

JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

SCHOOL OF GRADUATE STUDIES

FACULTY OF MATERIAL SCIENCES AND ENGINEERING

CHAIR OF POLYMER ENGINEERING

*A Thesis Submitted To School Of Graduate Studies For Partial Fulfillment Of Msc
Degree In Polymer Engineering*

*Synthesizing High Strength Biodegradable Polymer Film from Ethiopian False
Banana Pseudo stem.*

By

Hawi Ketema Hirpa

November 2020
Jimma, Ethiopia

Jimma University
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Declaration

I hereby declare that the thesis entitled: “*Synthesizing High Strength Biodegradable Polymer Film from Ethiopian False Banana Pseudo stem*” , was prepared by me, with the guidance of my advisor. The work contained herein is the original work of my own except where explicitly cited otherwise in the text, and that this work has not been submitted, in whole or in part, for any other degree or professional qualification.

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Abstract

Ethiopian false banana, locally known as “enset”, is an indigenous vegetable tree native to southern Ethiopia and mainly utilized as food source. In this thesis work, we investigated the possibility to use cellulose for bio-plastic production and its application for food packaging. Enset contain about 67.63% of cellulose in dry weight base. Cellulose was extracted from enset by combination of alkaline treatment by 1M NaOH and bleaching by H₂O₂ and the film were produced by solution casting method. To improve the strength of the films POSS and chitosan is added in different amount (10, 25, 35, 50, 75%) and glycerol is used as a plasticizer. The effect of the fillers on the mechanical properties, morphological structure, biodegradability Crystallinity and thermal stability were investigated. The increase of the fillers (POSS and chitosan) content led to increase the films tensile strength and slightly thermal stability. But when the content of POSS and chitosan increased to 75% tensile strength decreased. POSS and chitosan did not change X-ray patterns of cellulose films however degree of crystallinity increased at 50% POSS, and as the content of chitosan increase degree of crystallinity also increase.

Key words: cellulose, extraction, POSS, chitosan, glycerol, bio plastic.

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Acronyms

ASTM:- American Society for Testing and Materials

CCH: - Cellulose Chitosan

CP: - Cellulose Polyhedral Oligomeric Silsesquioxanes

DNA:- Deoxyribonucleic acid

FBF: - False Banana Fiber

FT-IR:- Fourier-transform **infrared** spectroscopy

POSS : - Polyhedral Oligomeric Silsesquioxanes

SEM: Scanning Electron Microscope

TGA:-Thermo Gravimetric Analysis

XRD :- X-ray powder diffraction

CHAPTER ONE

Introduction

1.1 Back ground of the study

In today’s world a million tons of petroleum based polymers are produced each year. A large amount of this petroleum based polymers are used for producing commodity materials that have short service lives. The large use of this polymers due to their good properties, good processing ability and low cost has led to significant problems in terms of health and environmental concern[1, 2]. Non-biodegradability and the prolonged effect in the natural environment and the consequent landfills are the major concerns regarding these materials. Packaging materials contribute the highest percentage of landfills; as world packaging organization reported that in 2009, global packaging market has reached US\$ 564 million and 30% was in plastic form and also the waste from this packaging has been highlighted as a key environmental issue[3]. The most commonly used polymers for making films are polyethylene terephthalate (PET), polyvinyl chloride(PVC),and High–density polyethylene(HDPE), low-density polyethylene(LDPE).

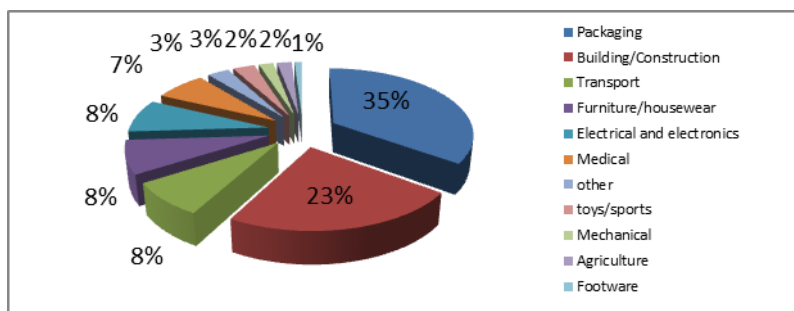


Figure 1:- Percentage usage of plastic in various sectors [4]

Consequently, there is a need to develop materials that are biodegradable in the natural environment as a substitute to non- environmentally friendly materials. In addition the rapid increase in the human population contribute a great roll towards pollution due to various practices such as illegal dumping and incineration, it is necessary to develop greener materials that are compatible with the environment. Therefore now day’s researchers are in search for

potential alternatives which are biodegradable and biocompatible to replace the traditional polymers used for packaging.

The feasible strategy to minimize the utilization of non-biodegradable polymer films is to develop bio based polymeric films as a substitute for these materials. Because of their compatibility, biodegradability and renewability, biodegradable polymer based films can be employed for a broad spectrum of applications where biodegradability is a key.

The purpose of this work was to produce high strength biodegradable film from Ethiopian false banana pseudo stem by mixing the polymer film derived from the stem with POSS and chitosan as filler to improve the physical and mechanical properties of the film.

1.2 Statement of problem

Global warming has forced researchers to enhance the quality products for saving the environment and energy. Many researchers studied producing biopolymers from natural based materials that replace synthetic polymers to solve the global warming problem and to save our environment from pollution. Ethiopia has a considerable amount of false banana plants, which has a great potential for the use of bio plastic material. Moreover as a result of lack of awareness of this plant and unavailability of experimental tools, research on the contribution of false banana cellulose has not been well researched before. On the other hand large amount of synthetic films are used in the country for packaging, which can cause environmental pollution after disposal. In this work the film produced from false banana pseudo stem cellulose mixed with natural filler like chitosan and POSS is expected to replace synthetic films and reduce environmental pollution

1.3 Objective of the study

1.3.1 General objective

The main objective of this research is to produce high strength biodegradable packaging film from false banana pseudo stem using POSS and chitosan as fillers and characterizing the properties of the film.

1.3.2 Specific objective

- Syntheses of biodegradable film from false banana pseudo stem using POSS and chitosan as filler.
- Characterizing the morphological, chemical, thermal, mechanical property and

biodegradability of the film.

- Determine the effect of POSS and chitosan on the property of the film.
- To compare the strength of false banana pseudo stem film with commercially available packaging films.

1.4 Significance of the study

Plastics production exceeds 180 million Mg (tons) per year, with a yearly increase in supply and demand. These plastics turn to solid waste after their end of life and will accumulate in the environment. Hence, from an environmentally friendly point of view, the production of biodegradable plastics is important to reduce the accumulation of plastic waste in the environment.

1.5 Research Design

In conducting this research some required steps has been accomplished, to mention some of them;

- i. Collecting some secondary data (information) related to biodegradable polymers, reading and making a comprehensive literature review to get the gap on the area.
- ii. Collecting raw sample (Ethiopian false banana pseudo stem) and required chemicals.
- iii. Designing the experimental procedure to study the effect of fillers (POSS and chitosan) on the films.
- iv. Analyzing the experimental data to reach to the conclusion
- v. Forwarding the concluding remark and recommend for further study.

1.6 The Thesis Layout

This thesis contains five main chapters. The first chapter is introduction part, includes background of the study, problem statement, objective of the study and significance of the research. The second chapter explains the finding from the review of different literatures including; the research papers, books, historical record and websites, which are relevant to the study. Chapter three describes methodologies used in this thesis including material collection, cellulose extraction followed by sample preparation and characterization and data analysis. The

fourth chapter presented the result and discussion of the laboratory test results. Chapter five includes conclusion, and recommendation for further studies.

CHAPTER TWO

Literature Review

2.1 Plastic Waste, World Overview

According to some reports, in 2016, the world generated 242 million tons of plastic waste 12 % of all municipal solid waste. Based on World Bank report ;this waste primarily originated from three regions 57 million tons from East Asia and the Pacific, 45 million tons from Europe and Central Asia, and 35 million tons from North America. The visibility of plastic waste is increasing because of its accumulation in recent decades and its affecting the surrounding environment and human health. Unlike organic waste, plastic can take hundreds to thousands of years to decompose in nature [5]. Plastic waste accumulated on an environment is causing floods by clogging drains, causing respiratory issues when burned, shortening animal lifespans when consumed, and contaminating water bodies when dumped into canals and oceans [6].In oceans, plastic wastes are accumulating in swirling gyres that are miles wide. When exposed to sun light the ultraviolet light in the sun makes the plastic degrading into “micro plastics” that are very difficult to resist and disrupting food chains and destroying natural habitats. The Ellen MacArthur Foundation (2016) predicates that, “by weight, there will be more plastic in the oceans than fish by 2050 if nothing is done”.

