Addis Ababa University

School of Graduate Studies

Addis Ababa Institute of Technology

School of Chemical And Bio Engineering

Production of Bioplastic from Corn Starch and Sugarcane Bagasse

Gadissa Mosisa

A Thesis submitted to

The School of Chemical and Bio Engineering

Presented in Fulfillment of the Requirements for the Degree of Master of Science
(Process Engineering)

Addis Ababa University
Addis Ababa, Ethiopia
June, 2017

Addis Ababa University

Addis Ababa Institute of Technology

School of Chemical and Bioengineering

This is to certify that the thesis is prepared by Gadissa Mosisa, entitled: **Production of Bioplastic from Cornstarch and Sugarcane Bagasse** and submitted in partial fulfillment of the requirements for the Degree of Master of Science in Process Engineering complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the Examining Committee:

Internal examiner: Prof. Eduardo. Signature _____ Date _____

External examiner: Eng. Gizachew Sh. Signature _____ Date 18/07/2017

Advisor: Prof. Belay Woldeyes Signature _____ Date 17/07/2017

_____

School or Center Chair Person

ACKNOWLEDGEMENT

First, I would like to thank the Almighty GOD for giving me all his astonishing provisions, strength and patience for the successful accomplishment of this study.

At the end of my thesis, I want to thank and give credit to all individuals who have provided me with invaluable assistance. My deepest thanks go to my mother Desta Gerbiche. Mam, seeing what you have reached is a true inspiration, I would not have been able to do any of this without you're pray and support for me.

My sincere thanks also goes to all my brothers and sisters who have been always besides me, helping me psychologically, emotional, physically and materially to over-come all the obstacles I faced during my life. Thanks to them I arrive to this level and I will remain always grateful toward them for what they have been doing.

Moreover, I would like to express my heartfelt appreciation and thank to my Advisor Belay Woldeyes (Professor) for his sustainable and appreciable guidance, tireless advising, for sharing his knowledge, skill ,experience and fine-tuning up to the successful completion of this thesis. Equally thanks goes to all of my dearest colleagues specially Gemechu B., Tamitrat E., Teshale T. and Rebira W. for their cooperation and sharing experiences during my studies.

Thank you all!!! You are the best!!! Sincerely yours!!!

DEDICATION

This work is dedicated to my brothers Lemma M. , Dessalegn M. and my sis. Mulunesh M. I owe you my ever bit.

TABLE of CONTENTS

List of Tables

List of Figures

ACRONOMYS

AAiT	Addis Ababa University Institute of Technology
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
CCD	Central Composite Design
CF	Cellulose Fibre
DMTA	Dynamic Mechanical Thermal Analysis
DT	Drying Temperature
EB	Elongation at Break
FAO	Food and Agricultural Organization of Unites Nation
FRP	Fibre Reinforced Polymer
FTIR	Fourier transforms infrared
LDPE	Low-density polyethylene
MC	Moisture content
OM	Optical microscopy
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
RSM	Response Surface Methodology
SCB	Sugarcane Bagasse
SEM	Scanning Electronic Microscopy
TPS	Thermoplastic Starch
UTS	Universal Tensile Strength

ABSTRACT

There is an increasing need for biodegradable plastics because they are environmentally friendly and can replace petroleum-based non-degradable plastics which pollute the environment. Recently huge efforts are exerted in substitution of petroleum based polymers by biodegradable ecofriendly composites because of the toxic effect of the synthetic polymers. Petroleum base polymers are not sustainable as they depend on depleting fossils. This work studies the effect of bagasse (sugarcane byproduct) fiber weight fraction on starch based composite.

This study also investigated the potentials of starch and sugar cane cellulose fiber for bioplastic productions. The effect of oven drying and starch-cellulose fiber ratio was also studied. The experimental design was employed using design expert 6.0.8 two factor three level central composite designs (CCD) including five replicates at the center point of optimization study requiring 13 experiments on the 3 responses were analyzed namely tensile strength, water absorption and elongation at break.

Results have shown that the addition of cellulose fiber (5 wt%, 10 wt% and 15 wt%) to selected gram of corn starch(5g), the value obtained were for tensile strength (13.27MPa, 24.45MPa and 22.18MPa, respectively), water absorption (36.90, 23.6 and 24.01% respectively) and elongation at break (20.25, 5.268 and 9.58% respectively), these values are the averages of replication treatment.

From the analysis of experimental results the maximum and minimum value of tensile strength (26.81 and 11.55MPa), water absorption (39.02% and 20.45%) and elongation at break (25.99% and 4.32%) was obtained respectively. Starch-derived bioplastic reinforced with cellulose fiber at the optimal point of the responses namely tensile strength, water absorption and elongation at break, which are biodegradable, have been prepared and characterized for FTIR, compound microscope, Transparency, solubility, and density.

Results obtained under optimal condition were found that Transparency of reinforced bioplastic reduced by 5% with respect to the control. Also its solubility decreased from (14.78% to 10.17%) while density was increased from (1.059g/ml to1.069g/ml). Evidence of the existence of strong interactions between the starch matrix and the cellulose fibers was revealed from detailed Fourier Transform Infra-red (FTIR) and compound microscopic evaluation.

1 INTRODUCTION

1.1 Background

The word polymer is derived from the Greek, poly and meros meaning many and parts respectively. Scientists also use the word macromolecule meaning large molecule instead of polymer. The long chains of atoms which comprise polymers and the bonds within and between the chains determine plastics 'properties. Polymers alone can not be plastics. Plastics are polymers or macromolecules which have been modified with additives and mechanically strong plastic structure that adopt a dimensionally stable form. Plastics have become indispensable to modern living and no longer represent only luxury and novelty as they did in the nineteenth century. Almost 35 million tonnes of synthetic polymers are produced annually in the USA and growth is expected as long as petroleum and other feedstocks last and consumer demand continues (Mo,X.Z. 2010).

In the last 60 years, the synthetic polymers have experienced a progressive growth, constituting an important area in the polymer science. During this period these materials have invaded almost all human activities. This fact is due to their low cost, repeatability at high velocity of production and its durability, and high resistance to the physical aging and bacteriological attacks. In diverse countries the problem originated by the handling of non-biodegradable solid wastes fabricated with synthetic polymers derived from the petrochemical industry, is growing day by day. These solid wastes take about 150 years to degrade only a few grams and reintegrate to the environment (S. L. Ezeoha, *et al.*, 2013). Nowadays, plastic utilization is increasing rapidly. This is because plastics can be used in many applications such as packaging,construction and automobile parts, etc. The need for such large quantities of conventional plastics and their dominance over other materials is due to their excellent "long life" properties. These properties include resistance to chemical reactions, especially enzymatic reactions. Diverse research has been conducted to reduce the amount of plastic waste and to elaborate less aggressive products to the environment. Although the practice of recycle would seem a viable response to this problem, this is a limited solution, nevertheless not all the countries have the economic and technological infrastructure for its implementation. Thus, there is a great interest in the production of diverse biodegradable materials with similar functional characteristics that can replace the commercial plastics (Mantia et al, 2011).

Biodegradable polymers, specifically from renewable resources, are being examined for replacement of synthetic plastics. The most common ASTM definition of biodegradable polymers, states that a degradable polymer is one in which "degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Biodegradable polymers may be converted back into carbon dioxide after their use. With this ability, polymers that are produced by renewable resources may create a "carbon neutral" life cycle in which the net amount of carbon dioxide released into the environment remains relatively constant. A variety of renewable polymers are produced by plants such as cellulose, starch, and protein. Agra-polymers, typically starch and bagasse, are being examined for their sustainable nature due to vast agricultural resources available for use (Abdul Khalil et al, 2012).

The resources used in the production of renewable biopolymers are continually replenished which becomes advantageous over traditional plastics for sustainability. Typical commercial biopolymers are polylactic acid (PLA), polyhydroxyalkanoates (PHA), starches, and bagasse. Some applications for PHAs range from stiff packaging to flexible coatings (B.P. Mooney, 2009). PLA can be used for flexible packaging or drinking cups as well as similar applications to polypropylene (PP) and polystyrene (PS) (Cao *et al.*, 2006). Applications for starches reside mainly with food packaging (Janssen and L. Moscicki, 2009). Where starch products are known for their highly hydrophilic nature, current applications are limited. When comparing the mechanical properties of synthetic and biodegradable plastics, there is a wide range of values for the strength of both classes of materials, but generally synthetic plastics are stronger than biodegradable plastics (Abdul Khalil et al, 2012). The degradation period of synthetic plastics may last up to 450 years in a landfill whereas some biodegradable polymers, starch and bagasse composites, may degrade within a few months (Fengel *et al.*, 1984). Some alternatives used for elaboration of "biodegradable plastics", are the biopolymers (starch, proteins and others). These macro-molecules are biologically synthesized or fabricated by chemical processes from natural sources (Guilbert 1992), and can be modified by diverse processes. However, most of these biopolymers individually processed showed poor mechanical properties and lack of dimensional stability resulting in very fragile products. An alternative to diminish this problem is the incorporation of reinforcing materials within the matrix of the polymer like natural fibers. The amount and type of fiber added to the thermoplastic starch compositions will vary depending upon the desired properties of the final molded article, with tensile strength, mechanical

resistance, toughness, flexibility, dimensional stability and cost. Natural fiber is mainly formed of cellulose, which is the most abundant natural polymer that has been investigated, with its derivatives, as potentially biodegradable raw materials. However, the natural cellulose, in case single, cannot be processed easily to be used like biodegradable material, it can be used like a reinforcement agent of other polymers, or by means of chemical modifications that alter their ordered structure this can be used individually as it is the case of cellulose acetate (Armelin, 2002), although any type of modification made to the raw materialinvolvesve additional costs.

Basically the technique used to manufacture synthetic plastics can be used for the manufacturing of biodegradable materials. The solvent casting process of thermoplastic solution is the most utilized technologies at laboratory scale for the plastic manufacturing. Some researchers have reported that these processes can be utilized individually or together for the development of new thermoplastic products which can be used like biodegradable materials for the production of diverse degradable materials with similar or better characteristics than those of commercial plastics, although, with the advantage of decreasing the adverse effect of waste disposal on the global environment (Carr and Cunninghan, 1989).

In this research, environmental friendly plastic was produced using the addition of cellulose fiber as a reinforcement material in corn starch matrix and glycerol as a plasticizer in the process of solvent cast method.

1.2 Statement of the problem

The world production of plastics is estimated to be more than 100 million tons per year. Therefore, such large quantity of conventional plastics and their dominance over other materials is due to their excellent long life properties. These properties include resistance to chemical reactions, especially enzymatic reactions. For example, it can take up to five hundred years to degrade only a few grams of plastic (such as polyethylene) under normal environmental conditions. Degradation at high temperature, such as in pyrolysis (burning) tends to cause emission of toxic fumes. Plastic accumulation in the environment, thus creates tremendous problems for the world, presently and in the future. Plastics, though useful, has become a serious environmental problem of the plant and many countreis when though is a put. Environmental problems caused by plastic include changes in the carbon dioxide cycle, problems in composting, and increased toxic emissions. Being non-biodegradable, they choke the earth for hundreds of years, making the soil infertile. By clogging sewer pipes, plastic grocery bags also create stagnant water; stagnant water produces the ideal habitat for mosquitoes and other parasites, which have the potential to spread a large number of diseases, such as encephalitis and dengue fever, but most notably malaria (Lem Ethiopia, 2006).

Among the most disgusting and not attractive yet seeming to be in all place items in solid waste in Addis Ababa today are the discarded low-density polyethylene (LDPE) plastic bags. The quantity of LDPE plastic bags in solid waste management has increased dramatically during the last 10 years and is expected to increase due to their convenience for carrying groceries and subsequently for refuse. Shops usually hand out these bags free of charge to shoppers. These thin plastic bags do not contribute much in terms of volume to municipal solid waste, but the main problem is the disposal of these bags in streets, streams, rivers, ditches, gardens, parks, and trees and they are therefore a serious environmental hazard as well as compromising the aesthetics of the urban and rural landscape. The plastic bags are usually made from non-biodegradable substances, which do not break down readily in the environment but take several thousand years to degrade. The other thing is films formed from starch are brittle and difficult to handle. Plasticizers are normally added to the film-forming solution before casting and drying procedures, as a way to overcome films brittleness.

Unfortunately, plasticizers generally decrease the film water vapor permeability (Gontard *et al*, 1993). In order to improve starch-based film characteristics, many researchers reported results with the addition of natural fibers as a suitable reinforcing component for thermoplastic materials. Most of these works focused on films' mechanical properties and have shown that fibers incorporation increases films' tensile strength and elasticity modulus and decreases their elongation capacity (Curvelo, 2001; Dufresne *et al*, 2005).

Plastic grocery bags also have the potential to leach their chemical components and toxins into soil and water sources, which can be passed on to humans, resulting in health dangers such as neurological problems and cancers. Loss of livelihood is another major social impact connected to the use of plastic grocery bags. Two examples are the loss of livestock and impacts on tourism. Concerning livestock, plastic grocery bags are often caught in trees or along fences, where they are mistakenly eaten by animals, leading to suffocation or blockage of digestive tracts, and eventually death (FAO, 2007).

The depletion of petroleum resources coupled with awareness of global environmental problem provides the alternatives for new green materials that are compatible with the environment and their development is independent of petroleum based resources. There are a number of alternatives by which one can avoid the impact of waste plastic on the environment. Among these developments of natural fiber (agricultural and industrial by product) reinforced biodegradable plastic promotes the use of environmentally friendly materials (Ave´rous *et al.*, 2001).

1.3 Objectives of the research

1.3.1 General objective

The general objective is to develop and evaluate bio-plastic from corn starch reinforced with sugar cane bagasse cellulose fiber.

1.3.2 Specific objectives

- To prepare and evaluate mechanical properties of bioplastic namely Tensile strength and elongation at break
- To investigate the water absorption of produced bioplastic
- Optimization of oven-drying temperature and cellulose fiber concentration
- To characterize physicochemical properties of bioplastic such as fouirier tranisform infrared spectrophotometery, water solubility, transparency and density of the film.

1.4 Significance of the study

Successful completion of the research will able to play a great role by providing a remedy for the bottle necked problems of environmental pollution due to the discharge of the waste plastics. One of the advantages related to the use of biodegradable plastics is the minimal emission of carbon in the air during the process of manufacturing bio-plastics.

The manufacturing process of bio plastics requires less amount of energy. Since less energy is needed, more bio plastics can be produced while there is less pollution in the environment when disposed. Plastics that are non-biodegradable are brought to landfills to discard them with seriously environmental damage. If bio-plastics are used, there is no need to add more landfills since these plastics can be absorbed by the soil and be converted to compost or humus.

Therefore, the research contributes much of the management of plastic wastes with the content of environmental protection. The research can also be used as a benchmark for further study and it revealed the potential usage of natural fiber and starch as a raw material for the production of bio plastic, which in turn reduces emission of carbon that is added to the greenhouse effect and global warming.

2 LITERATURE REVIEW

2.1 Global overview of bioplastics

According to the European bio-plastics organization, bioplastics can be defined as plastics based on renewable resources (bio based) or as plastics which are biodegradable and/or compostable. Bioplastics have many different renewable sources such as vegetable oil, corn starch, potato starch, fibers obtained from pineapple, jute, hemp, henequen leaves and banana stem (Siracusa et al, 2008). Major source of starch for bioplastics is corn, although starches from potato, wheat, rice, barley, oat and soy sources are also used nowadays (Guilbert *et al*., 1997). The bioplastic aim is to emulate the life cycle of biomass, which includes conservation of fossil resources, CO_2 production and water (Wikipedia, 2017).