2.2 Biodegradable polymer

Biodegradable polymers are polymers that can be broken down and catabolized into both carbon dioxide and water in the natural environment by microorganisms. Biodegradable polymers may be classified into biodegradable polymers and biopolymers based on whether the dominating ingredient is synthetic oil-based polymer or a biologically derived polymers. Biodegradable polymers are oil based synthetic polymers which either have certain degrees of inherent biodegradability such as polycaprolactone, polyhydroxybutyrate and poly(vinyl alcohol)[7] or chemically modified plastic to improve the biodegradation ability. Biopolymers are naturally

occurring long chain molecules like cellulose, polysaccharide, proteins and DNA are among the common. Unlike synthetic polymers, most of them are biodegradable, i.e. decomposable by biological activity such as through bacteria or fungi and give rise to natural metabolic products. Different measurements can be considered to classify biodegradable polymers. Table below shows the classification of biodegradable polymers based on their origins, families, and common examples in each category. Nevertheless, among the different biomass-based polymers, cellulose has outstanding characteristics that make it favorable, whereas starch has difficulties in processing and is brittle[8]. In addition, cellulose is abundant, as it can be obtained from various sources ranging from plants to microorganism.

Table 1: Classification of biodegradable polymers

Origin	Family	Common Examples	Refs.
Biomass	Polysaccharides	Cellulose, Starch, Chitin, etc.	[9, 10]
	Proteins	Collagen, Gelatin, Albumin, Soya, Glutan	
Microorganisms	Polyhydroxyalkanoates (PHA)	Polyhydroxybutyrate (PHB) Poly (γ -glutamic acid) Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)	[9-11]
Petroleum oil	Polyesters	Poly (ϵ -caprolactone) (PCL) Poly (butylene succinate) (PBS) Poly (butylene succinate-co-adipate) (PBSA) Poly (butylene adipate-co-terephthalate) (PBAT)	[10-12]
Bio-derived	Polyesters	Poly (lactic acid) (PLA)	[10]

Among all biopolymer sources, cellulose is the most abundant [13, 14], and it has been estimated that globally around 10^{12} tones are synthesized also destroyed each year [15]. These lignocellulose fibers possess many characteristics like: low cost, low density, specific resistance, biological degradability, neutral CO₂, renewability, good mechanical properties and non-toxicity which make their use advantageous[16].

Following disposal, biodegradable polymers are expected to undergo through complete mineralization. Such degradation usually occurs via a two-step process.

1. Breakdown of the polymer into lower-molecular mass species by means of abiotic or biotic reactions.
2. Natural digestion of the polymer parts by microorganisms and their mineralization[11, 17].

It is essential that the degradation products are not toxic to the environment and do not persist within the environment [18].

In addition to this they can be easily modified by chemical agents [19]. The development of low cost sustainable and renewable resources is critical to meet the growing environmental concern and energy demand.

2.3 Lignocellulosic Biodegradable films

Packaging material which has good quality is indispensable to increase the shelf life of packed products. Conventionally, no biodegradable plastics were the common choice for packaging materials owing to their easy process ability, lower price, and high resistance to chemical and mechanical stress [20]. Polymers that are petroleum oil based like polystyrene, polypropylene, and polyvinyl chloride have a good mechanical and barrier characteristics like tensile, tear strength, oxygen permeability, carbon dioxide permeability, and aroma transmission. However, such polymers cause major environmental problems due to their poor recyclability, from nonrenewable resources, and non-biodegradability, thus leading to serious ecological problems[20]. Considering such drawbacks, in the last few years, research has been focused on developing packaging materials from renewable resources and in this case, biopolymers have gained increasing attention. Packaging biopolymers are highly safe due to the absence of harmful chemicals or toxins that affect nature; furthermore, being biodegradable, they break down into harmless products that get absorbed and fertile the soil[21]. Over the last two decades, the development and use of biopolymer-based packaging materials to extend the shelf life of fresh products has been receiving increased attention. However, researchers have been exploring the utilities of bio based films for more than 100 years. A maize kernel protein film was developed by Osborne in 1897[22]. A patent has been filed in 1972 for the fabrication of wheat gluten-based film[23] and also in the year 2000, films were synthesized from apple puree for fresh-cut

fruits [24]. Generally, there have been many studies done for the development of biodegradable packaging for food applications.

2.4 False Banana Pseudo Stem

Ethiopia has a huge amount of false banana plant which has close similarity with domesticated banana, but unlike banana it's not grown for its fruit. In south and southwestern parts of Ethiopia, most areas of lands are covered with inset plant which is used as a source of food. Central statistics agency of Ethiopia has reported that, 302,000 ha of land are covered by inset plant in Ethiopia. The main edible parts of the inset plant are the starchy rhizome and pseudo stem. The carbohydrate portion of the vast majority of false banana fiber is composed of cellulose and hemicellulose polymers with minor amount of other sugar polymers such as pectin and starch. The composition of cellulose and hemicellulose are called holocellulose and usually accounts for 65-70 percent of the plants dry weight. The composition of false banana fiber (FBF) is mentioned in Table 2.

Table 2 :- Composition of false banana fiber [4]

Constituents	Reported values	
	Range	Average
Cellulose	67.4-67.89	67.63
Lignin	4.8-6.13	5.41
Ash	1-1.4	1.2
Moisture	10-15	12.5
Cold water soluble compounds	1.9-2.61	2.37
1% NaOH soluble compounds	28.5-29.9	29.4

False banana plant has the ability to withstand drought condition. Harvesting the inset for food is a laborious process that involves prying the entire plant out of the ground 3 persons can process 2 inset plants in a day.

The fiber extracted from the pseudo stem after its starch has been harvested is used for making ropes, mats and sacks, this woven material has high strength and less cost [25].



Figure 2:- False Banana (Inset) plant[26]



Figure 3:- Inset Fiber (kancha)[26]

2.4.1 Cellulose

Cellulose is the most abundant natural polymer found on Earth which is discovered by Anselme Payen back in 1838. This renewable and biodegradable material has got good attention due to its physical and chemical properties, which are different from those of synthetic polymers. Cellulose can be obtained from different living organisms, like plants, bacteria, and algae. Figure 4 shows the structure of cellulose. Cellulose was one of the key research areas during the emergence of polymer chemistry, and its structure was first demonstrated by the pioneer in polymer science, Herman Staudinger, in 1920[8, 27]. An in-depth understanding of this material, its structure, reactivity, and possible modification routes that can be followed is crucial for fine-tuning of its parameters for various purposes.

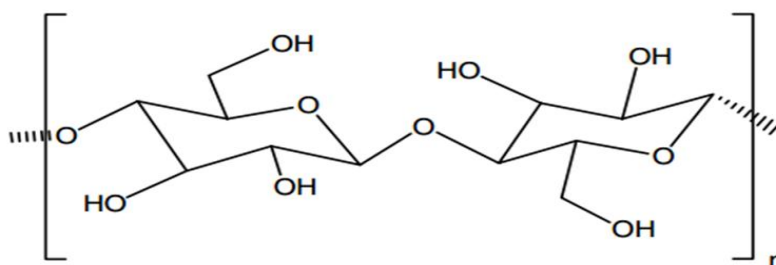


Figure 4:-Chemical structure of Cellulose [28]

Banana is a complex Lignocellulosic natural fiber consisting cellulose 70%, hemicellulose 6%, lignin 5%, pectin 3%, ash 1%, extractives 3%, residual gum, moisture regain [29]. Hemicellulose is a constituent of the plant cell wall that consists of a simple structure than cellulose. Hemicellulose consists of β -(1 \rightarrow 4)-linked backbones. The types of monomers involved in the polymerization of hemicellulose are xylose, galactose, mannose, rhamnose, and arabinose. Hemicellulose cross-links with either cellulose or lignin, strengthening the cell wall.

Banana pseudo stem is a promising potential source of ecofriendly cellulose based biodegradable plastic [13, 30]. As reported by [31] banana pseudo stem have the relatively high amount of cellulose, which is approximately 31-54% on a dry basis.

Banana pseudo stem film has relatively high tensile strength and low flexibility [1, 30]. Mechanism to improve the flexibility of cellulose film is by adding plasticizer or polymer additives into polymer matrix [18, 30].

2.5 Additives and plasticizers used for biodegradable films

Polymer additives play a crucial role in the modern plastics industry in order to overcome the difficulties in processing, to enhance material durability and which will help product designers to manufacture a pliable, fashionable, user friendly and productive materials. Most of the plastics synthesized were mixed with either organic or inorganic compounds to enhance the properties of the developed material. Nanometer-sized fillers have a large surface-area-to-volume ratio and are of particular interest, because they can be easily dispersed in a polymer, hence facilitating the enhancement of a desired property, such as elasticity, modulus, strength, heat resistance, porosity (barrier property) and flammability.

2.5.1 Polyhedral Oligomeric Silsesquioxanes (POSS)

POSS are class of compounds with an inorganic silicon-oxygen core and bulky organic substituents on the outer surface. POSS is one of many kinds of silsesquioxane molecules. The term silsesquioxane refers to the molecules, whose chemical structure follows the basic composition of $R_nSi_nO_{1.5n}$, for example $Me_8Si_8O_{12}$, the R-group, also called the vertex group for polyhedral molecules, may be hydrogen, alkyl, alkylene, aryl arylene, among others. Such silsesquioxane can form oligomeric organosilsesquioxanes ($CH_3SiO_{1.5}$) through chemical reactions and the chemical structures of the derivative silsesquioxanes are quite different [32].