Bioplastics are organic polymers, which can be processed in various different ways. Polymers (from the Greek Poly = many, mirrors = particles) are long-chain molecules (macromolecules), that can also be branched. Their technical properties, such as formability, hardness, elasticity, rigidity, heat resistance and chemical resistance, can be varied across a wide range by selecting the correct raw materials, manufacturing process, and additives. Plastics are lighter and more economical than many other materials. For these reasons, plus their extreme versatility and excellent process ability, they are the material of choice in many industrial and commercial applications (Obara, 1995). Since the widespread availability of petroleum at the beginning of the 20th century, most traditional plastics have been produced using petroleum.

Bioplastics consist in a large part, or even completely, of renewable resources. Thus bioplastics are bio based plastics. Biodegradable, but petroleum based plastics, is not considered as bioplastics. The first modern plastics from renewable resources, which appeared on the market at the end of the 1980s, were generally biodegradable. The new products were also advertised with this feature. This revealed that the term “bioplastic” was often linked less with the renewable resource base, but more with the property “biodegradation”. From today’s perspective, the biodegradability is not a mandatory criterion for a bioplastic, but merely a special property of some biobased, but also some of petrochemical plastics (Endres & Siebert-Raths, 2009). Oil and natural gas are the major raw materials used to manufacture most plastics. Replacing petroleum-based plastics with plastics made from renewable raw materials, such as plants, reduces our

dependence on fossil fuels. Replacing petroleum-based plastics with plastics designed to degrade, biodegrade, or compost can provide even more environmental benefits.

2.2 Potential of bioplastic production in Ethiopia

The bio-plastic has a significant contribution. Thus, developing in a wider range of disposal at lower environmental impact worldwide but, in Ethiopia it is not considered as legislative attention even Ethiopia has many options to produce bio-plastics from agro – industrial wastes and other byproduct those has a potential to produce and commercialize this environmentally friendly bio-plastic which can eliminate environmental problems. Also, it creates job opportunities from raw material collection to produce the product. This paper was done to explore this potential to produce environmentally safe product for huge amounts of wastes generated throughout our country.

According to the literature (Endres & Siebert-Raths, 2009) production of bio-plastics from cornstarch and sugarcane bagasse fiber is not a new technology but improving the mechanical properties of the product should baddressedss. The plastics made in this work were supposed to be used as packaging material. So, the aim of this work was to investigate how the addition of cellulose fibers in a starch matrix using glycerol as a plasticizer and water as a solvent improves mechanical properties of bio-plastic at different concentration and investigate the optimum concentration which gives better mechanical and improved water absorption resistant properties. These results are not available in the literature and very important to evaluate possible applications of these films as packaging material.

2.3 Challenges and opportunities for development of bioplastic from renewable resource

Over the last several years, production of polymers from renewable resources has shown significant growth. Some of the plastics produced from renewable resources such as vegetable oil, corn, and pea starch have been synthesized by microbes and are known as bioplastics. Their development is driven by current demands to replace fossil fuel-based polymers. It all starts with growing plants such as sugar cane and corn that are high in starches. Limitation in fossil fuel resources, price volatility, impact on the environment, and waste disposal problems are some of the main reasons for this shift toward bio-based plastics. The environmental impact caused by

petroleum-based packages have been increasing researches aiming the use of biodegradable materials based on renewable resources (Moad, 2011). Natural fibers have recently become attractive to researchers, engineers and scientists as an alternative reinforcement for fiber reinforced polymer composites. Due to their low cost, fairly good mechanical properties, high specific strength, non-abrasive, eco-friendly and bio-degradability characteristics, they are exploited as a replacement for the conventional fiber, such as glass, aramid and carbon. The tensile properties of natural fiber reinforce polymers (both thermoplastics and thermosets) are mainly influenced by the interfacial adhesion between the matrix and the fibers. Several chemical modifications are employed to improve the interface matrix–fiber bonding resulting in the enhancement of tensile properties of the composites. Sugarcane crop and its principal as well as byproducts are cheaper because the manual labor is far cheaper and easily available whenever and wherever it is needed in developed and developing countries. In these regions, bagasse fiber has been used since ancient times to prepare ethanol, chop wood, paper, bioelectricity, and used as growth substrate in biological sulfate reduction processes (Abdul Khalil *et al.*, 2012). Compared to locations, butyrates, valerate and other monomer used for synthesis of biodegradable polymers, starch is an inexpensive product whose transformation into a thermoplastic polymer can be accomplished in a rather straight-forward manner (Teixeira, 2009). Thermoplastic starch is considered one of the most promising biopolymers for large scale application (Cha & Chinnan, 2012). As a result, numerous works have been published evaluating their mechanical and thermal properties, water uptake behavior, and degradation kinetics in an attempt to adapt these parameters to the technical demands of potential applications (Aydinli, M. and Tutas M. , 2000). Starch-based films have promising application in food packaging, because of their environmental appeal, low cost, flexibility and transparency. Nevertheless, their mechanical and moisture barrier properties should be improved. The aim of this work was to enhance these properties by reinforcing the films with cellulose fibers. Besides, the influences of both the solubility coefficient of water in the films and the diffusion coefficient of water vapor through the films on the films' water vapor permeability were investigated. Films were prepared by the so-called casting technique, from film-forming suspensions of corn starch, cellulose fibers, glycerol and water. Films based on starch and fibers have suitable mechanical properties and could be used for packaging production (Muller *et al.*, 2009). One possible application for these films is in the manufacture of bags for packaging materials with "dry" surfaces (e.g.,

tomatoes, apples clothes, among others). The characteristics of polymer-based films are strongly dependent on the film formation process (Lafargue *et al*. 2007). Classically, these films are made by the casting technique, which consists in spreading a film-forming solution or suspension on Petridis or plates, in which the film thickness is controlled by the mass of suspension poured onto the plate. The drying process of these films usually takes place at room temperature or in an oven with air circulation at temperatures of 30–40°C (Müller *et al*. 2009; Javanmard *et al*. 2011). Properties of certain bioplastics like thermal instability, difficult heat solubility, brittleness, low melt strength, high water vapor and oxygen permeability of PLA limit their use as films in food packaging applications (Rhim et al., 2009). Other starch- and cellulose-based packaging materials due to their hydrophilic nature possess low water vapor barrier, which is responsible for poor process ability, brittleness, vulnerability to degradation, limited long-term stability and poor mechanical properties (Cyras et al., 2007). Many different methods have been employed to enhance the properties of bioplastics especially improving gas and water barrier properties. Some of the strategies are coating, blending, addition of nanoparticles, addition of cellulose, chemical/physical modification, etc.

According to valentes (Nishino *et al.*, 2013) untreated sugarcane bagasse reinforced in starch matrix results high water absorption properties and also incompatibility between the fiber and matrix. This suggested that changes in surface chemistry caused an increase in the affinity of the fibers for water absorption. During chemical pulping of the fiber, hemicellulose and lignin were removed (SGRICCIA, 2008 and OGUNSILE, 2006), thus making the cellulose available for composite formation. The hydroxyl group of the cellulose reacted with the functional group, which in turn bonded to the polymer matrix and thus established a good fiber/matrix bonding interaction (MARIATTI, 2008). Strong intermolecular fiber-matrix bonding decreases the rate of moisture absorption in bio composites. Thus, the chemical treatments of the sugarcane bagasse fiber resulted in a decrease in the water absorption of the bio-composites. Furthermore, the tensile strength and modulus of the untreated SCB was improved relative to the treated fibers. The pretreatment of the fiber by pulping improved the fiber-matrix interaction, leading to a higher value of modulus and tensile strength (Rasidi et al.2014). There are previous studies about fiber damage during processing (Janssen and L. Moscicki, 2009) they analyze mainly the effect of shear rate and temperature of manufacturing on final fiber length. The presence of bubbles in the specimens was attributed mainly to the gelatinization process and to improper mixing

(Torres F. Arroyo, 2007). However, the effect of fiber concentration of damage is not completely analyzed and understood. In recent years, some companies have started the mass production and commercialization of several starch-based biodegradable polymers. Nevertheless, research is still needed to properly adapt the mechanical properties, water uptake and/or degradation kinetics of TPS to any particular application (flower et al. 2012). In the particular case of mechanical properties, the most common way to increase them is through the utilization of reinforcing elements and optimization of those properties. Give the eco-friendly character of the TPS matrix, the use of biodegradable fiber, such as those obtained from natural plants seems that most adequate option (Faruk et al. 20012). This work, attempted to take advantage of the high toughness of cellulose fibers from sugarcane bagasse fiber to use them as the reinforcing element of a thermoplastic matrix. Sugar cane bagasse fiber submitted to chemical treatment to isolate cellulose fiber. After isolation of cellulose fiber were used to prepare fully biodegradable fiber reinforced thermoplastic composite and their tensile, elongation at break and water absorption was evaluated. The obtained result was compared with that of zero fiber. In general, the tensile strengths, elongation at break and water absorption of the natural fiber reinforced polymer composites has a problem found in literature so in this work the ratio or concentration of cellulose from sugarcane bagasse fiber was studied and identify the fiber content, up to a maximum or optimum value which gives improved tensile strength and water absorption and also starch-cellulose fibre bioplastic was investigated for their optimal tensile strength, water absorption and elongation at break and may show the same trend with (Khoathane et al, 2008) found that the tensile strength and elongation at break of composites reinforced with bleached sugarcane bagasse fiber increased incredibly with increasing fiber loading.

2.4 Greening bioplastics

The use of synthetic polymer materials has caused significant environmental problems. Solid waste from these materials is a major contributor to environmental pollution as it can takes thousands of years to degrade. Therefore, a great deal of attention has been given to the development of various biodegradable materials. The worldwide consumption of biodegradable polymers has increased in the last few years. The natural biodegradable materials include packaging materials (trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable Nonwovens (engineered fabrics) and hygiene products (diaper back

sheets, cotton swabs), consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys), and agricultural tools (mulch films, planters). Starch based biocomposites can be produced by blending or mixing as different natural polymers. The tensile strength (TS), percent elongation at break (%E), tear resistance and impact strength of biocomposite films were made with different types of starches such as normal cornstarch, waxy corn starch, high amylose corn starch (50% amylose and 70% amylose), wheat starch, potato starch and tapioca starch have been used for the preparation of films (Lawton, 1996). Thermoplastic starch (TPS)/cellulose fiber composites have been prepared by using fibers from different sources, such as flax and ramie fibers, potato pulp fibers (Dufresne *et al*., 2000), bleached leaf wood fibers (Averous *et al*., 2001), bleached eucalyptus pulp fibers (Curvelo *et al*., 2001), wood pulp fibers (Carvalho et al., 2002), and cassava bagasse fibers (Teixeira et al., 2009, Sariffuddin *et al*., 2012). It was observed that the mechanical properties of TPS/cellulose fiber composites were found to be higher. Mao *et al*. (2000) have studied the improvement of the properties of cornstarch blended with poly (vinyl alcohol) (PVA) and glycerol. The blending of starch-glycerol with PVA resulted in significant improvement in both tensile strength (TS) and elongation at break. Bamboo fibers were used as reinforcement with biodegradable resin. It was observed that the mechanical properties of biocomposites were found to be higher. (Galicia-Garcia, 2011), have studied the tensile strength of composites prepared by starch/banana and starch/bagasse fiber by compression molding using glycerol and crude glycerin as plasticizers. Ramirez *et al*. (2010) studied the composites based on coconut fibers and cassava and corn starches. The increase in the tensile strength of the composites was observed. Native starch (corn, potato and waxy corn) and phosphorylated cornstarch blended with bagasse fiber and glycerol has been used for the preparation of biodegradable films (Garcia *et al*., 2011). Cellulose fibers from recycled newspaper were used as reinforcement for thermoplastic starch. The composites were prepared from corn starch plasticized by glycerol and cellulose fiber content ranging from 0 to 8% (wt/wt of fibers to matrix). The mechanical, thermal and water resistance properties of composite films were improved (Wattanakornsiri *et al*., 2011). Biocomposites of thermoplastic sago starch (TPSS) and kenaf core fiber (KF) were prepared at different fire loading (0-35 wt. %). Thermal and mechanical properties of the composite films were found to be improved (Sariffuddin *et al*., 2012).

2.5 Structure of bio-plastics

Biodegradable polymers tend to consist of ester, amide, or ether bonds. In general, biodegradable polymers can be grouped into two large groups based on their structure and synthesis. One of these groups is agro-polymers, or those derived from biomass (Luc Avérous, 2012). The other consists of biopolyesters, which are those derived from microorganisms or synthetically made from either natural or synthetic monomers. Agro-polymers include polysaccharides, like starches found in potatoes or wood, and proteins, such as animal based whey or plant derived gluten (Luc Avérous, 2012). Polysaccharides consist of glycosidic bonds, which take a homicidal of a saccharide and binds it to an alcohol via loss of water. Proteins are made from amino acids, which contain various functional groups (Cox *et al.*, 2008). These amino acids come together again through condensation reactions to form peptide bonds, which consist of amide functional groups (Cox *et al.*, 2008). Examples of biopolyesters include polyhydroxybutyrate and polylactic acid (Luc Avérous & Eric Pollet, 2012).

2.6 Plastic production from renewable resources

Polymers are very common in nature and used in many industrial processes. By the annually produced volume, cellulose, chitin, and lignin are most abundant. Currently, lignin and chitin have no notable commercial applications as plastic materials, but their use as filler for rubber and thermoplastics, and as prepolymers is being intensively studied (Chen *et al*., 2012). Among the natural polymers, only cellulose and starch is used for the industrial production of bio-based plastics. Biobased plastics can be produced from a wide range of plant-based raw materials. On the one hand natural polymers, i.e. Macromolecules that occur naturally in plants, etc., are used, and on the other hand smaller molecules, such as sugar, disaccharides and fatty acids (plant oils), are used as the basic raw materials in the production of bio plastics. All of these renewable resources can be obtained, modified and processed into bio-based plastics.

2.6.1 Matrix material: starch

75% of all organic material is present on earth in the form of polysaccharides (E.S. Stevens, 2002). An important polysaccharide is starch. Plants synthesize and store starch in their structure as an energy reserve. It is generally deposited in the form of small granules or cells with diameters between 1-100 μm (O.B. Wurzburg 1986). Starch is found in seeds (i.e. Corn, maize, wheat, rice, sorghum, barley, or peas) and in tubers or roots (i.e. Potato or cassava) of the plants (Abdillahi et al., 2013). Most of the starch produced worldwide is derived from corn, but other types of starch such as cassava, sweet potato, potato, and wheat starch are also produced in large amounts. Starch is one of the natural polymers that have been used as a matrix for the production of reinforced biodegradable materials due to its characteristics of thermoplasticity, strong hydrophilicity, and renewability, low cost and high availability (Cha and Chinnan, 2004). Native starch is basically formed of two polymers with different primary structures: the amylose (20-30%), and the amylopectin (70-80%) a branched molecule. The molecules of amylose and amylopectin have masses that vary from 105 to 107 g/mol respectively (Whistler et al 1984). Potato accumulates starch to approximately 75 % of the dry weight in the tubers with a yield up to 21 ton starch per hectare, while corn seeds consist of 65-80% starch by weight, with an average yield of 4.9 ton starch per hectare (Cox *et al*, 2008). Starch is a polymer of high availability in the nature, and it is extracted from diverse sources of cereals (corn, wheat, rice, and others), tubercles (potato, tapioca, and others), roots and in lesser proportion of some fruits and legumes. The world-wide starch production in 2000 was 48.5 million tons that were extracted principally from corn, wheat and potato. Starch molecules have two important functional groups: -OH groups, susceptible to substitution reactions, and the C-O-C linkages susceptible to the breaking of the chains. The modification affecting these functional groups or the introduction of some chemical agents modify the structure of the chain, increasing viscosity, reducing the water retention and increasing the resistance to the mechanical effort of starch. The thermoplastic starch is strongly hydrophilic, can be used as a matrix of biodegradable materials or in a partial substitution of some components in traditional plastics. The mechanical properties of the films from starches are generally inferior to those of synthetic polymers, however, when a plasticizing agent as water is added, these materials improve their mechanical properties (Cha and Chinnan, 2012).

2.6.2 Plasticizing agents

The plasticizing agents are additives frequently used in some types of polymeric materials, with the objective of improving processabillity and to increase the flexibility and extensibility, inducing changes in the photochemical and mechanical properties. The plasticizing agents are compounds of low volatility that can be solid or commonly liquids of high molecular mass. The basic requirements for a plasticizing agent are: a) compatible with the components in the formulation of the polymeric material, indicating the existence of similar intermolecular forces between the two components and b) null volatility. The mechanism of action of the plasticizing agent consists of a decrease in the intermolecular forces between adjacent polymeric chains, it makes that the plasticizing agent acts as lubricant allowing the macromolecules freely slip some over another. The types of plasticizing agent can affect the mechanical properties, since they cause a decrease of the cohesion and tension forces, the glass transition temperature and melting temperature, however, the plasticizing does not alter the chemical nature of the macromolecules (Guilbert *et al.*, 1997). The effect of the glycerol content has been evaluated on the mechanical and rheological properties of extruded corn starch and its relation with the change in the glass transition temperature in the production of new biodegradable plastics (Yu L *et al*, 2006). The reports indicated that the glycerol is an excellent plasticizing agent for starch and improves in a great extent its technological properties. An increasing in the glycerol content decrease the values of apparent viscosity, resistance to the tension and the melting and glass transition temperatures, although, increase the percentage of elongation. There are several substances used as plasticizer for the preparation of thermoplastic starch (TPS), such as water and polyols (glycerol, glycol, sorbitol, sugars) (Yu, *et al* 2005). The use of water as a plasticizer is not preferable, because the resulting product will be brittle when equilibrated with ambient humidity (Forssell *et al.*, 1997). The use of other plasticizers (for example, glycerol) results in a rubbery material, with better properties than virgin starch in various applications. Yu, *et al* (2005) discovered that the elongation of the break of the thermoplastic starch is significantly improved by plasticization with glycol, glycerol, and hexylene glycol. The plasticized starch properties may be tuned by changing the temperature of processing, water content, and the properties and amount of plasticizers. For instance, the thermal properties of glycerol-plasticized starch are a function of water content (Gracida *et al.*, 2004). At intermediate water levels, phase separation may still occur. A biodegradation study, according to ISO/CEN 14852 and ASTM D5209-92

standards (ASTM, 2008) on films made from starch–glycerol–water mixtures confirmed that the films are easily biodegradable. Although thermo plasticization seems to be a promising method, TPS synthesized from polyol and sugar plasticizers have the tendency to re-crystallize (retrogradation) after been stored for a period of time, which results in embrittlement. Another issue is the poor water resistance and low strength, which still limits their use. The plasticizers are also usually hydrophilic and can bewashed out by water (Armelin, 2002). Solutions to improve the properties of TPS are blending, or coating with hydrophobic polymers (Ma *et al.*, 2005).

2.6.2.1 Functions of plasticizers in bioplastic production

Films prepared from pure polymers tend to be brittle and often crack upon drying. The addition of plasticizers to film-forming solution alleviates this problem (McHugh and Krochta,1994). When a plasticizer is added, the molecular rigidity of a polymer is relieved by reducing the intermolecular forces along the polymer chain. Plasticizer molecules interpose themselves between the individual polymer chains, thus breaking down polymer polymer interactions, making it easier for the polymer chains to move past each other. The plasticizer improves flexibility and reduces brittleness of the film. Polyethylene glycol, glycerol, propylene glycol, and sorbitol are the most commonly used plasticizers in edible film production (Aydinli and Tutas, 2000). Several researchers have conducted studies to evaluate the efficiency of different plasticizers in protein-based films, and have developed empirical models to describe the observed phenomena. According to (Bourtoom T & Chinnah MS, 2009) increasing the plasticizer concentration will decrease tensile strength and the type and concentration of plasticizers can affect the film solubility. Increasing the plasticizer concentration results in higher solubility. The amount of plasticizer added can cause adverse effects on film properties such as increasing mass transfer through the films. When the plasticizer concentration exceeds its compatibility limit in the polymer, it causes phase separation and physical exclusion of the plasticizer. This leads to the development of a white residue on edible films which have been referred to as “blooming” (Aulton et al., 1981). During the film-forming process, shrinkage of the films due to evaporation of water or rapid drying often causes defects such as cracks or curling in the films (Obara & McGinity JW, 1995). The addition of plasticizers such as glycerol or sorbitol is often used to reduce such defects (Ahmed, 2008).

2.6.3 Corn starch gelation processes

Thermoplastic starch is biodegradable plastic based on starch. The semi-crystalline starch granules must be broken by thermal and mechanical processing to obtain TPS (Kim et al., 1997). The important role of a plasticizer, accompanied with heat and pressure, is to break up the crystalline structure of starch granules and form a continuous amorphous polymer phase (Willett *et al.,* 2002). After TPS is produced, slight recrystallization cab occurs which improves the tensile strength, but allows more ductility (Janssen & Moscicki, 2009). Gelation of starch occurs by disrupting the crystalline structure, freeing the starch helices, producing amorphous thermoplastic starch. Heating the mixture of starch and the plasticizer is important to make the starch granules swell and amylase disperses out of the starch granules, while amylopectin is held in. Thus the gluten breaks down starch-starch –OH bonds and forms new interactions between starch and the plasticizer (R. Smith, 2005). Starch granules need at least 33% moisture to be plasticized when water used as the plasticizer. The amount of water in the mixture affects the glass transition temperature and melt flow index. However, addition of glycerol results in stronger thermoplastics due to the strong interaction forces between the starch monomer units and glycerol (Janssen and L. Moscicki, 2009). Since starch is extremely abundant from several sources, thermoplastic starch is inexpensive, biodegradable and renewable. The materials produce can also be modified by adding another additional material such as fillers (Wattanakornsiri, 2012). Owing to the ease and the ability to produce TPS using the same industrial processing techniques of the current commercial plastics including extrusion, injection molding and vacuum forming (Janssen & L. Moscicki, 2009), TPS can be an alternative to some non-degradable plastics, especially those used in short-lifetime applications.

2.6.4 Reinforced material: cellulose fiber

Sugar cane bagasse is a residue produced in large quantities every year by the sugar and alcohol industries, and is mainly used as a fuel to power the sugar mill, but a huge amount is still not used (Teixeira *et al*., 2009). Ethiopia's cane field produces 540 000 tonnes of cane tops and 270 000 tonnes of trash each year (380 000 tonnes of dry matter) and the factories produce about 476 000 tonnes (235 000 tonnes of dry matter) of bagasse (FAO, 2007). In Ethiopia production of bagasse is 1200 metric tons (http//:www.factfish.com/statistic/bagasse/Ethiopia). Several

processes and products have been reported that utilize bagasse as a raw material for industrial applications. These include electricity generation, pulp and paper production, and products based on fermentation. Recently, the interest to find new uses for natural fibers is growing due to the high production of agricultural residues and agro-industrial co-products. These materials are available, renewable, biodegradable, and recyclable; researchers (Funke, 1998) have reported that the use of cellulose fibers as reinforcement material in thermoplastic matrices, as well as its use in thermoplastic starches increased the force of tension. The lignocelluloses material is constituted by cellulose, lignin and hemicellulose in an approximate relationship of 4:3:3 varying sensitivities between the different species (Fengel and Wegener, 1984). Fibers may be added to the mouldable mixture to increase the flexibility, ductility, bendability, cohesion, elongation ability, deflection ability, toughness, and fracture energy, as well as the flexural and tensile strengths of the resulting articles. Fibers are one-dimensional, long and thin structures which principal function is the tissue formation. The useful polymers as fibers are those that have a high degree of crystallinity and strong interaction between adjacent chains; this orientation increases the tensile force (Billmeyer, 1984). Fibers have a high length to width ratio (or "aspect ratio") and are oriented throughout a single axis. They have great molecular cohesion, which makes them stronger than plastics, and for this reason they are used as reinforcement materials. Glass transition temperature and melting point are two important properties of fibers; a glass transition temperature (Tg) too high makes difficult the stretching, and therefore, the orientation of the fiber, and if the Tg is too low, the orientation of the fibre is not maintained at room temperature. A wide range of fires can optionally be used in order to improve the physical properties of the thermoplastic starch compositions because they readily decompose under normal conditions. Thermoplastic materials were synthesized by esterified modification of cellulose. The cellulose esters exhibited plasticized behaviors due to the destruction of inter- and intra-molecular hydrogen bonding in cellulose. Sugar cane bagasse is a natural composite of lignin, hemicellulose and cellulose with plenty of hydroxyl groups, which could be substituted by ester groups to enhance the material properties of sugarcane bagasse.

2.7 Starch extraction processes

Corn kernels were hand-picked and cleaned to remove foreign material, mold, and broken kernels before analysis. Starch is generally extracted from the plant by wet milling processes (Boundy *et al.*, 1967). The plant material is grounded in water, the debris is filtered from the slurry, and starch granules are obtained after centrifugation from the suspension. The starch is present in the endosperms (floury and horny), and is embedded in a proteinaceous cellular matrix. After initial cleaning to remove cob, sand, and other foreign materials, the corn kernel is softened by steeping in warm water containing (0.67% SO_2) at 45°C until the volume of the kernel increases with 55-65%. Followed by manual removal of the pericarp, germ with forceps and the rest of the kernel, which is again fed to a second milling process. The resulting suspension from the mills contains fiber, gluten, and starch. The fiber is removed using washing screens. The low density gluten is separated from the starch suspension by centrifugation. The resulting starch is further washed in a cyclone and finally dried (John *et al.*, 1999).

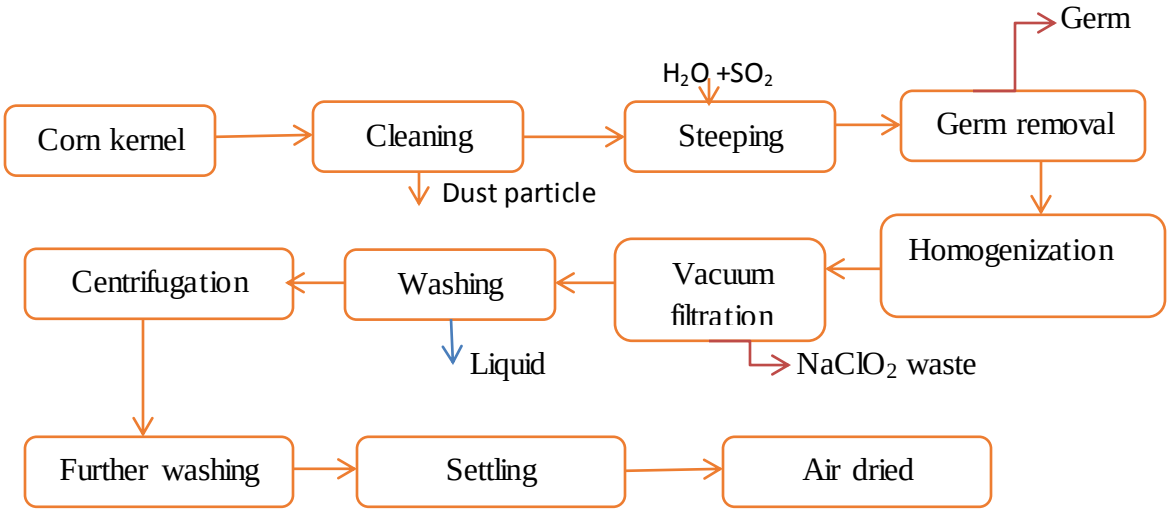


Figure 2.1 Corn starch production process flow diagram a) Typical corn-milling operation b) Cross-sectional view of a corn kernel **(**White, 2005**)**

2.7.1 Structure and properties of starch

Starch is a polymer consisting of anhydroglucose (AHG) units (see Figure 2.2a.) (Wurzburg, 1986). Two types of AHG polymers are usually present in starch: amylose and amylopectin (Muller *et al.*, 2009). Amylase is essentially a linear polymer in which AHG units are predominantly connected through α-D- (1, 4) -glucosidic bonds. The molecular weight of amylase is a function of the plant source and processing method, but usually in the range of 1.6-7 x 105 Da (Sarifuddin & Norshahida, 2012). Amylopectin is a branched polymer, containing periodic branches linked with the backbones through α-D- (1, 6) - glucosidic bonds (Wurzburg, 1986). Each branch contains about 20-30 anhydroglucose units. The molecular weight of amylopectin is higher than that of amylose and is typically 4-5 x 10^8 Da (SGRICCIA, 2008). The content of amylose and amylopectin in starch varies and largely depends on the starch source. Typically, the amylose content is between 18-28% (Wurzburg, 1986).

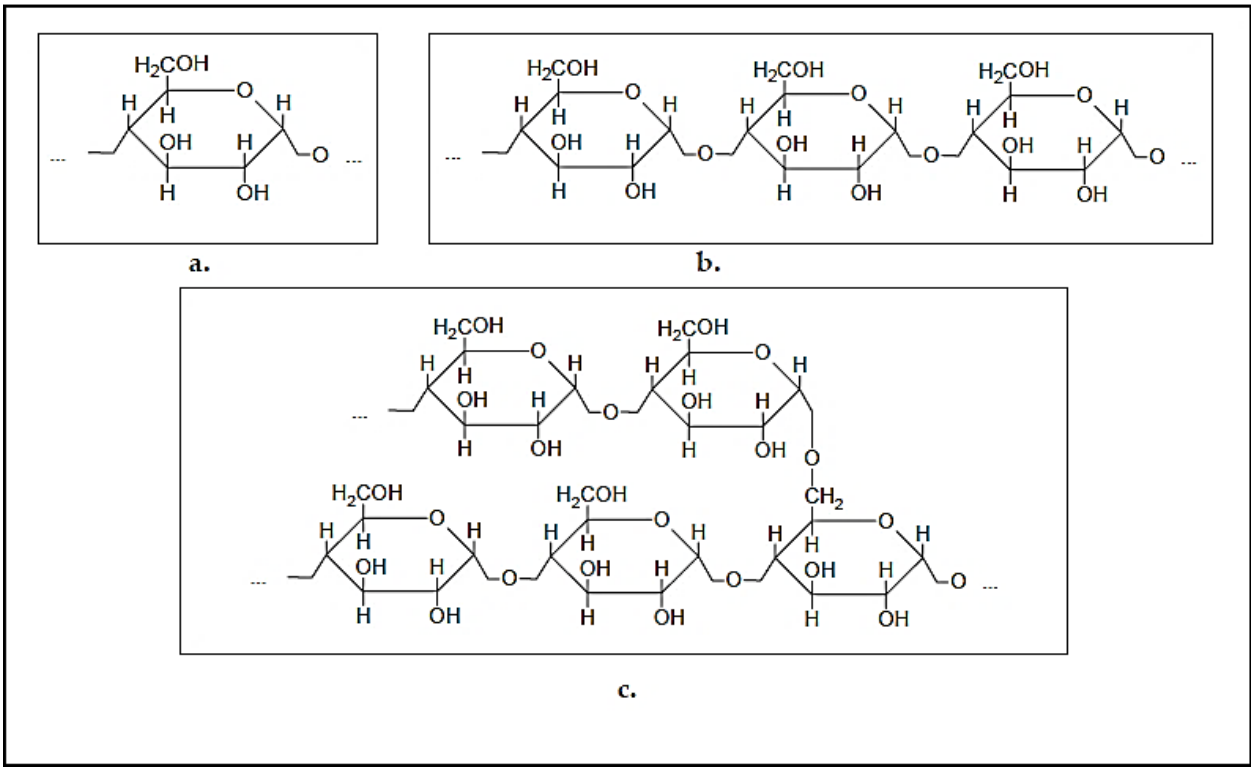


Figure 2.2 Chemical Structure of Starch: a) Anhydroglucose (AHG) unit b) Amylose c) Amylopectin

Starch is insoluble in cold water, but it is very hygroscopic and binds water reversibly. Heating a starch solution leads to loss of hydrogen bonding in the interior of the starch granule and the starch will start to gelatinize. The starch granules will swell rapidly in many times of its original volume. The linear amylose molecules leach out of the granules into the solution. The resulting suspension contains a mixture of linear amylose molecules, swollen granules, and granule fragments, and, depending on the amount of water present, will form a thick paste or gel. The gelatinization temperature range can be defined as the temperature at which granular swelling begins until the temperature when nearly 100% of the granules are gelatinized (Whistler, 2005).