The molecular architecture of silsesquioxanes can be divided into two categories:

- (a) Non-caged structure and
- (b) Caged structure.

Cage-like silsesquioxanes are usually called polyhedral oligosilsesquioxanes or Polyhedral Oligomeric Silsesquioxanes, abbreviated as POSS. This class of well-defined, highly symmetric molecules usually features a nanoscopic size, approximately 1.5 nm in diameter when the vertex (R) groups are included. They can be loosely regarded as the smallest possible silica particles [33]. POSS molecules with a T8 cubic inorganic core composed of silicon-oxygen ($R_8Si_8O_{12}$ or $R'_1R_7Si_8O_{12}$) are the most prevalent system studied, although the Q8 structure ($R_8Si_8O_{20}$) has also been given significant attention [34]. The hybrid organic-inorganic framework renders POSS thermally and chemically robust, in order that one of the promising applications of POSS-based polymers is to be used with in the highly oxidizing environment of orbiting space vehicles [35, 36].

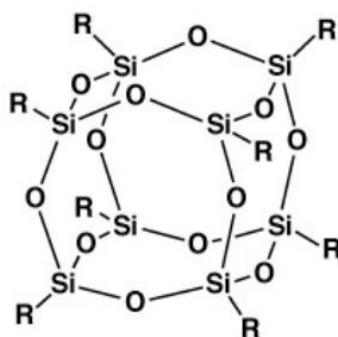


Figure 5:- Molecular structure of POSS [30]

In a similar fashion to atomic oxygen resistance, POSS can improve the oxidative stability and flame retardance of polymers in terrestrial applications[37, 38]. They have gained attention as a polymeric additive because they can be modified to achieve good interfacial adhesion with the polymer matrix and, once well dispersed, have the ability to improve a variety of polymer properties, including increased strength, oxidative resistance, increased toughness, increased thermal stability, and reduced flammability[39].

2.5.2 Chitosan

Chitosan, a β -(1-4)-2- amino -2- deoxy β -D- glucopyranose, is a hydrophilic, biocompatible and biodegradable polysaccharide prepared by N-deacetylation of chitin, which is the main structural component of crab and shrimp shells[28, 40]. Chitosan has various properties including biodegradability, biocompatibility, non-toxicity, and antimicrobial activity. Because of these properties, chitosan has been studied and used as a material across many fields, including biotechnology, pharmaceuticals, agriculture, food, cosmetics, and so on. In particular, there has been a growing interest in using chitosan as a coating material for various applications, because of its remarkable film-forming properties coupled with its antimicrobial activity and antifungal properties[41]. Besides these properties, chitosan films or coatings have been investigated because of their barrier properties, i.e. the ability to retard the mass transfer rate of moisture, oxygen, aromas, oil and solutes, their flexibility and their potential improvement of mechanical and resistance properties of the final materials.

2.6 Related works

Many studies have been conducted researches on cellulose based biopolymers. Some of them are:

FitriFaradilla et al have studied the effect of additives (glycerol as plasticizer, nano clay and graphine oxide as nano fillers) on physico chemical properties of biodegradable nano cellulose plastic sourced from banana pseudo stem. In their work they isolate nano cellulose from banana pseudo stem through TEMPO mediated oxidation and mild mechanical treatments and a thin film was prepared from isolated nano cellulose by solution cast method. Modification was made to the control by adding additives: nano fillers (nano clay and graphine oxide) improved the tensile strength and the contact angle of the films but not their elasticity. Whereas glycerol which acted as plasticizer increased the elasticity of the films, but thermal stability, tensile strength and contact angle is reduced[30].

Abraham et al have studied extraction of nano cellulose fibrils from lignocellulosic fibers by using three different fibers: banana pseudo stem, jute stem and pineapple leaf fiber (PALF). They develop a simple process to obtain an aqueous stable colloid suspension of cellulose nano fibrils. They use steam explosion technique with mild chemical treatments like alkaline extraction, bleaching and acid hydrolysis to extract cellulose from these raw fibers. As a result the percentage of cellulose components was found to be increased during steam explosion and the additional bleaching process for all the studied fibers. The lignin and hemicellulose components were found to be decreased from raw to the bleached fibers. Steam explosion combined with acid hydrolysis has been found to be successful in obtaining fibers in the nano dimension from various plant fibers[26].

FitriFaradilla et al aimed to characterize a free standing film produced from banana pseudo stem nano cellulose that was prepared by TEMPO- mediated oxidation. The nano cellulose was dispersed in water and cast to form a film. During film formation inter fibrillar hydrogen bonding is formed that connects the nano cellulose chain together. The film obtained from this work was translucent with transmittance 30.3% at 463 nm. But at first they expected transparent film considering the diameter of the nano cellulose was much smaller than the visible light wave length. According to their study they found calcium oxalate crystals in the film which affects the

properties of the film especially its optical property by absorbing the visible light and obstacle transparency. And also due to the presence of this calcium oxalate crystals the film become rough and the roughness of the film also reduce transparency. Generally they confirmed that banana pseudo stem nano cellulose can be used for making a free standing film that has promising potential as a bio plastic[13].

Deepa et al have studied the characterization of cellulose nano fibrils isolated from five different sources (banana rachis, sisal, kapok, pineapple leaf and coir) using acid coupled steam explosion process. The main goal of their work was to examine the effect of the extraction process and raw material sources on many of the key properties (structural, morphology, Crystallinity, surface energy, thermal stability and the yield) in the resulting nano cellulose. As a result they produced a transparent smooth surface film out of nano celluloses suggesting the absence of crystals in the nano celluloses[42].

The main difference between **FitriFaradilla et al and Deepa et al** was a Nano cellulose isolation method used. A combination of chemical treatments such as alkaline treatment bleaching and acid hydrolysis is used in [13]where as in[42] Nano cellulose was isolated by TEMPO- Mediated oxidation.

Mechanism to improve the flexibility of cellulose film is by adding plasticizer into cellulose matrix. One of the plasticizer mainly used to improve the elasticity characteristics of bio plastics is glycerol[30, 43].

The elasticity of the film produced by [30] was increased by adding glycerol as plasticizer, but the flexibility is still poor. This is may be due to the selected Nano fillers i.e. Nano clay (NC) and graphine oxide (GO).

Jiwookyag.et.al has studied the effect of Cellulose and chitosan solutions prepared in 60% LiBr and mixed with a different weight ratio. The washing and drying of the prepared cellulose–chitosan composite films were performed under identical conditions. The color of the liquefied mixtures and films was initially transparent but changed from colorless to brownish yellow depending on the amount of chitosan in the solution. The cross section observed with in the SEM results shows that the film developed with a higher ratio of chitosan was more robust and possessed greater antibacterial properties. FT-IR analysis of the films showed that hydrogen bonds between cellulose and chitosan in composite films were successfully achieved and

retained excellent mechanical properties. The proper ratio of chitosan and cellulose solution can increase the mechanical properties, like tensile strength and the elongation of the films; however, the E-modulus property was consistently reduced. The antibacterial activity and mechanical properties of the films were greatly improved because the amount of chitosan with in the film increased[44].

Sofiah et al have studied the mechanical properties of bio plastics produced form *Musa paradisica* formatyca concentrate, sorbitol and glycerol plasticizer substance is added. The purpose is to make bio plastics produces more flexible and more elastic. They determined the effect of the composition of sorbitol and glycerol plasticizers that optimal biodegradable plastics are able to obtain. The other ingredients utilized are acetic acid, chitosan, and aquedest. The results obtained in the form of thin sheets of bio plastic were tested mechanically in the form of tensile strength and percent elongation. Based on the analysis of tensile strength and elongation percent technique, it was found that bio plastics were close to the standard, i .e., in the sample 3% glycerol (% v / v) with a tensile strength of 46.4201 Mpa and percent elongation of 15.15152% and a sample of 5% sorbitol (% v / v) tensile strength 31.4228 MPa and elongation percentage 15.15152%[45].

CHAPTER THREE

MATERIALS AND METHODOLOGY

This experimental section is primarily concerned with the investigation of biodegradability of the films and the effect of the fillers POSS and chitosan on increasing the strength of the film production. Banana pseudo stem is removed as a waste dumped on land after harvesting banana fruit from it. The use of waste biomass to substitute fuel based polymers has become an attractive topic for researchers due to its dual advantages: economic and environmental. Paying this hot issue in to consideration, the experimental program of this research was carried out to explore the synthesis of biodegradable polymer film and consequently finding the effect of the fillers on increasing mechanical properties the film following the testing procedure of specifications of ASTM.

3.1 Materials and Methodology

The material used in the experiment as well as the methodology to synthesize the films has been presented in this chapter. Moreover, characterization used to examine the physical property, the chemical composition, mechanical property and morphology also stated.

3.1.1 Sample Selection

False banana pseudo stem is selected due to its availability, low cost and cellulose composition. The raw materials will be collected from cultivation areas in southern part of Ethiopia. To produce a free standing film we have to improve the mechanical, physical and chemical properties of the cellulose. Through the vast literature survey, it can be concluded that additives effectively improve various properties of natural material based films. In this research chitosan and POSS are selected as filler due to the obvious compatibility of the two poly saccharides, which can be processed without any chemical modification and in aqueous media. And also cellulose – chitosan combinations are of particular interest because of the structural similarity, resulting in compatible composite materials that combine the excellent mechanical properties of cellulose fibers with physicochemical properties of chitosan. One practical application of cellulose –chitosan composition is their processing into films with high strength, good biocompatibility, biodegradability and hydrophilicity[46].

3.1.2 Experimental sites

False banana pseudo stem was collected from Jimma town farm land. The chemicals used for the extraction process of cellulose NaOH, H₂O₂ and citric acid are collected from Jimma university material lab and chemistry lab. Chitosan and POSS are received as a gift from expertise. Besides, extraction of cellulose and film preparation was made in Jimma University, Materials Science and Engineering lab, Most of the characterization has been done in Jimma Institute of Technology Laboratories.

3.1.3 Apparatus and equipment's used in the experiment

To accomplish the objectives, the following material has been used; electronic cutter, digital beam balance, severs mechanical mixer, sonicator, miller, beakers, oven, Petri dish, centrifuge and electrical furnace has been used. Moreover, for of characterization purpose instruments like XRD, TGA, SEM, and Mechanical strength (Compressive strength tester called UTEST) were used. In addition, some mathematical method applied to analyze the collected data.

3.2 Methodologies

3.2.1 Cellulose Extraction

Cellulose was isolated from the outer layer of the banana pseudo-stem by the modification of the method suggested by Pelissari et al. (2014) and Lin et al. (2014). The outer part (layered part) of banana pseudo stem was sliced using a slicer with a blade size of 10 mm and dried in a cabinet dryer at 40°C for two days. Dried pseudo-stem was then milled using a miller. The pseudo-stem flour (10 g) was soaked in 300 mL of 1MNaOH with continuous stirring for 16 h. After that, the pseudo-stem was washed by centrifugation (5 min) with distilled water to remove remaining NaOH. NaOH treated flour was then bleached for farther delignification with 200 mL of 1% H₂O₂ for 1 h at 70°C. After 1 h, the mixture was cooled down and stirred for 1h. Bleached pseudo-stem flour was washed again by centrifugation (5 min) with distilled water to remove remaining H₂O₂. The aqueous suspension will homogenized with a mixer and sonicated with a batch sonicator to form cellulose dispersion. For the control sample (purely cellulose film), the cellulose suspension was mixed with distilled water so that the Solid content was 0.7%. The mixture was homogenized with Ultra Turrax sonicator for 10 min and sonicated with a batch

sonicator for 30 min to form cellulose dispersion. The dispersion was then poured into plastic petri dish and dried in the oven (40°C, 2 days) to produce a film through solution casting method.

3.2.2 Sample Preparation

1. Cellulose (control) film preparation

After the dispersion was prepared 15ml of the dispersion was boiled in 250ml beaker until bubble is formed. After that the boiled cellulose was poured on Petri dish of 9cm diameter, and then dried in the oven for 48hrs at 40°C

2. POSS containing cellulose film preparation

POSS containing cellulose film was prepared with different amount of POSS labeled as CP10, CP25, CP50, and CP75 containing 1%, 2.5%, 5% and 7.5% POSS. respectively. Cellulose and POSS dissolved in separate solution. Cellulose solution was prepared just like for control and POSS solution was prepared by dilute citric acid and oil since POSS is hydrophilic. After that the two solutions added together and stirred for 1minute for fine dispersion of POSS in cellulose. Then the dispersion 15ml was poured on Petri dish and dried for 48hr at 40°C.

3. Chitosan containing cellulose film preparation

Chitosan containing cellulose film was prepared just like that of POSS, different amount of chitosan labeled as CCH10, CCH25, CCH50, CCH75 containing 1%, 2.5%, 5% and 7.5% chitosan respectively. Cellulose and chitosan dissolved in separate solution. Cellulose solution was prepared just like for control and chitosan solution was prepared by dilute citric acid since chitosan is hydrophilic. After that the two solutions was added together and stirred for 1minute for fine dispersion of chitosan in cellulose. Then 15ml of the dispersion was poured on Petri dish and dried for 48hr at 40°C.

3.3 Characterization techniques

The morphologies of the cross section of the films were characterized by scanning electron microscopy (EM-30 Mini SEM, COXEM Co., Ltd., Daejeon, South Korea).

Crystallinity profile of chitosan, POSS, and cellulose composite films was analyzed using X-ray diffraction (XRD-7000 Drawell made in china). Sample was placed on a 30 mm sample holder with mask 10 and slit 2θ. The radiation source was Cu Ka at 40 kV, 30 mA. Scanning was done

in 2hrange from 4 to 40 with step size of 0.02, time per step 50 s, and scan speed 0.04/s.

Thermal properties of the films were analyzed by thermo gravimetric analysis (TGA) (TGA Q 5000 TA. Analysis was done in duplicate.

Mechanical Test

Mechanical properties of the films were measured, such as tensile strength and percent elongation at break, using tensile testing following the ASTM Standard D882-12. Films were then cut into bone-shaped specimens. Width, thickness, and length of each specimen were measured using a digital caliper. Measurements were done with load cell 50 N.

Biodegradability

Five 400 ml beakers and 4cm ×4cm of a preweighed piece of bio plastics were taken, the preweighed bio plastic material prepared was placed under the beaker containing soil at a depth of 5cm from the surface. Some amount of water was sprinkled on the soil so that bacterial enzymatic activities could be enriched. These samples were kept in the beaker for about 15 days and each 3 days of interval we observed the decrease in the weight of the bio plastic material and results were recorded accordingly. Weight loss were measured and taken as an index of the biodegradability of each corresponding sample. The weight loss was calculated using the following equation;

$$\%WL = [(W1 - W2)/W1] \times 100 \dots\dots\dots\text{Eq.1}$$

Where %WL is weight loss percent, W1 is preweight of the sample, W2 is weight of the sample after burial.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Introduction

The result of synthesized film with different compositions of POSS and chitosan has been analyzed in this part. Generally, this chapter is composed of the result and discussion of the characterization of the morphological, Mechanical strength (compressive strength) data, and physical characteristic data of the sample film.

4.2 Morphological analysis

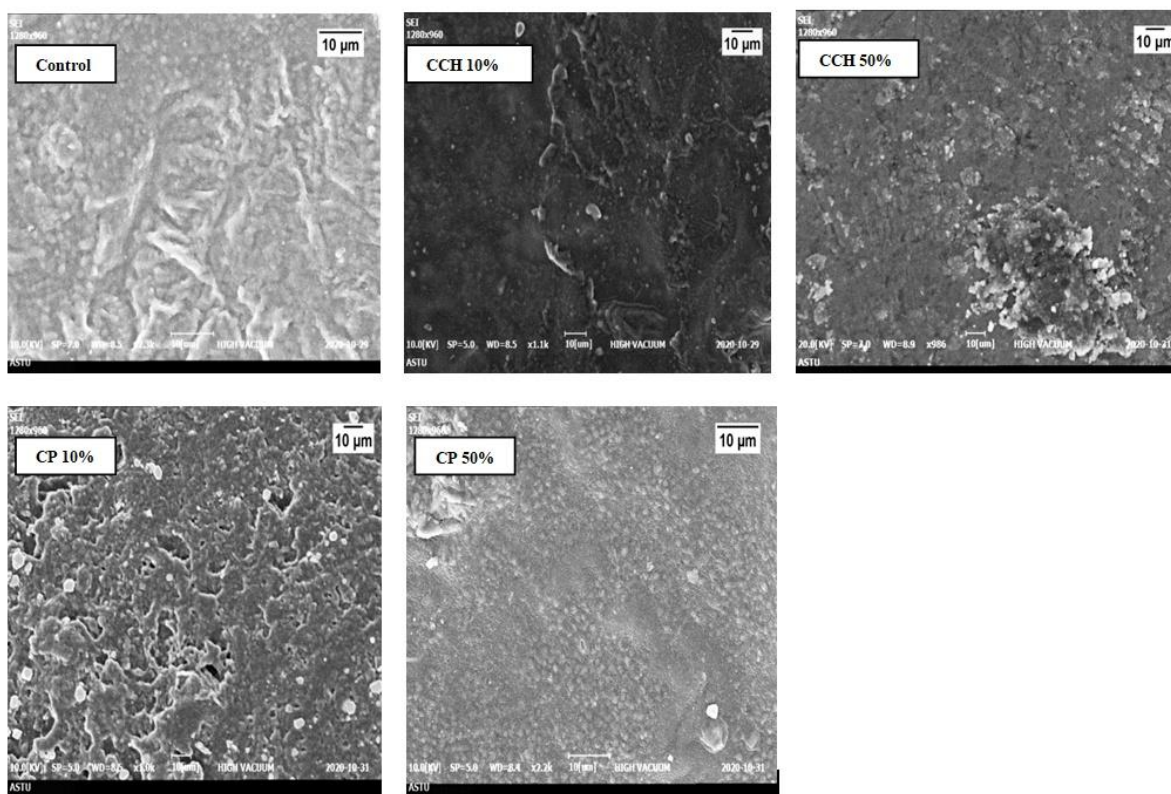


Figure 6:- SEM images of (a) control cellulose film (b) 10% chitosan containing cellulose film (c) 50% chitosan containing cellulose film (d) 10% POSS containing cellulose film (e) 50% POSS containing cellulose film

Figure 6 shows SEM images of the cross section of the control, CCH10, and CCH50 films (a-c). The cross section of control, which contained no chitosan, exhibits a uniform layer structure. CCH10 have a similar layer structure with uniform spread out of chitosan in the matrix, on increasing the percentage of chitosan to 50% aggregates of chitosan start to emerge within the matrix and makes the surface appear relatively rougher. This is probably because of chitosan agglomeration and phase separation[44]. The homogeneous matrix of films is an excellent sign of their structural integrity, and as a result, good mechanical and physical properties would be probable[47]. Figure 6d and 6e are for POSS containing film the dispersion POSS in cellulose for both films are homogenous and uniform which shows good interaction of POSS and cellulose. The SEM image of 50% POSS is smoother than 10% POSS this is probably indication of improved mechanical properties of the film as the amount of filler added increases.