Table 2.1 Amylose content of common starches raw material (Whistler R. L., 2005)

Starch	Amylose (%)
Arrowroot	20.5
Corn	28
Hybrid amylomaize class V	52
Hybrid amylomaize class VII	70-75
Oat	27
Manioc	15.7
Potato	20
Rice	18.5
Sago	25.8
Sweet potato	17.8
Tapioca	16.7
Wheat	26

Table 2.2 Gelatinization temperature range for different types of starch raw material (Whistler R. L., 2005)

Types of Starches	Gelatinization temperaturerange (^{o}C)
Potato	59-68
Tapioca	58.5-70
Corn	62-72
Waxy corn	63-72

2.8 Composition of sugarcane bagasse fiber

Bagasse consists of approximately 50% cellulose and 25% each of hemicellulose and lignin. Chemically, bagasse contains about 50% α-cellulose, 30% pentosans, and 2.4% ash. Because of its low ash content, bagasse offers numerous advantages in comparison to other crop residues such as rice straw and wheat straw, which have 17.5% and 11.0%, respectively, ash contents, for usage in microbial cultures. Also, in comparison to other agricultural residues, bagasse can be considered as a rich solar energy reservoir due to its high yields and annual regeneration capacity (Ashok Pandey *et al.*, 2000).

2.8.1 Physico-mechanical properties of bagasse fiber

The physical properties of bagasse fiber are critical, and include the fiber dimensions, defects, strength and structure.

Table 2.3 Physico-mechanical properties of bagasse fibers (Hattallia *et al.*, 2002)

Properties	Values
Tensile strength (MPa)	290
Young's modulus (GPa)	17
Density [g/cm^3]	1.25

2.9 Chemical modification of sugarcane bagasse fiber by sodium chlorite treatment

Alkalization treatment is one of the most used chemical treatments for cellulose fibers when used to reinforce thermoplastics. An important modification done by the alkalization treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness (Li, 2008). Addition of sodium hydroxide (NaOH) to botanical cellulose fibers promotes the ionization of the hydroxyl group to the alkoxide as shown in the following Equation. Therefore, the alkalization treatment directly influences the cellulose fibers, DP, and extraction of lignin and hemicellulose compounds (Jahn, 2002).

$$\text{Fiber-OH} + \text{NaOH} \rightarrow \text{Fiber-O-Na} + H_2O$$

The chemically modified natural fibres have gained the properties such as hydrophobic and hydrophilic character, heat resistant, resistance to microbial attack, thermo-sensitivity, pH sensitivity, and potential adsorbent for hazardous dyes removal, sorption, and fabrication of drug delivery system, removal of metal ions and as reinforcing material for thermoplastic, thermosetting and biodegradable polymer composites. The interest in using natural fibres for the preparation of composites has increased in recent years due to their lightweight, nonabrasive, combustible, nontoxic, low cost and biodegradable properties. Hydrophilic nature of natural fibres reduces their potential as reinforcing agents due to the low interfacial properties between fibre and polymer matrix. However, lack of good interfacial adhesion, low melting point and poor resistance to moisture absorption, make the use of natural fibre reinforced composites less attractive. The pretreatments of the fibre clean the fibre surface, chemically modify the surface, stop the moisture absorption process, increase the surface roughness and improve the fibre matrix interaction. The chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix. Many chemical treatments such as mercerization, isocyanate treatment, permanganate treatment, acetylation, silane treatment and peroxide treatment with various coupling agents etc., have been attempted for the modification of fibre surface and enhance its properties (Teixeira *et al.,* 2009)

Sodium chlorite ($NaClO_2$) is usually used for bleaching the fibres. It also delignify the lignocellulosic fibres. Flax fibres were treated with sodium chlorite for the surface modification (Liu and Huang 2013). Mishra *et al.* (2002) have been investigated the treatment of sisal fibre in sodium chlorite with a liquor ratio of 25:1 at 75°C for 2 hours. Tensile strength of bleached sisal fibre-phenol formaldehyde composite was found less than other chemical treated fibre composites. It may be due to the fact that the delignification of the fibre lowered the tensile strength of the fibres. Textile strength of okra bleached fibres has improved by grafting acrylonitrile (AN) using potassium persulphate as redox initiator. (Jacob *et al.* 2004) have investigated the thermal resistance and crystalline structure of Kenaf fibre (Hibiscus cannabinus) fibre. Rich cellulose content was found in sugarcane bagasse after treating it with sodium chlorite (Liu and Huang 2013).

2.10 Cellulose fiber from sugarcane bagasse

Cellulose fibers are derived from plants, e.g. bast, leaf, seed and wood. They are a class of hair-like materials being continuous filaments and their molecular chains are very long and strong (Kaushik *et al.*, 2010). They are aligned along the length of the fibers that provide maximum tensile and flexural strengths as well as support rigidity. Mechanical properties are mainly determined by the cellulose content, degree of polymerization (DP), and fibrillar angle. Typically, the reinforcing efficiency of cellulose fibers depends on the cellulose nature and their crystallinity. Importantly, a high cellulose content and low fibrillar angle are desired properties of fiber to be used as reinforcement for biological composites (John and Thomas, 2008). Cellulose is a polysaccharide and natural linear crystalline polymer comprising D-anhydroglucose ($C_6H_{10}O_5$) repeating units linked together by α-1,4-D-glucosidic bond (Rasal, 2010) as shown in Figure 3. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability of hydrogen bonding play an important role in directing the crystalline packing and control the physical properties of cellulose (Bourtoom, 2009). Solid cellulose forms a microcrystalline structure with regions of crystalline and amorphous material. Besides, cellulose is also formed of slender rod like crystalline microfibers (Mo *et al.*, 2010). Cellulose has received more attention for green composites since it is attacked by a wide variety of microorganisms and represented an appreciable fraction of waste products and composites that make up sewage and refuse (Lu *et al.*, 2009).

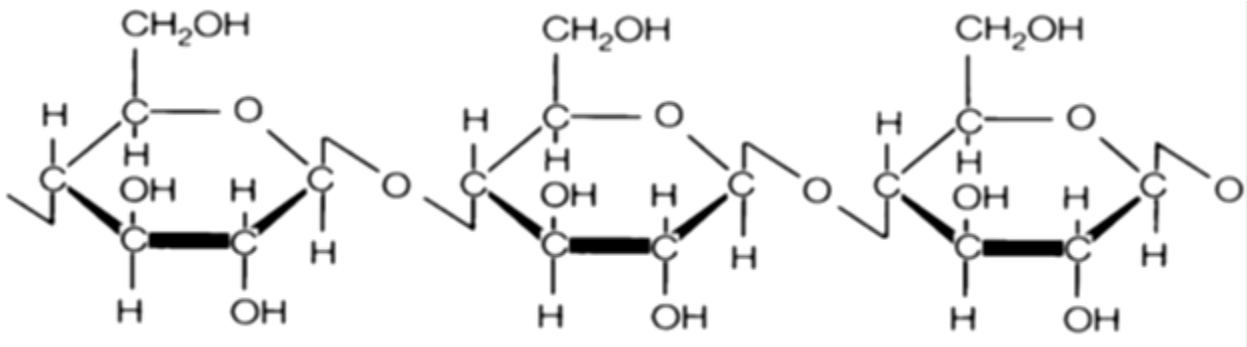


Figure 2.3 Chemical structure of cellulose (Bourtoom, 2009).

2.11 Classification of bioplastics

Bioplastics or organic plastics are a form of plastics derived from renewable biomass sources, such as vegetable fats and oils, corn starch, pea starch, or microbiota, rather than fossil-fuel plastics which are derived from petroleum.

2.11.1 Starch-based plastics

Starch is a very attractive source for the development of biodegradable plastics (R. Smith, 2005). Starch may become an attractive raw material for plastics in the future, because the price of oil based polymers may still increase due to the rise in the crude oil prices. The global production capacity of starch-based bioplastics in 2010 is estimated to increase to 200-300 kiloton per year from 77-200 kiloton in 2003. Starch is a polysaccharide produced by green plants for the storage of energy. Due to its semi-crystalline structure, which undergoes thermal degradation before the melting point is reached, native starch cannot be applied to thermoplastic processing. A bio-based plastic that is based on starch is thermoplastic starch (TPS). It can be prepared from starch granules by mixing and heating them in the presence of one or more plasticizers, typically water and glycerol, in a process called destructurization. TPS is an attractive bio-based material because starch is cheap, biodegradable, and abundantly available in large volumes. Furthermore, TPS is processable with common equipment. However, TPS is very hydrophilic which renders it unsuitable for applications in humid environments (Liu et al., 2009). This currently limits the applicability of TPS to niche products like fast dissolving dishwasher tabs or adhesive tapes. Several solutions to improve the properties of TPS were developed including the use of less volatile and less water sensitive plasticizers like sorbitol or xylitol and the addition of suitable hydrophobic fillers like lignin. Major source of bioplastics is the storage polysaccharide of cereals, legumes and tubers i.e. starch which is a renewable and widely available raw material (Park *et al.*, 2002; Tharanathan, 2003). For processing of starch, flexibilizer and plasticizer such as sorbitol and glycerine are added. After addition of plasticizers and application of thermal and mechanical energy, these constitute thermoplastic starch (TPS) could be used as substitute for polystyrene (PS). Starch works as effective packaging material when it is modified to form films that provide adequate mechanical properties of high percentage elongation, tensile and flexural strength. Starch is modified by either plasticization, blending with other materials, genetic or

chemical modification or combinations of different approaches. These starch-based thermoplastic materials such as, polyethylene-vinyl alcohol or polyvinyl alcohol, polycaprolactone have found wider industrial applications ranging from extrusion applications, injection moulding, blow moulding, film blowing and foaming (Mensitieri *et al.*, 2011; Müller *et al.*, 2009).

2.11.2 Cellulose based plastic

Cellulose is a biodegradable polysaccharide from which cellophane film can be made by dissolving it in a mixture of sodium hydroxide and carbon disulphide to obtain cellulose xanthate which is then dipped into an acid solution (sulphuric acid) to yield cellophane film (Averous *et al.*, 2001). Another way of obtaining cellulose derivatives is the derivatization of cellulose from the solvated state, through the process of esterification or etherification of hydroxyl groups (Cyras *et al.*, 2007). Further, additives are added to these cellulose esters viz. cellulose (di)acetate and cellulose (tri)acetate in order to convert them into thermoplastic material. These are processed by laminating, injection or extrusion moulding and exhibit good film forming properties (Zepnik *et al.*, 2010). Biodegradable plastics, based on cellulose acetate (CA), were studied and the produced plastic decomposed in soil or water within a few years. However, the material can be recycled, also, or incinerated without residue. There were studies of the important properties of CA including mechanical strength, impact resistance, transparency, colorability, fabricating versatility, moldability, and di-electric strength (Fischer et al., 2008). Also, CA could be used for the manufacturing of photographic films, ultra -filtration membranes, fibers and some plastic tools (Cosimo, 2013). Natural plastic is produced in a fluid form and, therefore, it is shaped easily and does not require a large amount of energy. This is to be compared with the conventional plastic which is stored usually as granules and needs a massive amount of energy so that it can be shaped by molding, injection, or extrusion (Xiaoyun and Shuwen, 2013). Many researchers used acetylation of plant cellulose fiber, such as cotton by-products; rice, wheat, rye and barley straws; and cornhusk and poplar wood fiber for the production of CA. The acetylation process was performed in supercritical carbon dioxide (Nishino *et al.*, 2011), or in an ionic liquid (Cao *et al.*,2007) and also, by phosphotungstic acid or by iodine and acetic acid (Cosimo, 2013).

2.12 Composite materials

The world production of plastics is estimated to be more than 100 million tonnes per year. This large quantity of conventional plastics and their dominance over other materials is due to their excellent long life properties. These properties include resistance to chemical reactions, especially enzymatic reactions. Under normal environmental conditions it can take up to five hundred years to degrade only a few grams of plastic (such as polyethylene). Degradation at high temperature causes emission of toxic fumes. Also plastic accumulation in the environment thus creates tremendous problems for the world, presently and in the future. Environmental problems caused by plastic include change to the carbon dioxide cycle, problems in composting, and increased toxic emissions. Being non-biodegradable, they choke the earth for hundreds of years, making the soil unfertile. By clogging sewer pipes, plastic grocery bags also create stagnant water; stagnant water produces the ideal habitat for mosquitoes and other parasites, which have the potential to spread a large number of diseases, such as encephalitis and dengue fever, but most notably malaria (U.S EPA, 2005). Plastic grocery bags also have the potential to leach their chemical components and toxins into soil and water sources, which can be passed on to humans, resulting in health dangers such as neurological problems and cancers (Kebbede, 2004).

Loss of livelihood is another major social impact connected to the use of plastic grocery bags. Two examples are the loss of livestock and impacts on tourism. Also the depletion of petroleum resources is global environmental problem. Therefore, there is demand to replace these materials with biodegradable ones derived from plant sources which provide the alternatives for new green materials that are compatible with the environment and their development is independent of petroleum based resources (Yu et al., 2006). Currently the need for a material with light weight, biodegradable and high performance is increasing day to day to avoid the entire problem. Starch-based polymers are one such material, becoming popular because of their low cost, their abundance, and ease to be chemically modified. Unfortunately, these materials are hydrophilic and absorb moisture from air and so cannot directly be used in many applications. Also, they have a tendency to undergo ‘retro gradation’ (i.e. recrystallization on storage) and become brittle and fragile with time. To overcome some of these intrinsic properties, additives (e.g., plasticizers), cross-linking agents or blending with natural fillers (e.g. cellulosic fibres) has been used (Chen et al., 2009).

The improvement of the performance for a material is limited when there is only one composition. Therefore, there have to be a new material with high performance which constitutes two or more conventional materials. According to (Averous *et al.*, 2001)composite materials refers to materials in which two or more distinct materials are combined together but remain uniquely identifiable in the mixture, having strong fibers surrounded by a weaker matrix material. The matrix serves to distribute the fibers and also to transmit the load to the fibers. Lignocellulose materials have great potential as reinforcing fibres for starch because they contain cellulosic fibres, are abundant, renewable, and have high tensile strength. Bagasse is a lignocellulose material, is a good source of cellulose fibre, and has an average tensile strength of 222 MPa (Satayanarayana et al., 2009).

2.12.1 Green composites of thermoplastic starch and cellulose fibers

TPS can be reinforced with cellulose fibers in order to improve its low resistance to mechanical stresses and moisture (Teixeira *et al.*, 2009). TPS is first introduced as matrix and cellulose fiber is then reinforced as biodegradable filler to preserve their biodegradability. There have been many studies on different starch types of TPS and varied types of cellulose fibers. Wollerdorfer and Bader (1998) first reported that the reinforced TPS prepared by wheat starch and flax and ramie cellulose fibers was four times better (37 N/mm2) than the pure TPS. The reinforcement of cellulose fibers and starch blends caused a stress increase of 52% (55 N/mm2) and 64% (25 N/mm2), respectively. Curvelo *et al.* (2001) applied cellulose fibers from *Eucalyptus urograndis* pulp as the reinforcement material for TPS in order to improve its mechanical properties. The green composites were prepared from regular corn starch plasticized with glycerol and reinforced with short cellulose fibers (16% wt/wt) from bleached pulp. The cellulose fibers were added directly to the TPS in an intensive batch mixer at 170^{o}C. The mixture was hot-pressed in 2-3 mm-thick plates and then cut to prepare the specimens for mechanical tests. The composites showed an increase of 100% in tensile strength and more than 50% in modulus with respect to the pure TPS.

Averous and Boquillon (2004) prepared green composites from wheat starch with glycerol with and without water, and incorporated natural cellulose fibers with varying lengths of 60 to 900 µm from leafwood. Particularly, TPS1 and TPS2 matrixes were prepared from the ratios of dried wheat starch/glycerol/water as 70:18:12 and 65:35:0, respectively; besides, all fibers were

supplied from companies. After extrusion and injection molding, mechanical, thermo-mechanical and thermal properties of the composites were analyzed. Dynamic thermal mechanical analysis (DMTA) showed important variations of main relaxation temperature, which can be linked both resulting interactions in a decrease of starch chain mobility and regular reinforcing effects. The results were consistent with the static mechanical behavior, which varied according to the filler content as well as fibers' nature and length. In addition, the results showed that the addition of cellulose fibers improves the thermal resistance of these green composites.

Table 2.4 Previous studies of green composites prepared from TPS reinforced with cellulose fibers.

Study	Starch type	Plasticize ratio(%wt/wt of plastcizer to starch)	Fiber type	Fiber ratio (%w/w)
Curvelo *et al.*, (2001)	Corn	30wt%(glycerol)	Eucalyptus urogradis	0 and 16
Averous and Boquillon, (2004)	Wheat	TPS1:18wt%(glycerol) and 12wt%(water) TPS2:35wt%(glycerol)		
Ma et al., (2005)	Corn	14.5wt%(urea), and 7.7wt%(formamide)	winceyette	0, 5, 10, 15 and 20
Muller et al., (2009)	Cassava	23%(glycerol)	Eyucalyptus	0, 7, 19 and 28
Teixeira et al., (2009)	Cassava	TPS1:30wt%(glycerol) TPS2:15wt%(glycerol) and 15wt%(sorbital)	Cassava bagasse	TPS_1 and TPS2: 0, 5, 10, and 20
Wattanakornsiri et al., (2012)	Tapioca	30wt%(glycerol)	Used office paper and newspaper	0, 2, 4, 6 and 8

2.13 Properties of bio-plastic developed from natural resource

2.13.1 Mechanical properties

The increase of mechanical properties, i.e. ultimate tensile strength (UTS) and elastic modulus (E), of green composites when compared with pure TPS confirms the interfacial adhesion and the strong interaction between matrixes and cellulose fibers (Martins *et al.*, 2009). Green composites prepared from corn starch (CS) plasticized by glycerol (30% wt/wt of glycerol to starch) as matrix that was reinforced with recycled paper cellulose fibers (CF) and newspaper fibers contents ranging from 0-8% (wt/wt of fibers to matrix) (Wattanakornsiri *et al.*, 2011). These results are favored by the chemical similarities between starch and cellulose fibers (Ma *et al.*, 2005). However, the percent elongation at break decreased with respect to those of pure TPS. These results could be due to the high crystallinity of the cellulose fibers, then providing higher stiffness of the green composites when compared to the pure TPS (Prachayawarakorn *et al.*, 2010).

2.13.2 Water absorption properties

Low water resistance is a major drawback of TPS for many practical applications. In fact, TPS could absorb an amount of water from the environmental humidity; as a result, the mechanical properties could drastically drop down (Kalichevsky and Blanshard, 1993). The presence of cellulose fibers decreased the amount of water absorption. This can be mainly ascribed by the addition of the cellulose fibers; in fact, they are less hydrophilic in comparison to starch (Ma *et al.*, 2005) and can absorb a part of glycerol with a reduction of the hydrophilic behavior of TPS (Curvelo *et al.*, 2001). Besides, the presence of less hydrophilic cellulose fibers significantly reduced the water absorption of TPS probably also because of the constraint exerted by the fibers at the interface on the matrix swelling (Wattanakornsiri *et al.*, 2011). Besides, amylopectin-rich TPS are more sensitive to water absorption than amylose-rich TPS (Curvelo *et al.*, 2001).

2.13.3 Functional groups

Fourier transform infrared spectroscopy (FT-IR) is a powerful technique for identifying types of chemical bonds of polymer composites in a molecule by producing infrared absorption spectrum, which is comparable to a molecular finger print. FT-IR spectra in the case of green composites, investigated by Wattanakornsiri *et al.* (2012), display the typical profiles of polysaccharide. where CS-NF_0, NF_4, and NF_8 are defined to non-reinforced TPS, and green composites containing 4 and 8% wt/wt of fibers to matrix. The peaks in the range of 1,026-1,027 and 1,079-1,155 cm^{-1} are attributed to C-O stretching of C-O-C group in the anhydroglucose ring and of C-O-H group, respectively. The wave numbers in the range of 1,414-1,454 cm^{-1} are designed for O-H bonding (Prachayawarakorn *et al.,* 2011). The peak positions in the range of 1,638-1,639 cm^{-1} are owing to the bound water present in the non-reinforced TPS and composites. The bands of 2,931 cm-1 are associated with C-H stretching. Besides, the bands belonging to hydrogen bonded hydroxyl (O-H) group appear in the range of 3,414- 3,420 cm^{-1} that are attributed to the complex vibrational stretching, associated with free, inter and intra molecular bound hydroxyl groups (Galicia-Garcia *et al.*, 2011). Especially in the last case, the bands slightly shifted to lower wave numbers by the presence of cellulose fibers; referring to an increase of intermolecular hydrogen bonding by the addition of cellulose fibers. This phenomenon is ascribed that when polymers are compatible, a distinct interaction, i.e. hydrogen bonding or dipolar interaction, exists between the chains of TPS matrix and cellulose fibers, providing the changes of FT-IR spectra on the composites, e.g. band shifts and broadening (Prachayawarakorn *et al.*, 2010).

Generally in this work, corn starch and cellulose extracted from sugarcane bagasse fibre has been selected to obtain novel natural biopolymer composite materials. This work, attempted to take advantage of the high toughness of cellulose fibre as the reinforcing element of a thermoplastic matrix. After isolation of cellulose fiber were used to prepare fully biodegradable fiber reinforced thermoplastic composite and their tensile, elongation at break and water absorption was evaluated. The obtained result was compared with that of zero fiber. The relationship between the structure and properties of the composite films were investigated using Fourier transform infrared spectroscopy (FT-IR) and compound microscope.

3 MATERIALS AND METHODS

The experimental procedure for the development of bioplastic is depicted in the Figure 3.1 below. Detailed description of the process is given in the text that follows.

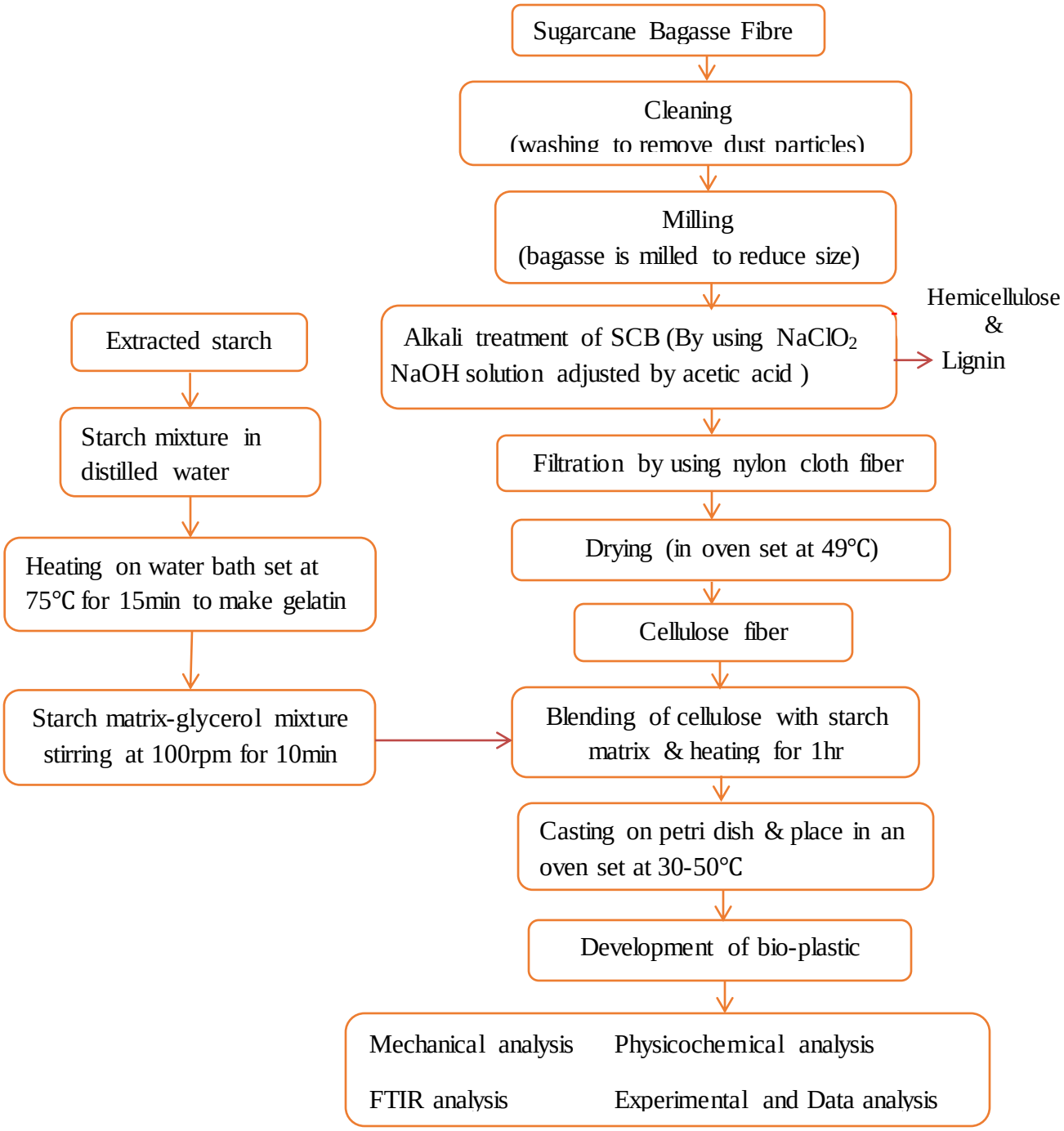


Figure 3.1 The experimental procedure for production of bioplastic from corn starch and cellulose fiber

3.1 Experimental location

Development of the bioplastic and evaluation of its physicochemical and mechanical properties are conducted at Addis Ababa University institute of Technology (AAiT), Leather Industry Development Institute and Addis Ababa University college of natural science (chemistry laboratory).

3.2 Materials

Raw materials used for this research were locally available sugarcane bagasse fiber and corn starch.

3.2.1 Laboratory equipments

Laboratory equipment for conducting mechanical, chemical and physical testing were: Analytical Weighing balance, thermometer, Beakers, water bath shaker, desiccators, measuring cylinder, burettes, micro pipettes, filter paper, magnetic stirier, heating oven, Different sized standard measuring flasks, Fume hood, UV spectrophotometer, compound microscope, Physical testing equipment (Universal Tensile Testing machine) and FTIR for functional group determination.

3.2.2 Chemicals for laboratories analysis

Chemical and reagents used used in this study are were sodium chlorite($NaClO_2$), buffer (glacial acetic acid), sodium hydroxide, glycerol, distilled water and acetone.

3.3 Methods

3.3.1 Development of bioplastic from corn starch and cellulose fiber

Materials

The raw materials used for this study were sugar cane bagasse fiber -it was kindly supplied by Fincha Sugar Factory located in horo guduru wellega zone, glycerol (chemical formula $C_3H_5(OH)_3$, Batch G120313) was purchased from Micron PLC, Addis Ababa and Corn starch which was used as a matrix were prepared in laboratory.

Equipments: The equipments used during the experimentations includes Wiley mill, sieve, strip road, Silica crucible, desiccators, digital weighing balance, weight bottle, stopper, tong, Erlenmeyer flask, water bath, vacuum suction, weighed sintered glass crucible, what-man filter paper, measuring cylinder, round bottom flask, cellulose extraction thimble, beaker, scissor, dryer, glove, mask, thermometer, stirring rod, air circulated oven.

Chemicals: chemicals used in the production of bioplastic were glycerol, sodium chlorite ($NaClO_2$), sodium hydroxide (NaOH), glacial acetic acid and distilled water was the chemicals those used in development process.

Methods

3.3.1.1 Extraction of starch from corn (maize)

Extraction of maize starch was done as described by White *et al*., (1990) modified by Krieger *et al*., (1997). First, we clean the shelled corn shipments to ensure that they are free from dust and foreign bodies. Once clean, the corn is soaked in water, called steep water, at 50˚C for between 24 hours, during which time it doubles in size. As the corn swells and softens, the mildly acidic steep water starts to loosen the gluten bonds with the corn, and to release the starch. The corn is coarsely milled in attrition mills to separate the germ from the rest of the components. The remaining slurry then leaves the separation step for fine grinding. After the fine grinding, which releases the starch and gluten from the fibre, the slurry flows over fixed concave screens which catch the fibre but allow the starch and gluten to pass through. The starch, gluten suspension is sent to the starch separators. The starch, gluten suspension passes through a centrifuge where the gluten, which is less dense than starch, is easily spun out.