4.3 XRD analysis

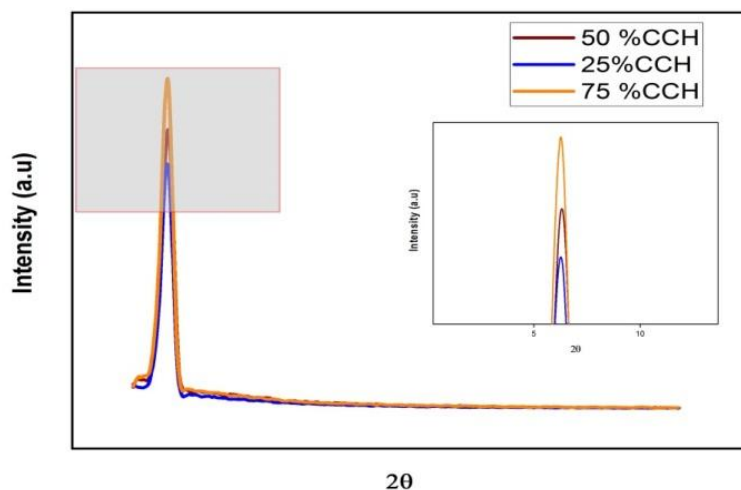


Figure 7:- XRD result for chitosan containing films

XRD suggests that the influence of chitosan particles on the intensity of the patterns. The XRD patterns of the main peaks suggests that the peaks at $2\theta = 6.4^\circ$ associated with the crystal

structure of the film. XRD confirmed the influence of chitosan molecule on the intensity of the patterns, as the amount of chitosan added increase the film intensity also increases.

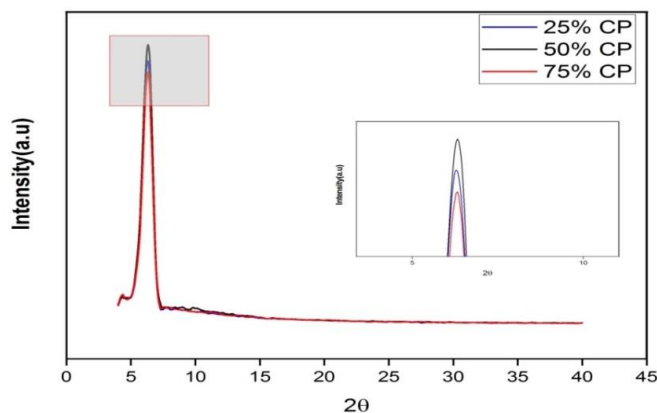


Figure 8:- XRD result for POSS containing films

XRD suggests that the influence of POSS particles on the intensity of the patterns.. The XRD patterns of the main peaks suggests that the peaks at $2\theta = 6.8^\circ$ associated with the crystal structure. XRD confirmed the influence of POSS particles on the intensity of the patterns, the film with 50% have high intensity than 25% and 75%. This indicates when this amount of POSS is added the film becomes more crystalline.

4.4 Mechanical test for cellulose films

Tensile strength and percent elongation at break were determined for all of the cellulose films. The ultimate tensile strength shows the maximum load that can be held per cross-sectional area of the film, while percent elongation at break shows the extent of the film can be stretched before it breaks [48].

Table 3: Tensile strength and elongation at break of glycerol containing films.

Amount of glycerol added (ml)	Tensile strength (Mpa)	Elongation at break (%)
2.5ml	21.325	13.125
4ml	18.67	20.24
5ml	13.219	25.185

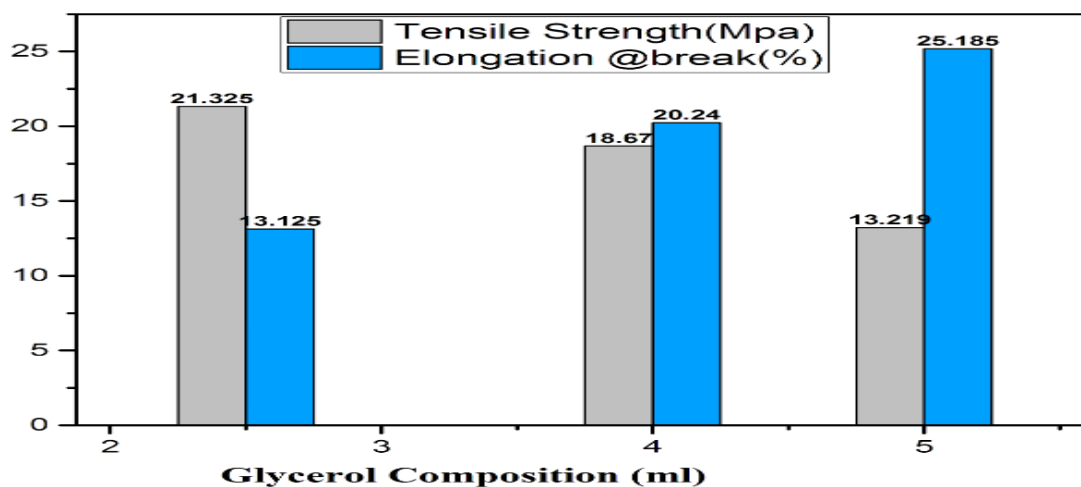


Figure 9:- Mechanical properties of glycerol containing films.

Good mechanical strength is the basis for a material, which is widely adopted. Tensile strength is the maximum pull that can be achieved until the film can survive before breaking up. The tensile strength values obtained by adding glycerol ranged from 21.325Mpa, 18.67Mpa and 13.219Mpa for 2.5 ml, 4ml and 5ml glycerol containing film. The tensile strength of cellulose films is strongly influenced by the amount of the added plasticizer where the elongation at break is significantly increasing as the amount plasticizer increase. From Figure 9 it can be seen as the amount of the glycerol increase in making cellulose film to the composition of 5 ml, the lower the tensile strength (13.219Mpa) of the cellulose film produced. And from the above table the elongation at break is increasing as the amount of glycerol is increasing to 5ml. This is due to the increase in the concentration of the plasticizer will reduce hydrogen bonds in the film to increase flexibility, by increasing the flexibility the tensile strength of the film will be smaller because the resulting film becomes flexible and soft. This behavior could be related to the structural modifications of cellulose network when plasticizer was incorporated. The matrix of the film becomes less dense, facilitating movement of polymer chains under stress, therefore decreasing the film resistance[47]. The tensile behavior of films with 5ml of glycerol could be associated to those of ductile polymers since tensile strength decreased and elongation at break increased significantly compared with less plasticized films. Similar results were obtained by [49] and [4] for acetylated corn starch and cassava starch films, respectively. Plasticizers interfere with polymeric chain association facilitating their slipping and thus enhancing film

flexibility. Glycerol decreases the rigidity of the network, producing a less ordered film structure and increases the ability of polymer chains movement [50]. Glycerol concentrations higher than 4ml modified the mechanical behavior of films drastically showing the typical pattern of very flexible materials. For these films, tensile strength values decreased and elongation at break increased significantly. The nonlinear decrease of tensile strength and the increase of elongation at break with plasticizer content were also reported by several authors for biodegradable Lignocellulosic based films [51]

Table 4: Tensile strength and elongation at break of chitosan containing samples.