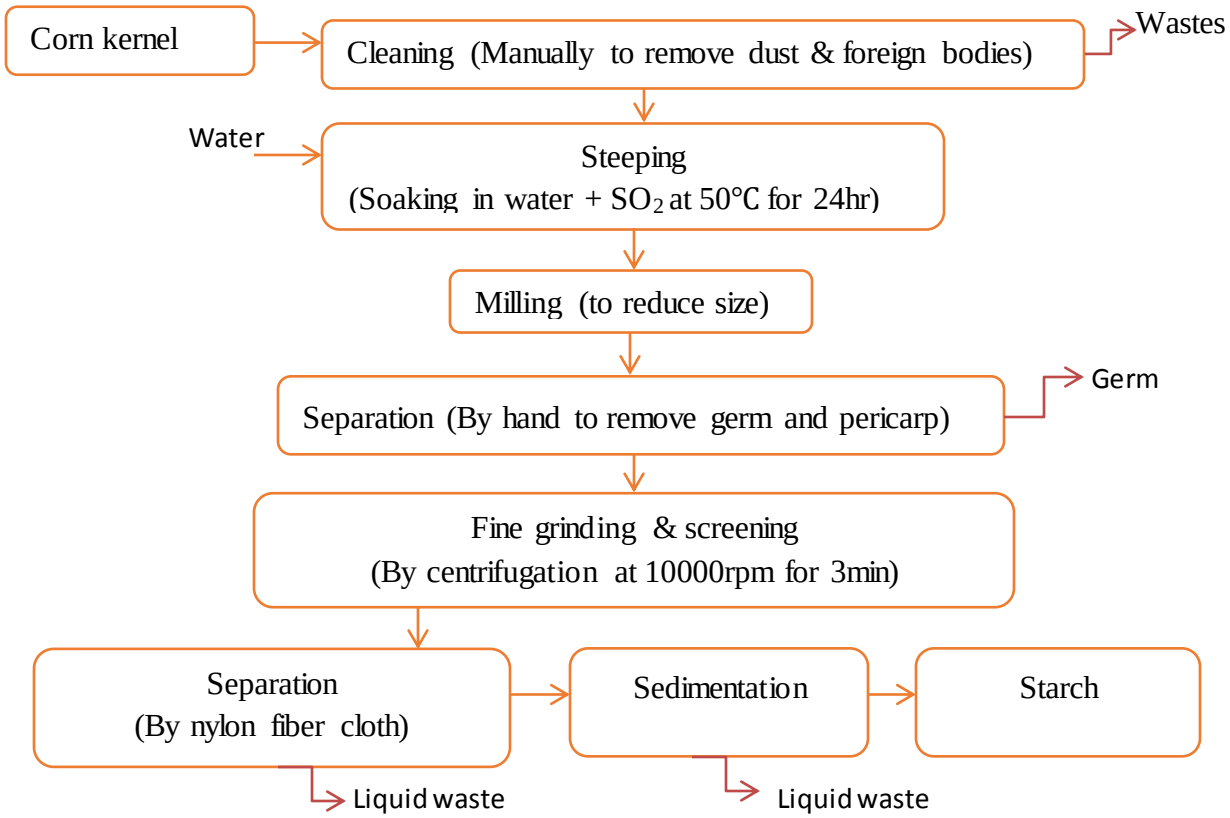


Figure 3.2 Extraction of starch process flow diagram

3.3.1.2 Delignification and isolation of cellulose from sugarcane bagasse fibre

In this work the particle size was selected as determined from the literature, the dried, milled and screened by 80µm sieve size (100g of SCB) was first bleached with 0.7%(w/v) sodium chlorite ($NaClO_2$) solution (fibre to liquor ratio of 1: 50) at pH4, adjusted by % acetic acid that was used to acidify $NaClO_2$ solution. The fibre was boiled in the solution for 2hours on water bath set at $75^{O}C$ to remove lignin completely and hemicellulose partially. The bleaching process was repeated for four to five times until fibre become white and then filtered. The holocellulose thus obtained was boiled with 250 ml 17.5% (w/v) sodium hydroxide solution for 5 h to remove the hemicelluloses.After being filtered, the residue was washed for several times with distilled water. At the end of extraction the insoluble residue (cellulose) was collected by filtration and it was oven dried.

3.3.1.3 Synthesis of bioplastic from corn starch and cellulose fiber

The sample was prepared by the procedure adapted from the method described by (Eraricar S.et al., 2009). A film forming dispersion was prepared by mixing the starch (10g) and distilled water (200ml). The dispersion was stirred manually on magnetic strier set at 70-80°C for 15 min while stirring at the same rate until it become gelatinized. Then glycerol(3.6ml) was added and stirred for 10 min. Cellulose fibre was then added at 0.00, 0.50, 1.00 and 1.5g (dry basis) based on a starch weight basis. Each mixture was stirred for homogeneity and to make the gelatin very strong and then allowed to cool to 75 °C before being cast on a non-stick tray. Then the solution, while still hot, the mixture was transferred into petri dishes using weight balance to keep its uniformity (Lafargue et al. 2007). Then dishes will place in an oven set at 50°C, 40^{O}C and 30^{O}C until the film was dry. Subsequently the dishes are removed from the oven and the films was peeled off, then stored at room temperature in polyethylene bag for further analysis. The analysis variables are drying temperature and fiber content in blends with starch.

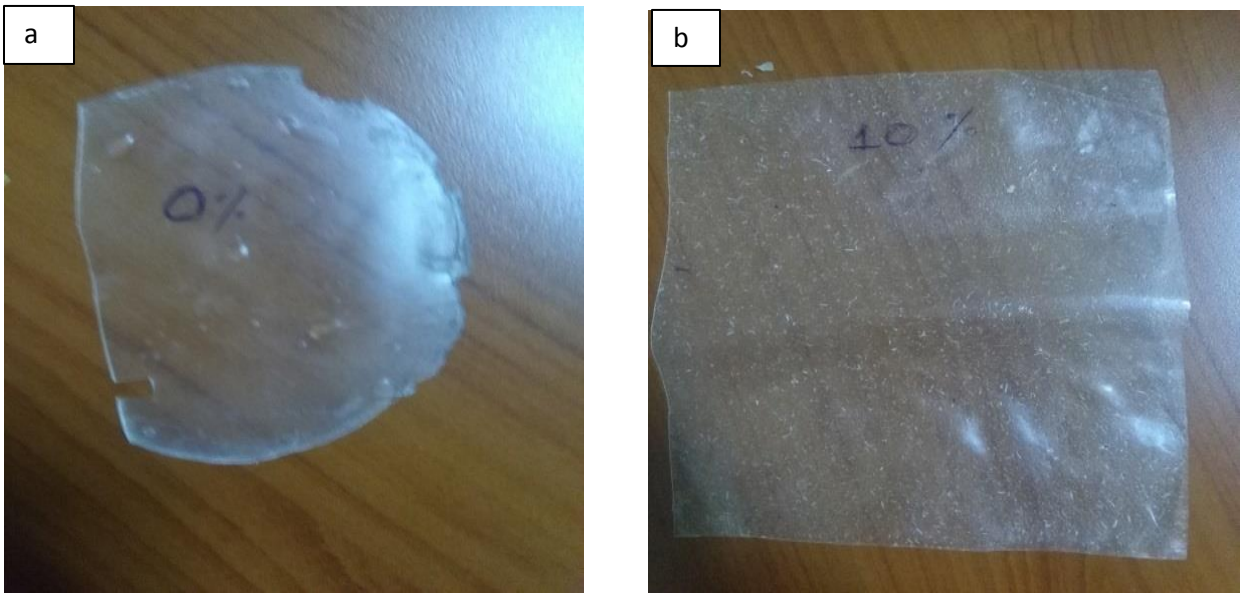


Figure 3.3 pictures of developed bioplastic with a) 0% starch matrix b) optimal cellulose fibre(10%wt)

3.4 Evaluation of mechanical properties of developed bioplastic

3.4.1 Tensile strength and elongation at break

Tensile strength and elongation at break are the most important mechanical properties of the packaging bio-plastic. So that it is favored to characterize the prepared bio-films with the aspect of its tensile strength and elongation at break. Tensile strength is defined as strength of material in terms of force per unit area of cross section while applying force in linear direction.

Materials

- **Sample:-**The sample was taken from butt area of developed bio plastic.
- **Apparatus and equipment:-**Apparatuses used for this test were: scissor, steel die of standard dimension, steel ruler, and thickness gauge, Tensile strength testing Machine (UTM) and PC system.

Methods

For this testing ISO3376:2002 standard testing method was used.

Procedures:-

- Dumbbell shaped of test pieces was cut with a required shape and size (10mmx50mm).
- The sample cutting positions were from parallel to back bone direction of the plastic sample (along direction) and three samples right angle to back bone direction (across direction).
- Then conditioned them in a controlled atmospheric condition (20±2^{o}C & 65±5 % R.H or 23±2^{o}C &50±5 % RH) for 48 hours
- The thickness of each test pieces were measured using thickness gauge at three places on grain side of the bioplastic test specimen and record the average thickness.
- The width of the bioplastic was measured using a steel ruler.
- The area of cross-section was calculated on the test specimen by multiplying its width and thickness.
- The distance between the grips of the tensile tester was set as 50 mm for standard test specimen.
- The test specimens were inserted between the grips, and then tighten the grips with sufficient pressure.

- The tensile testing machine was operated at a speed of 100±2 mm/minute until the bioplastic sample breaks.
- The machine was stopped immediately, and then the distance between the two grips was measured and recorded the maximum force found at plastic break.

Finally both Tensile strength and percentage elongation at break were calculated as follow

$$\text{Tensile strength at yield (MPa)} = \frac{\text{Force(N)}}{\text{Area(width in mm x thickness in mm)}} \quad 3.1$$

$$\%\text{Elongation} = \frac{\text{Increase in length}}{\text{Original length}} \text{x}100 \quad 3.2$$

3.5 Characterization of physicochemical properties of produced bioplastic

For every physical testing, before starting any test the sample was conditioned for 48hr in a specified temperature and humidity. For this purpose we use the standard test method (ISO 2418:2005 and ISO2419:2005, Sampling and Conditioning).

3.5.1 Water absorption

Materials

- **Sample:** The sample were taken from butt area, water and glycerol
- **Apparatus:** The apparatus used for this analysis were beaker, scissor, weighing balance.

Methods

The method used for this test was according to (Kuorwel, 2011)and the testing procedures are:-
The samples were taken, cut in to pieces and weighing. Then it was immersing into a beaker containing mixtures of 50% water and 50% glycerol (%v/v) at room temperature for 10min. the samples were removed from the beaker and wiped dry and weight was recorded. The experiment was performed in triplicates and the average was recorded.

Finally, the water absorption was estimated by using the following formula

$$\text{Water Absorption} = \frac{W_{f-} W_o}{W_o} \times 100\% \quad 3.3$$

Where, W_f = represents the final weight of the film after 5 minutes of absorption

W_o = is the initial weight of the film.

3.5.2 Water solubility

Materials

- **Sample:** The sample were taken from butt area.
- **Apparatus:** The apparatus used for this analysis were beaker, scissor, weighing balance, agitator and air circulated oven

Methods

The films' solubility in water was determined according to the method reported by (Cuq Gontard, 1996). Disks of film (20 x 20 mm) were cut, weighed (M_i), and immersed in a beaker containing 50 ml of distilled water. After 24 h of immersion at 25°C with agitation (60 rpm), the pieces of sample were taken out and dried to constant weight (M_f) in an air circulated oven set at 105°C for 24hr.

The amount of water solubilty was estimated using the following formula:

$$\text{Water Solubility} = \frac{M_{f-} M_i}{W_f} \times 100\% \quad 3.4$$

Where M_i = is the initial mass and

M_f = is the final mass of the sample.

3.5.3 Density of developed bioplastic

Materials

- **Sample:** The sample were taken from part of both control and reinforced plastic specimen.
- **Apparatus:** The apparatus used for this analysis were picknometer, measuring cylinder, beaker, scissor and weighing balance

Methods

The density of the starch based films was measured according to the following procedure using 25ml packnometer, three third of the total packnometer volume was filled by known weights of the film sample (Ws), then the packnometer was filled by water until over follow of the water had seen, next the weight of packnometer including film sample and water was measured, finally volume of the film sample (V) was calculated by subtracting 25ml from the total mass inside the packnometer. (Assumption1g=1ml).

3.5.4 Transparency of produced bioplastic

Materials

The materials used in this study were UV spectrophotometer (UV 7804C).

Methods

The transparencies of the films are determined using spectrophotometer (UV 7804C). The transmittance of films will be determined at 600nm as described by Bourtoom and Chinnah (2009).The film samples are cut into rectangles and placed in the internal side of the spectrophotometer cell.

$$\text{Transparency}(\%T) = \frac{-\log T600nm}{X} \qquad 3.5$$

Where T600 = is the transmittance at 600nm and X is the film thickness (mm).

3.5.5 FTIR analysis of bioplastic

The functional groups(chemical bonds) of produced bioplastic was identified by fourier transforms infrared spectroscopy (FTIR) and Compound Microscopy.

Materials

The sample used in this analysis were unfilled (sample used as a control) and reinforced bioplastic.

Apparatus : mortar, lid, metal pice, quick handy press and FTIR was used in this work.

Methods

The composite plastic (both the control and the sample developed at optimal) preparation was done by KBr pellet method from Science faculty in Chemistry department (AAU): ~ 1 mg of solid bio-plastic sample and ~ 100 mg of Potassium Bromide (KBr) was mixed; the contents were ground in the mortar wall with a pestle into a fine mixture (~ 2 minutes); small amount of the finely crushed mixture was put into the open chamber (2 piece metal), just enough to cover the bottom surface of the chamber; the lid was put on the chamber containing the finely crushed mixture and put this 3 piece metal set inside the Quick Handy Press, press hard and then release the press; Carefully take out the 3 piece metal from the Quick Handy Press and examine the Pellet formed within the middle metal piece of the 3 piece metal set. The Pellet should somewhat clear and free from cracks (redo procedure if the pellet is opaque or has cracks); Take the middle metal piece that has somewhat clear and un-cracked pellet formed and screw to the pellet holder; This was the method to prepare bio-film sample, then the FTIR spectrum was allowed to pass through the prepared sample and the spectrum responses were recorded, finally the peak plot of wave number (400-4000cm^{-1}) versus Transmitence (%) was plotted using Microcal origin software and identified the functional groups.

3.6 Experimental design and data analysis

Response surface methodology (RSM) will be adopted in the design of experimental combinations. The main advantage of RSM is to reduce the number of experimental runs needed to provide sufficient information for statistically acceptable results. A three variable (three levels of each) central composite experimental design was employed (Montogomery, 2001). The ratio of cellulose fiber concentrations has strong impact on the final performance of prepared bioplastic. For instance glycerol is used as plasticizer, making the films more flexible. Cellulose extracted from sugarcane bagasse is used to improve the mechanical properties of the starch based bioplastic for different application.

The first task before conducting the experiments was selection of potential parameters to be varied. The two main factors selected in this study were oven-drying temperature, concentration cellulose fiber. The level of the selected factors is determined from the literature research and is presented in table 3.1 The experiment performed as a completely randomized design with two main factors at three levels and three response variables. The processing variables (concentration of cellulose fiber

and drying temperature (^{o}C) were optimized using RSM to study their effect on the functional properties of prepared plastics. The responses that were considered during the optimization of the Processing variables are solubility, water absorption, tensile strength and elongation at break. The prepared bioplastics physical (solubility and water solubility) and mechanical (TS and EB) properties, and the effect of independent variables on the prepared bio-films were checked.

Table 3.1 Levels of independent variables for the development of bioplastic based on central composite design

Independent Variable	Units	Coded symbol	Coded Levels		
			-1	0	+1
Drying Temperature	^{o}C	A	30	40	50
Cellulose fiber to Starch	w/w%	B	5	10	15

Data analysis has performed by DESIGN EXPERT® 6.0.8 software using Response surface methodology design method and randomize the runs. Randomization ensures that the conditions in one run neither depend on the conditions of the previous runs nor predict the conditions in the subsequent runs. Randomization is essential for drawing conclusions from the experiment, in correct, unambiguous and defensible manner.

This design of the experiment helps us to differentiate the significance of the main and the interaction factors. This program software also used to develop the mathematical model that will describe the effects of the main and interaction factors on the response.

The proposed RSM design required 13 runs. Detail of the experimental runs with the set of input parameters that were conducted are given in Table 3.2

Table 3.2 Two factors, three levels face centered cube design with five center point formulation

Standard order	A:Temperature °C	B:Cellulose fiber (%wt)
1	30.00	5.00
2	50.00	5.00
3	30.00	15.00
4	50.00	15.00
5	30.00	10.00
6	50.00	10.00
7	40.00	5.00
8	40.00	15.00
9	40.00	10.00
10	40.00	10.00
11	40.00	10.00
12	40.00	10.00
13	40.00	10.00

4 RESULT AND DISCUSSION

The determination of mechanical properties involves not only scientific, but also technological and practical aspects (Gontard , 1993). Thus, the mechanical properties of the films were studied to determine the values of important parameters such as tensile strength (TS) and percent of elongation at break (E). The value of tensile strength, water absorption and Elongation at break for Bio-plastic at given level of two factors is depicted in table 4.1 below

Table 4.1 Experimental design and responses

Run order	Factor	Factor	Response 1	Response 2	Response 3
	A(°C)	B(wt%)	Tensile strength(MPa)	Water absorption(%)	Elongation at break(%)
1	30.00	5.00	10.79	44.54	27.3
2	50.00	5.00	15.47	37.35	24.41
3	30.00	15.00	15.58	30.24	15.89
4	50.00	15.00	25.75	22.23	7.85
5	30.00	10.00	17.87	30.37	14.88
6	50.00	10.00	24.83	22.23	10.42
7	40.00	5.00	16.55	37.02	22.99
8	40.00	15.00	25.23	20.45	9.01
9	40.00	10.00	26.25	20.88	5
10	40.00	10.00	26.01	19.97	7.56
11	40.00	10.00	25.89	20.52	4.32
12	40.00	10.00	26.81	20.25	4.7
13	40.00	10.00	26.47	19.97	4.85

The resulting data, Table 4.1; were analyzed using Design expert® 6.0.8 software to determine the effects of oven-drying temperature and concentration of cellulose fiber. The dependent variables used as a response parameter were the tensile strength, water absorption and elongation at break. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors. And the design summary for the experiment is shown in table 4.2.

Table 4.2 Design summery

Study Type	Central composite
Initial Design	Response surface
Center Points	0
Design Model	Quadratic
Runs	13
Blocks	No Blocks

Factor	Name	Units	Type	Low Actual	High Actual	
A	Temperature	°C	Quadratic	30	50	Levels: 3
B	Cellulose fibre	%	quadratic	5	15	Levels: 3

From table 4.1 it can be seen that the maximum tensile strength, minimum water absorption and elongation at break were obtained at the center level coded (0) of both factors that is at 40℃ and starch-cellulose composite of 10% (w/w) with 26.81MPa Tensile strength, 19.97% of water absorption and 4.32% of Elongation at break. From this result, increasing temperature up to 40℃ and fiber ratio up to 10% increase all three responses because an increase in baking temperature brought about an initial increase in the tensile strength of the films, i.e. increasing the temperature results tensile strength increase to a maximum for drying temperature of 40℃, the strength was slightly decreased slightly as the drying temperature is increased up to 50℃. An increase in drying temperature brought about an initial decrease in the elongation (extension at break) of the films which means lower value of elongation at break, with the drying temperature increase, the elongation decreases to a maximum of temperature of 40℃, the elongation decreases as the drying temperature was increased. This may be due to the individual molecules that make up polymeric materials are very large and have an extended chain-like shape that results in an entangled structure. This entanglement is beneficial in some respects. The relatively high levels of elongation that most polymers exhibit without breaking are due in large part to chain entanglement. However, this entanglement also restricts the freedom required at a molecular level to organize into crystals. Water absorption and elongation at break decreases with increasing tensile strength at a temperature of 40℃ and 10% of SCB cellulose blended in

starch matrix this is due to starch by itself is brittle and could not form a flexible material. Most biopolymers are brittle in nature with lower tensile strength and the addition of cellulose fiber enhances the tensile strength, water absorption and Elongation at break values by acting as reinforced material.

The addition of plasticizers to biopolymer relieves their brittleness and makes them tougher. The values of the tensile strength of the films which were made from various ratios of cellulose fiber to corn starch was shown in Table 4.1. The tensile strength of the film with incorporated cellulose fiber was much higher than that of pure starch film (control) due to strong interaction between the polymers(cellulose and starch matrix). The results showed that the addition of the cellulose fiber improved the mechanical properties of the material. When the cellulose fiber was added into the starch matrix, there was a gradual increase in tensile strength (Table 4.1). The significant increment in the tensile strength of the film with the incorporated cellulose fiber indicated the presence of intermolecular interactions in the films. Consequently, the Tensile strength value was 26.81 MPa at 10% content of cellulose fiber used, this is in agreement with literature in a study done by (Oskman et al 2003). The fiber content in the matrix of synthetic or biological polymers increased the values of elasticity modulus and maximum resistance to the tension and decreased the values of elongation at fracture (Oskman et al 2003; Alvarez et al 2004; Brahmakumar et al 2005). Probably this effect is due to an interaction of the fiber with the starch matrix, decreasing the molecular mobility and resulting in more rigid and less flexible materials (Wu et al, 2003).

The percentage elongation (E) values of the film with the incorporated cellulose fiber was the measure of a flexibility of the film and it was affected by the starch to cellulose fiber ratios. An increase in the percentage elongation with an increase in cellulose content is due to the reduction in the number of intermolecular cross-links and an increase in the inter-molecular distance. Structurally, starch contains amylopectin which is a branched polymer. As a result, the incorporation of cellulose fiber into the starch-based composite led to improvement in tensile strength due to the reinforcement effect as discussed earlier in this section. The increase in tensile strength indicates that the bonding between the starch matrix and cellulose fiber is strong enough to allow the transfer of strength from the cellulose fiber to starch during testing.

However, the decrease in film strength may be due to fiber aggregation during casting and/or lignin or other components reducing the fiber to starch matrix bond.

Tensile testing results obtained in the present study show the same trend reported in the literature (Vallejos *et al.*, 2011; Prachayawarakorn *et al.*, 2010). The tensile strength of starch/glycerol films containing up to 10 wt% fibre increased by 44% and 200% using de-lignified sugarcane bagasse (Vallejos *et al.*, 2011) and cotton fiber (Prachayawarakorn *et al.*, 2010) as reinforcement respectively. In both cases the authors found that increasing the fibre content to 15 wt% decreased the film tensile strength. Vallejos *et al.* (2011) suggested that bagasse fibre agglomeration and poor dispersion in the matrix took place if more than 10 wt% fibre was added. Prachayawarakorn *et al.* (2010) suggested that the decline of tensile strength was possibly due to the discontinuity of the starch matrix from fibre overloading.

In summary, as there was improvement in both water absorption and tensile strength properties with fibre addition, some bonding between starch and bagasse fibers must have taken place. Further improvement is currently being considered include the removal of the lining component of banjos prior to fibre size reduction and increasing the fibre aspect ratio. This would enhance surface bonding and improve adhesion between fibre and starch.

4.1 Development of regression model equation

Table 4.1 summarizes the result obtained with the experimental design which was aimed at determining the condition that favors maximum tensile strength reduce water absorption and increase elongation at break. A quadratic model equation 4.1, 4.2, 4.3 shown below was fitted to the data model for predicting responses; Tensile strength, Water absorption and elongation at break respectively. F ratio is calculated for 95% of level of confidence.

4.2 Tensile strength of produced bioplastic

The Model F value of 318.56 implies that the model is significant ($P < 0.05$). R^2 and Adjusted R^2 values of the model are 09956 and 0.9925 respectively. The adequate precision value of 47.199 indicates that the model can be used to navigate the design space as it is greater than 4.0 (Montgomery, 2001). On the basis coefficient in (equation 4.1) it was evident that tensile strength increases with temperature and cellulose fiber ratio. Cellulose fiber ratio to starch has a

more profound effect on tensile strength as expressed in equation 4.1. Temperature and cellulose fiber showed significantly linear effects on tensile strength which clearly indicated by largest positive linear regression coefficient 3.63 and 3.96 respectively. As shown in the final equation in terms of coded factor the response for tensile strength by both linear terms (A, B) and quadratic terms, pure quadratic terms (A^2, B^2) and interaction quadratic terms (AB). All coefficients of linear terms and interaction terms were positive and the response of tensile strength was positively affected by linear terms and interaction term, but the coefficient of both quadratic terms were negative and the response of tensile strength was negatively affected by quadratic terms. From ANOVA analysis The Model F-value of 318.56 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicates model terms are significant. In this case A,B, A^2, B^2 and AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant see appendix B. The "Lack of Fit F-value" of 2.76 implies the Lack of Fit is not significant relative to the pure error. There is a 17.59% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Final Equation in Terms of Coded Factors:

$$\text{Tensile Strength} = +26.16 + 3.63 * A + 3.96 * B - 4.48 * A^2 - 4.94 * B^2 + 1.37 * A * B \quad 4.1$$

Final Equation in Terms of Actual Factors:

$$\text{Tensile strength} = -76.77115 + 3.67341 * A + 3.64608 * B - 44805 * A^2 - 0.19762 * B^2 + 0.027450 * A * B \quad 4.2$$

Where: A = Oven-drying temperature

B = Cellulose fiber

4.3 Water absorption of bioplastic

Water absorption is an important factor for biodegradable plastic material for their application, typically in the packaging industry. The measurement hydrophilicity of polymeric film was evaluated by measuring the water absorption capacity of the film surface. The Equation 4.3 represents the quadratic model of water absorption capacity. For water absorption on the basis of coefficient in equation 4.3 it was evident that water absorption decreases with increasing oven-drying temperature and cellulose fibre to starch ratio. As expressed in equation 4.3 both linear terms negatively affect water absorption of bio-plastic which was clearly indicated by large negative regression coefficient -3.89 and -7.67 of oven-drying temperature (A) and cellulose fiber (B) respectively. Equation 4.3 indicates that the final equation in terms of coded factors responses of water absorption was affected by both linear terms (A, B) and quadratic terms (pure quadratic) (A^2, B^2) and interaction term (AB). Both coefficients of linear terms and interaction terms affect negatively, but both quadratic terms (pure quadratic) affect positively. For linear terms drying temperature (A) had the highest effect on water absorption and also from quadratic terms (A) had the highest effect, but interaction terms had the highest effect than both linear terms. In terms of R^2 and Adjusted R^2values of the model are 0.9968 and 0.9945 respectively. The adequate precision value of 58.128 indicates that the model can be used to navigate the design space as it is greater than 4.0 (Montgomery, 2001)

From ANOVA analysis The Model F-value of 433.18 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicates model terms are significant. In this case A,B, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant see appendix B.

The "Lack of Fit F-value" of 4.70 implies the Lack of Fit is not significant relative to the pure error. There is a 8.46% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good - we want the model to fit.

Final Equation in Terms of Coded Factors:

$$\text{Water Absorption} = +21.78 - 3.72 * A - 6.33 * B + 6.35 * A^2 + 4.29 * B^2 - 0.70 * A * B \quad 4.3$$

Final Equation in Terms of Actual Factors:

$$\text{Water Absorption} = +21.78379 - 3.72333 * A - 6.33167 * B + 6.35172 * A^2 + 4.28672 * B^2 - 0.70500 * A * B \quad 4.4$$

Where: A = Oven-drying temperature

B = Cellulose fiber

4.4 Elongation at break for bio-plastic

As depicted in equation 4.5 in terms of coded factors the response elongation at break affect by both linear terms (A, B) and quadratic terms (pure quadratic) (A^2, B^2) and interaction term (AB). Equation 4.5 showed elongation at break was negatively affected by linear terms and interaction term and also positively affected by quadratic terms. For linear terms drying temperature (A) had a highest negative effect on response elongation at break, whereas from quadratic terms A2 had highest positive effect on response.

The Model F-value of 51.54 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, 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. The "Lack of Fit F-value" of 2.83 implies the Lack of Fit is not significant relative to the pure error. There is a 17.03% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Final Equation in Terms of Coded Factors:

$$\text{Elongation at break} = +5.91 - 2.57 * A - 7.00 * B + 5.20 * A^2 + 8.55 * B^2 - 1.28 * A * B \quad 45$$

Final Equation in Terms of Actual Factors:

$$\text{Elongation at break} = +137.28264 - 4.15822 * A - 7.21422 * B + 0.051957 * A^2 + 0.34183 * B^2 - 0.025550 * A * B \quad (4.6)$$

Where: A = Oven-drying temperature

B = Cellulose fiber

4.5 Effect of process variables

The effect of each independent variable on the physical and mechanical properties of the bio films was investigated by keeping other variables constant. Moreover, from the model equation, the coefficients of the independent variables show the effect of each independent variable on physical as well as mechanical properties of the bioplastic.

4.5.1 Effect of individual process variables

4.5.1.1 Effect of drying temperature on tensile strength of bio plastic

The effect of drying temperature on Tensile Strength of bio-plastic was shown in Figure 4.1 below. From the graph it can be observed that as temperature start to increase from low level coded (-1) up to center point coded (0) tensile strength also increases, but beyond center point the tensile strength shows slight decreasing and become parabolic. This can be caused by the influence of higher temperatures that can cause intermolecular bonds in starch chains becoming weaker. The hydrogen bonds between amylose chains undergo termination of the bond. Then further heating will break glycosidic bonds (bonds between monomers) in amylose. Based on research Haryanti *et al.*, (2014) increasing the heating temperature can cause depolymerization in amylose chain, the straight chain amylose falater and become shorter, thus decreasing amylose content (Halley, 2001).