Amount of chitosan added (%)	Tensile strength (Mpa)	Elongation at break (%)
10%	22.711	21.01
25%	27.031	26.76
35%	31.615	33.18
50%	34.527	35.54
75%	32.407	30.02

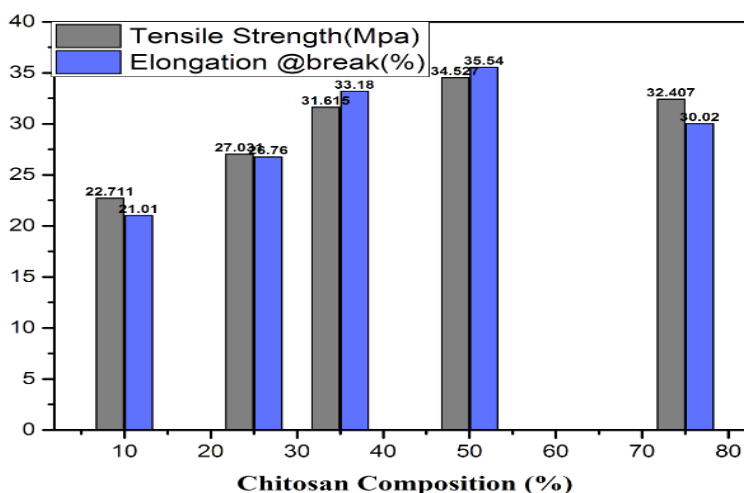


Figure 10:- Mechanical properties of films containing chitosan

The chitosan content in the films varied from 10% to 75% (by weight). Figure 10 shows the tensile strength and elongation at a break of the composite films across the different ratios of

cellulose and chitosan. It was found that the TS values of cellulose-based films were improved gradually with the addition of chitosan. The tensile strength of the 10%, 25%, 35%, 50% and 75% addition of chitosan cellulose films were found to be 22.711, 27.031, 31.615, 34.527 and 32.407Mpa, respectively. The tensile strength increased from CCH10 to CCH50, further increase of chitosan beyond 50% gave negative. The EB values of the cellulosic films also increased gradually. Table 4 showed the effect of chitosan on the elongation at break (EB %) of the films. The EB % values of 10%, 25%, 35%, 50% and 75% chitosan content films were 21.01%, 26.76%,33.18%,35.54% and 30.02%respectively. The elongation increased from CCH10 to CCH50 but rapidly decreased at CCH75.The increase in tensile strength and elongation can be attributed to a certain amount of chitosan causing an increase in the intermolecular interaction between the –OH group of cellulose and the –OH and –NH₂ groups of chitosan—this works as a reinforcement for the cellulose matrix. However, the addition of more than a certain amount of chitosan caused tensile strength and elongation decrease. This is because chitosan intramolecular bonds rather than intermolecular bonds with cellulose are formed. It occurs during phase separation between two components, thus causing nonhomogeneous interaction in the film and weakened mechanical properties [52].

The best proportion for films was 50% chitosan and 50% cellulose because the films with these proportions showed excellent mechanical properties.

Table 5: Tensile strength and elongation at break of POSS containing samples.

Amount of POSS added (%)	Tensile strength (Mpa)	Elongation at break (%)
10%	25.9	25.24
25%	29	27.13
35%	32.401	30.08
50%	36.801	31.12
75%	31.254	21.35

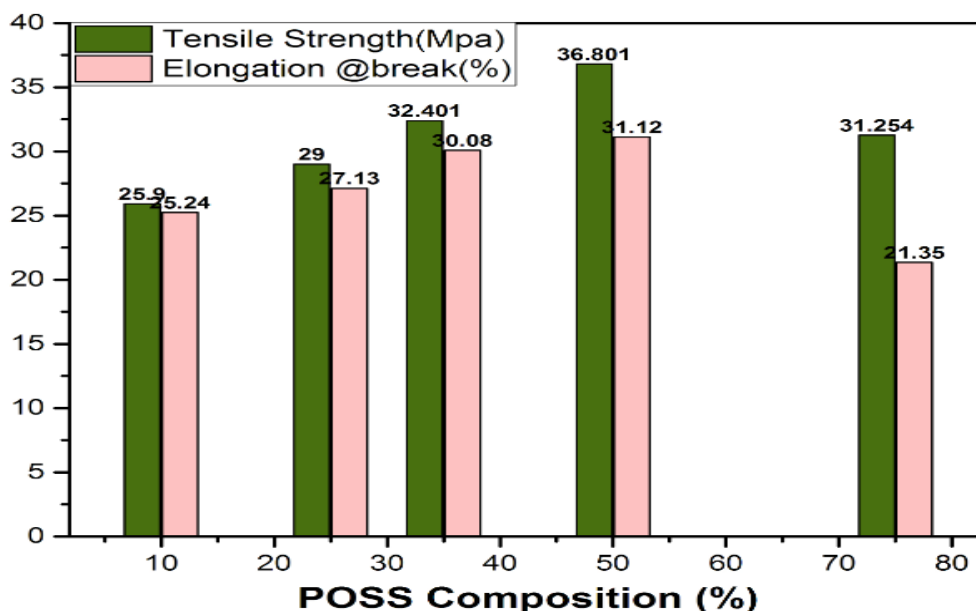


Figure 11:- Mechanical properties of film containing POSS

The mechanical properties of the cellulose/POSS films, including the tensile strength and elongation at break, are summarized in Figure 11. As seen from the results of the tensile test, the films possessed good tensile strength of 25.9-36.801 MPa and elongation at break of 21.35-31.12 MPa, which were almost in the same range with those of conventional commercial polyolefin films, such as polyethylene (PE) and polypropylene (PP) (the tensile strength = 20–40 MPa). The tensile properties of the cellulose/POSS increased with the content of POSS up to 50 %, and then decreased at 75%. The cellulose/POSS film with 50% POSS achieved a maximum tensile strength of 36.8 MPa. This phenomenon is probably correlated to the dispersion-aggregation state of POSS nanoparticles and the interfacial interaction of organic/inorganic between POSS and cellulose.

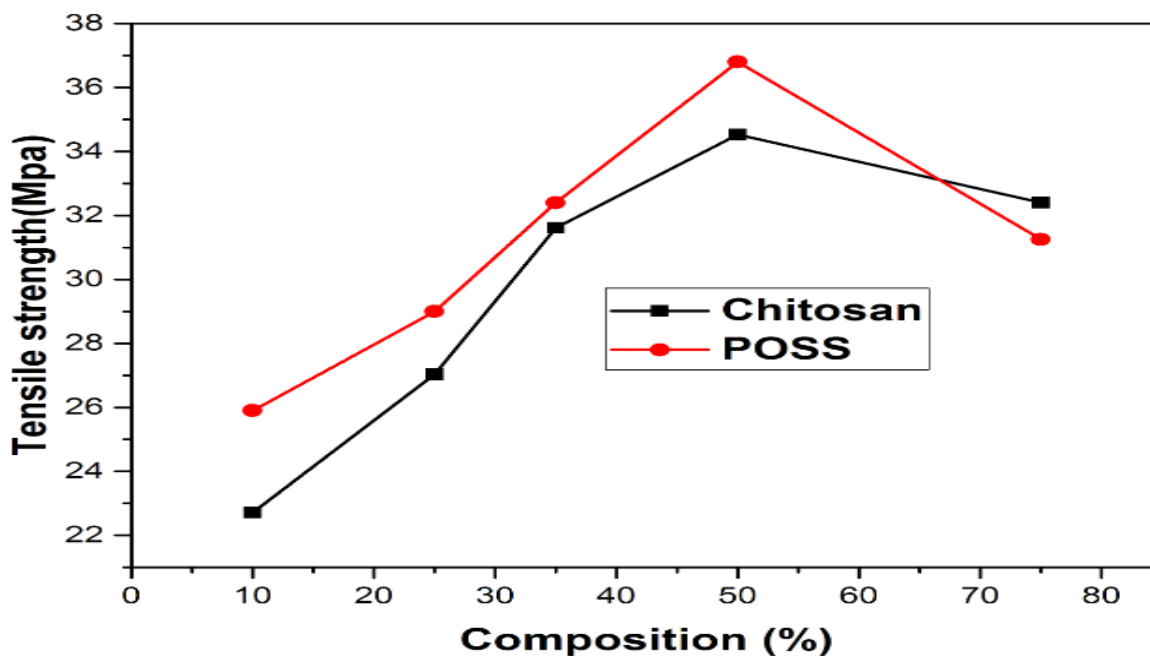


Figure 12:- Tensile strength comparison of chitosan and POSS containing films

From Figure 12 the addition of POSS and chitosan improved the tensile strength of the films; tensile strength of the film as expected, CPs (films contained cellulose and POSS) was 25.9-36.801 Mpa, and CCHs (films contained cellulose and chitosan) was 22.7-34.45Mpa. The cellulose films which have POSS as filler shows improved tensile strength than film which have chitosan. In contrast, the addition of glycerol slightly reduces the tensile strength of the films (13.911-21.699 Mpa), but improved the flexibility, which was indicated by significant increase in percent elongation (13.127–25.2%). The reduction of film strength and improvement in flexibility due to the presence of glycerol has been reported in several studies[53]. These phenomena could be due to glycerol reducing the internal hydrogen bonding of the polymers, in this case, cellulose, and thus increasing the space between polymers and reducing the crystallinity [53]. However, when POSS or chitosan was combined with glycerol in cellulose films, a further increase in percent elongation was observed without compromising the tensile strength. Even though the addition of fillers and glycerol increased the percent elongation of the films significantly, but percent elongation of these composite films was still lower than the percent elongation of the synthetic films .It shows that the cellulose film could bear heavier food

products than the synthetic films, but could not be stretched as long as the synthetic films. Therefore, more investigation is needed to improve the flexibility of these cellulose films.

4.5 Soil Burial Test

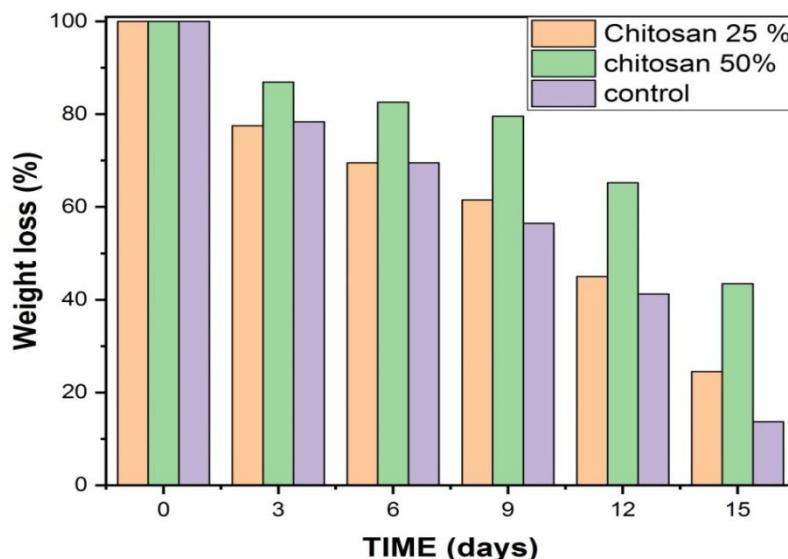


Figure 13:- Soil burial test for control and chitosan containing films

Soil burial test is used to measure the degree of film degrade after being expose to the decomposition condition. Cellulose chitosan film was a biodegradable product that has the degradation properties. Thus, soil burial test was applied to the film in order to know the degree of degradation of the film. Figure 13 has shown the weight change during the degradation of Cellulose chitosan and cellulose film. The slower degradation rate in the Cellulose chitosan film was due to the resistance in water uptake and diffusion through the composite compared to pure Cellulose film, which readily takes up water. After day 9, Cellulose chitosan films starting experience huge weight loss over time, 50% chitosan in Cellulose chitosan film having lowest weight loss compared to 25% chitosan and control film. This was because the function of filler, chitosan mostly filled all the voids in the cellulose film, thus, the reaction between the film and soil lesser as the amount of filler in the cellulose film increases. On the other hand, pure cellulose film was experienced huge weight loss due to the substitution of OH group in

cellulose with soil and there was many void inside the cellulose chains compared to others. From the result, cellulose film which adding chitosan as filler having low degree of degradation compared to pure cellulose film. This was because chitosan has antimicrobial properties which prevented the microbial attack. Therefore, cellulose chitosan film has low weight loss compared to that of pure cellulose film. There was degradation mechanism taken place from day 3 on the surface of the film. However, starting from day 10, cellulose chitosan film experienced degradation inside the film and begin to break the chains. cellulose chitosan film was then having huge weight loss due to chain break and the degradation were faster [54]. After day 15, the cellulose film was almost fully degraded while cellulose chitosan film left some residues. Table 6 shows the cellulose chitosan film condition before and after 6 days. From the Table 6 it can be seen clearly that there was some parts of cellulose chitosan film started to degrade after 6 days. This result of significant weight loses in cellulose chitosan film. There were microbial attacks by the microbial colonies on the cellulose chitosan film. The microbial attack causes the discoloration on the surface of cellulose chitosan film. Microbial colonies were microorganisms that will generate the enzymes to causes the breakage of the cellulose and chitosan backbone chain[54] . Hence, the film will degrade fully after a certain period. From, the above graph, pure cellulose film was degraded faster as compared to cellulose chitosan film after 15 days. And also amount of chitosan present in the film can affect the degradation time of the biodegradable film.

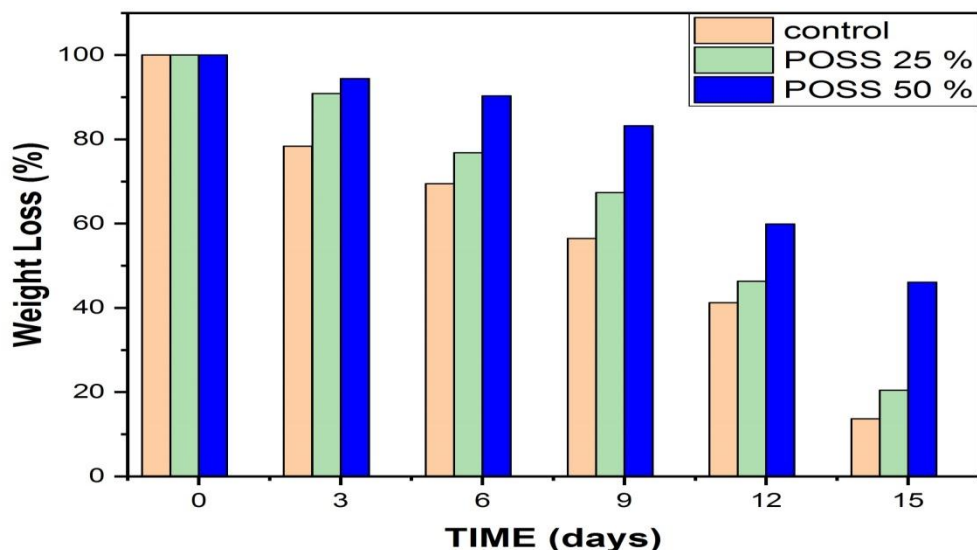


Figure 14:- Soil burial test for control and POSS containing films

The biodegradability of cellulose POSS film is shown on the Figure 14. The cellulose POSS films start degradation when checked after 3 days. As shown on the above graph control film degrades faster than POSS containing films and also as the composition of POSS increases the degradability decreases. . After day 12, Cellulose POSS films starting experience huge weight loss over time, 50% POSS in Cellulose POSS film having lowest weight loss compared to 25% POSS and control film. This was because the function of filler, POSS mostly filled all the voids in the Cellulose film, thus, the reaction between the film and soil lesser as the amount of filler in the cellulose film increases. On the other hand, pure Cellulose film was experienced huge weight loss due to the substitution of OH group in Cellulose with soil and there was many void inside the Cellulose chains compared to others. From the result, Cellulose film which adding POSS as filler having low degree of degradation compared to pure Cellulose film. Therefore, Cellulose POSS film has low weight loss compared to that of pure Cellulose film. There was degradation mechanism taken place from day 3 on the surface of the film. However, starting from day 12, Cellulose POSS film experienced degradation inside the film and begin to

break the organic/inorganic chains. This is due to POSS is inorganic filler that results in organic/inorganic interaction of cellulose and POSS.

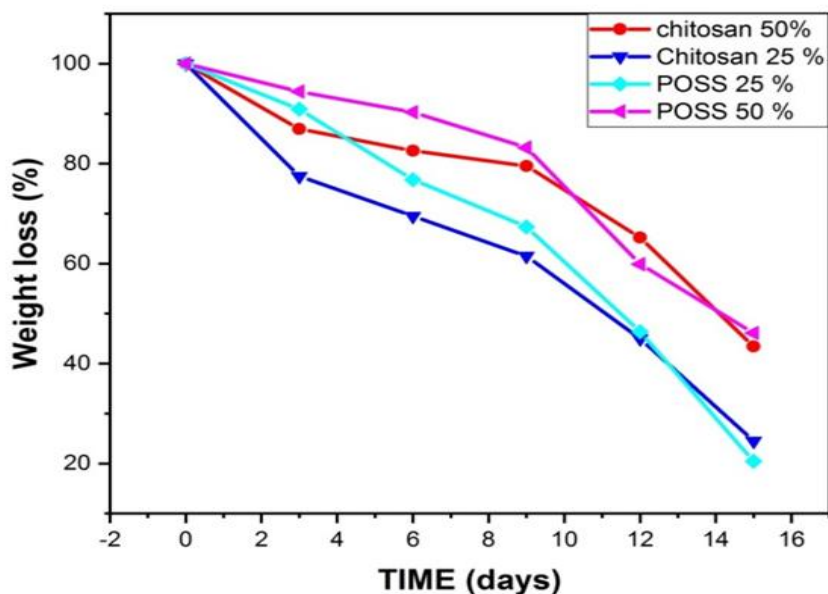


Figure 15:- Comparison of soil burial test for chitosan and POSS containing cellulose films.

In general when we compare cellulose-POSS and cellulose-chitosan containing films biodegradability, all films show biodegradability property in different percentages, Where POSS containing films show slow degradation when compared to chitosan containing film. As shown on the above figure the film containing 25% chitosan degrades faster than 25% POSS and 50% containing chitosan film degrades faster than 50% POSS containing cellulose film. Generally when we see the films degradation property as the amount fillers in cellulose film increases the slower weight losing property is observed. This was because the function of filler mostly filled the voids in the Cellulose film.











Sample name	Before burial	After six days
Control		
2.5% Chitosan		
5% Chitosan		
25% POSS		
50% POSS		

Figure 16:- Comparison of samples before and after soil burial test

4.6 Thermal decomposition of the films

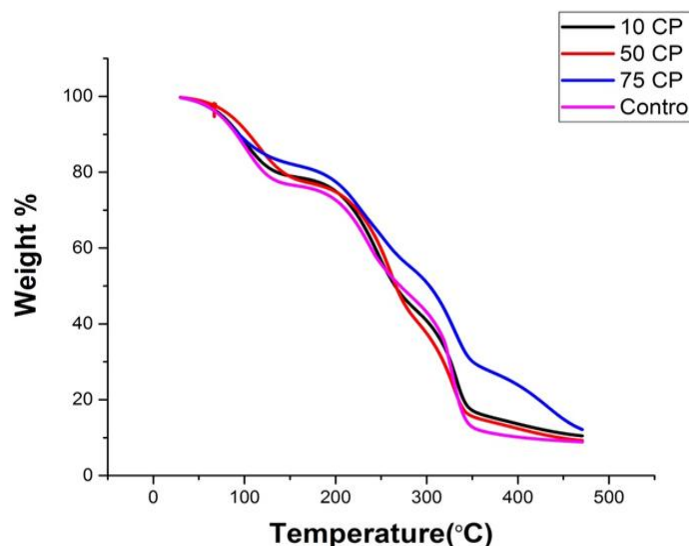


Figure 17:- TGA graph of POSS containing samples

The results of the TGA of the cellulose-POSS film are shown in Figure 17. The thermal analysis of the samples is carried out under a stream of nitrogen at a heating rate of 10 °C/min. For the TGA results, temperatures from 10 to 500 °C are used, and the observed weight loss appears in three stages, as follows: The first stage of degradation is from 65 to 100 °C, the second stage of degradation is from 100 to 250 °C, and the third degradation is from 250 to 350 °C. The population of the silanols and water molecules (65 to 100 °C) corresponds to the water molecules that are released in the hybrid composites that are present in the outer spherical surface of the particles, as well as on the inner-pore walls. The surface of the spherical silica consists of a very small portion of free silanols, a large amount of hydrogen-bonded silanols, and adsorbed water molecules. The intensive thermal degradation of the cellulose-POSS film is observed approximately between 100 and 250 °C for the cellulose-POSS film. And also as the amount of POSS in a cellulose film increase the thermal stability also increase. This increase of the degradation temperature shows that the strong organic/inorganic-phase interaction greatly influences the thermal resistance. The third step of the thermal-decomposition curve indicates a correspondence to the cellulose-POSS with the addition of inorganic content. The third degradation shows losses from 250 to 450 °C. Therefore, from this result as the amount of

inorganic moieties that are present in the cellulose-POSS film is increased the thermal stability increases.

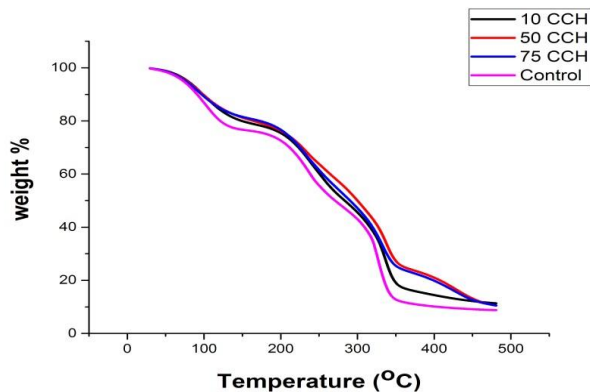


Figure 18:- TGA graph of Chitosan containing samples

From Figure 18 the degradation occurred in three steps. The first thermal event around 60-120 °C was denoted dehydration of the samples. The second step of degradation occur from around 120-250°C and the third step is from 250-350°C, where the main mass loss step is occurred. The cellulose film in which chitosan was added shows more thermal stability than control film. Also as the added amount of chitosan increases the thermal stability is increasing.

The films with filler shows improved thermal stability when compared with control film. Among the fillers the film prepared by composition 50% of POSS shows slightly improved thermal stability when compared with other films.

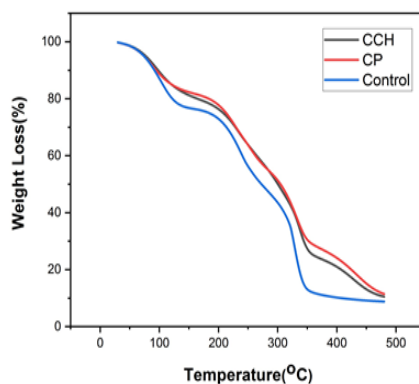


Figure 19: comparison of TGA for POSS and chitosan containing films.

CHAPTER FIVE

Conclusion and Recommendation

5.1. Conclusion

Generally, in this study on the preparations and characterizations of enset cellulose based bio-plastic and investigation of its physicochemical properties we lead to draw the following conclusions.

- ✓ Bio-based packaging materials offer a versatile potential in case of packaging industry. The selection of packaging form and materials should be primarily based on considerations of food safety, followed by quality, cost, etc.
- ✓ Cellulose is a desirable candidate for making plastic material due to its abundance, world wide availability, low cost and promising film forming properties. Enset is comprised of high quantity of cellulose to approximately 67.76 % of the dry weight base.
- ✓ A combination of alkaline extraction by NaOH and bleaching by H₂O₂ is used for the extraction process of the cellulose from inset pseudo stem.
- ✓ To enhance the strength of the films produced from inset pseudo stem POSS and chitosan was added in different amount as filler and glycerol is used as a plasticizer.
- ✓ The physicochemical properties of the bio-plastic film under the optimized condition were found to be mechanical property, thermal property and biodegradability.
- ✓ The added fillers show improvement in mechanical properties of the films when compared to the films produced without fillers. Additionally the film produced from POSS containing cellulose film shows good tensile strength (25.9-36.801 Mpa) than the film produced from chitosan containing cellulose film (22.7-36.45Mpa). The film which has 50% fillers (POSS and chitosan) shows optimum properties than others.
- ✓ In this study the produced plastic was tested for in terms mechanical strength (tensile and elongation at break), thermal degradation, soil burial test to check biodegradability, morphological structure by SEM and crystallinity by XRD of bio-based film produced from enset cellulose showed comparable properties to those of petroleum-based films.

- ✓ In general, bio plastics would be an appropriate alternative for food packaging materials from the viewpoint of the environmental preservation and sustainability and for its cost effectiveness.

5.2. Recommendation

While conducting this study, many interesting questions came up that were not possible to investigate further within the time frame and availability of equipment's for the project. Those are;

- To get a better insight to the enset based cellulose film one could extract the cellulose by making it Nano cellulose to see the difference with cellulose film to see how the properties change between these films.
- Future researchers could also continue with improving the blend preparation method used in this study by changing different variables such as extraction methods, drying condition, concentration and molding methods in order to gain a more even, whole and flexible film.
- Furthermore, a wider range of test and analyzing methods could be conducted. For example mass transfer rate of moisture, oxygen, aromas, oil and solutes, water-vapor-transmission test, contact angle test and dynamic mechanical thermal analysis.

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APPENDIXES

Laboratory figures

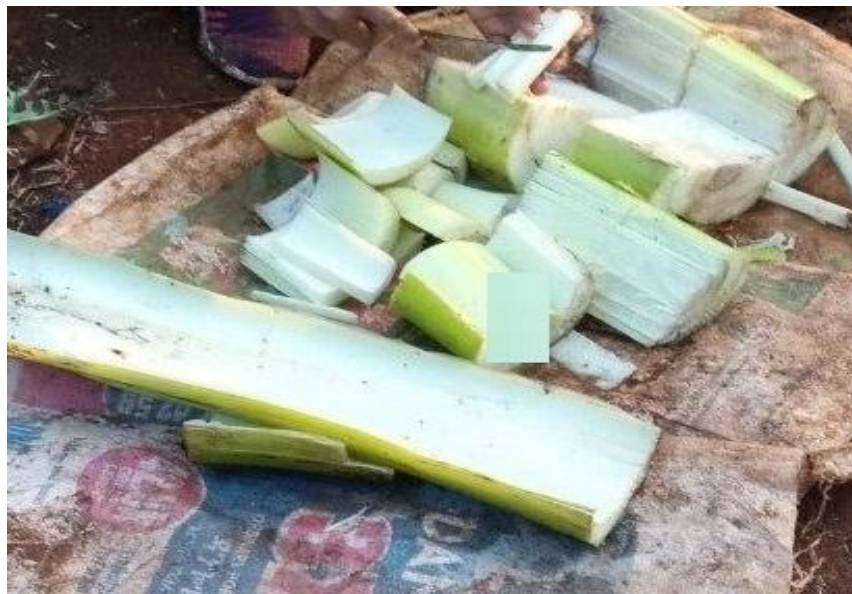


Figure 20: collecting row Ethiopian false banana pseudo stem.



Figure 21: dried false banana pseudo stem



Figure 22: Extracted cellulose



Figure 23:- electronic beam balance



Figure 24:- mechanical stirrer with combination of stove



Figure 25:- produced films