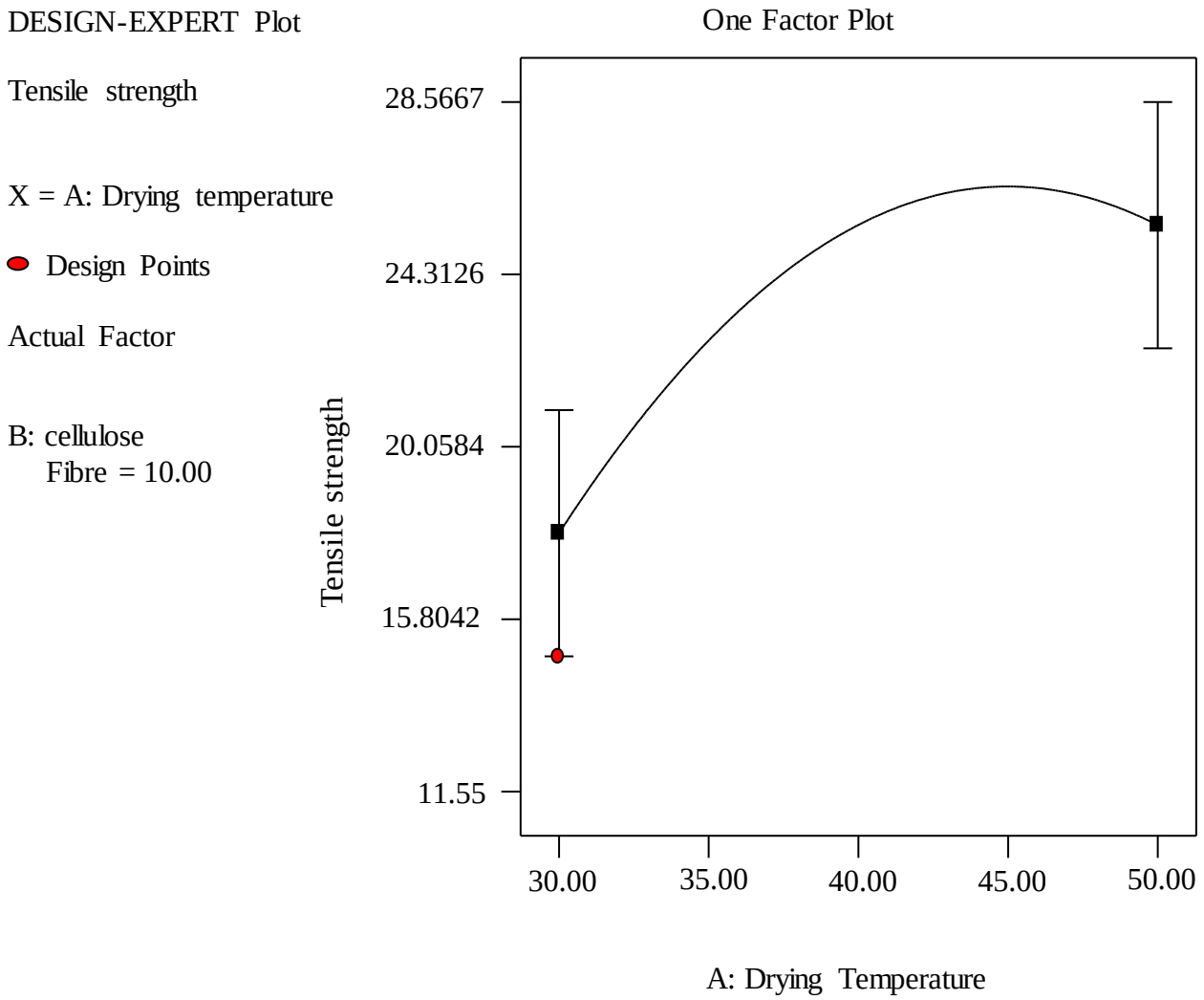


Figure 4.1 Effect oven drying temperature on tensile strength of developed bio-plastic

4.5.1.2 Effect of cellulose fiber concentration on tensile strength

As depicted in figure 4.2 below the effect of Cellulose fiber to starch ratio on tensile strength can be observed that as the ratio of Cellulose fiber increases the response of tensile strength increases up to center point coded (0) and beyond to some extent and become decreases as cellulose fiber increases further up to higher level coded(+1). Probably this effect is due to an interaction of the fibre with the matrix, decreasing the molecular mobility and resulting in more rigid and less flexible materials (Wu *et al.*, 2003). The fibre content in the matrix of synthetic or biological polymers increased the values of elasticity modulus and tensile strength of bioplastic;

and decreased the values of elongation at fracture (Oskman *et al.*, 2003).

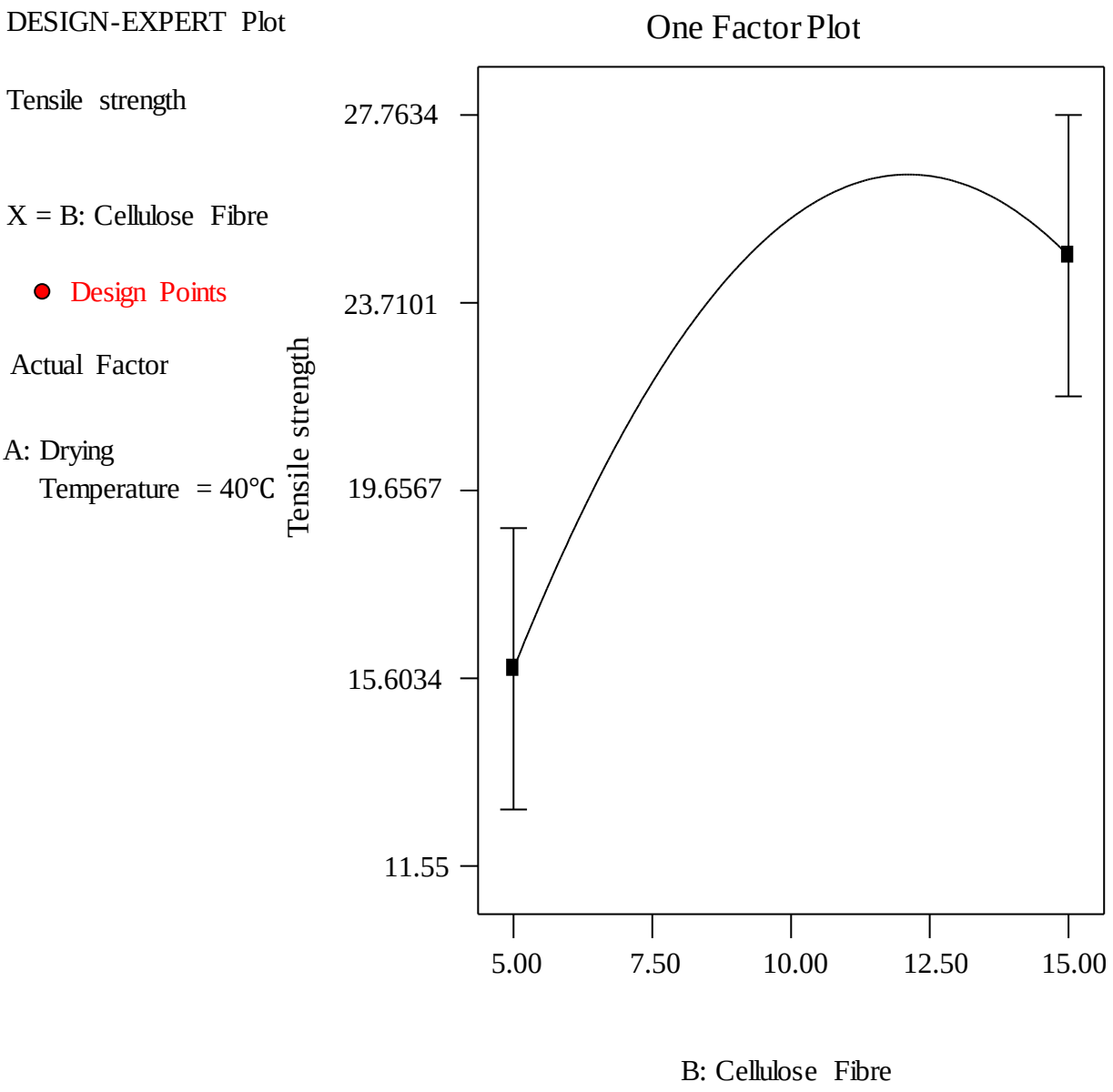


Figure 4.2 Effect of cellulose fiber concentration on tensile strength of developed bioplastic

4.5.1.3 Effect of drying temperature on water absorption of bioplastic.

The effect of drying temperature on water absorption of bio-plastic was shown in figure 4.5. As shown in the figure, the lowest water absorption was observed at center point coded (0) or at 40℃. As we move from lowest coded level(-1) to center point the water absorption decreases, and as drying temperature increases from center point to higher level coded(+1) water absorption start to increases this was in agreement with some literature results.it was found out that in the work of (Ahmed *et al.*, 2014)

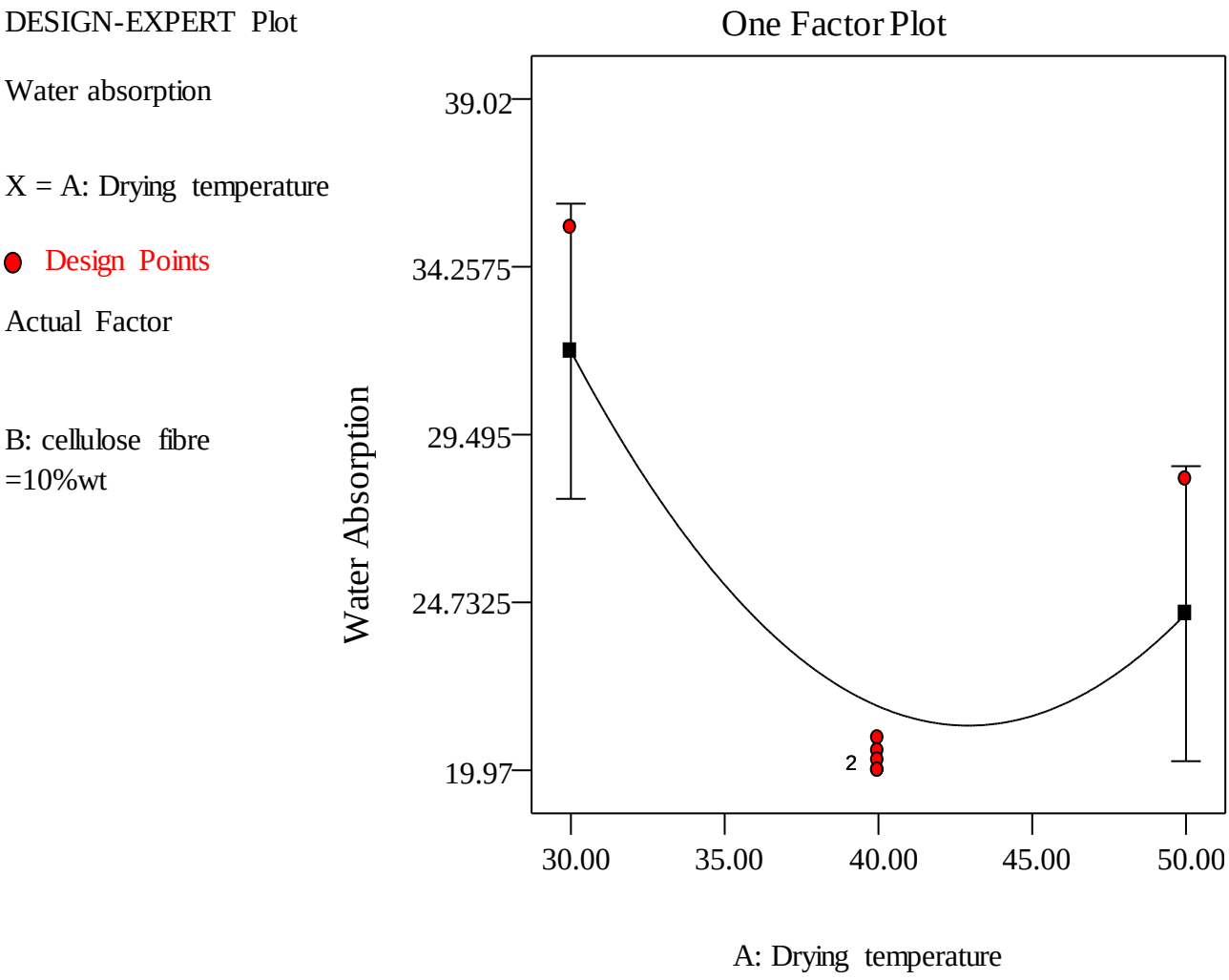


Figure 4.3 Effect of oven drying temperature on water absorption of developed bio-plastic

4.5.1.4 Effect of cellulose fiber on water absorption of bioplastic

Sensitivity of the composites(bioplastics) to water absorption from the environment may be one of the most important parameters to consider for some applications, as water absorption affects the properties of starch-based composites (Müller *et al*. 2009). As shown from the figure bellow the water absorption decreased when the percentage of Cellulose fiber increased from lowest level to center point coded (0) or up to 10% of Sugarcane bagasse cellulose in the bio-composites, as we move from center point to higher level water absorption starts to increase slightly and become a show parabolic line.According to Sarifuddin *et al.* (2012), this moisture absorption reduction in bio-composites can be attributed to stronger hydrogen bonds between the matrix and the reinforced material. Furthermore, Müller *et al.* (2009) demonstrated the resistance to water absorption in TPS when cellulose fibers are incorporated. In fact, they proposed the incorporation of fibers in TPS as an alternative for reducing water uptake in bio-composite exposed to high humidity environments.

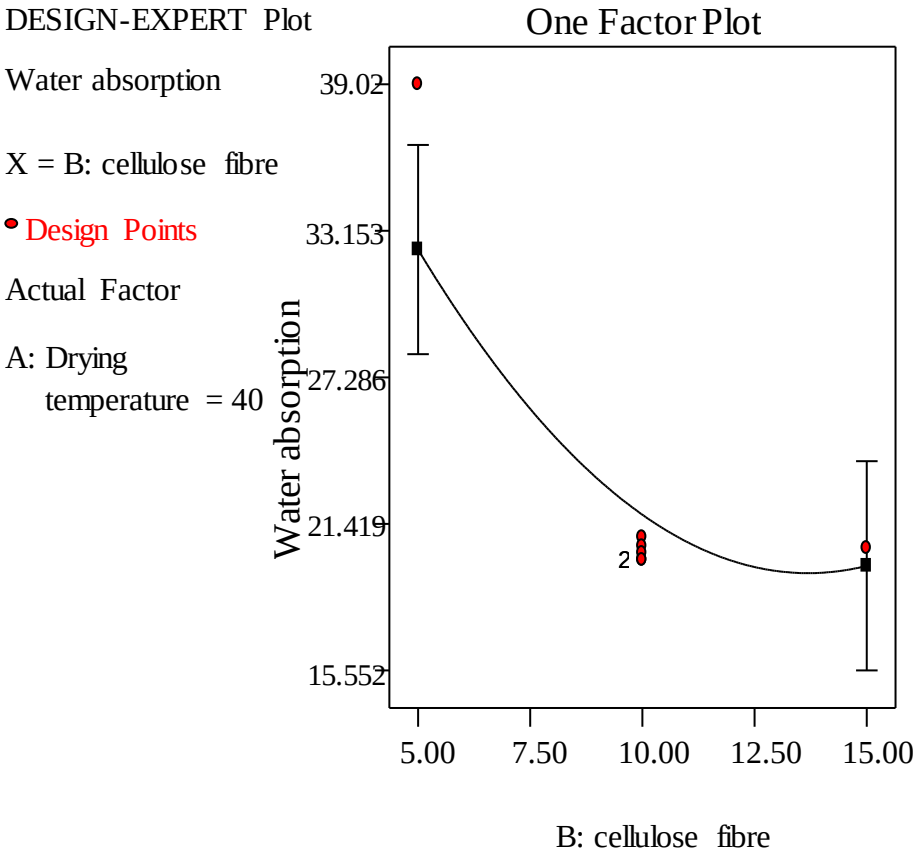


Figure 4.4 Effect of cellulose fiber on water absorption of bioplastic

4.5.1.5 Effect of drying temperature on elongation at break of bio-plastic

From figure 4.5 it illustrated that increasing oven drying temperature of the bio - plastic solution causes the value of elongation at break decreases until it reach the center point (see figure 4.5). Which was due to increasing the tensile strength of bio-plastic as well as increasing drying temperature from lower level coded(-1) up to center point coded(0). The result of elongation at break decreases with increasing the temperature and as shown from the figure as drying temperature increases to high level coded (+1) elongation at break start to increases smoothly. This is because the heat that is given causes an increase in the kinetic energy of the molecules in which the molecules vibrate and create a free volume to allow larger molecular chains rotation (Patrycja, Wojciechowska, 2012).

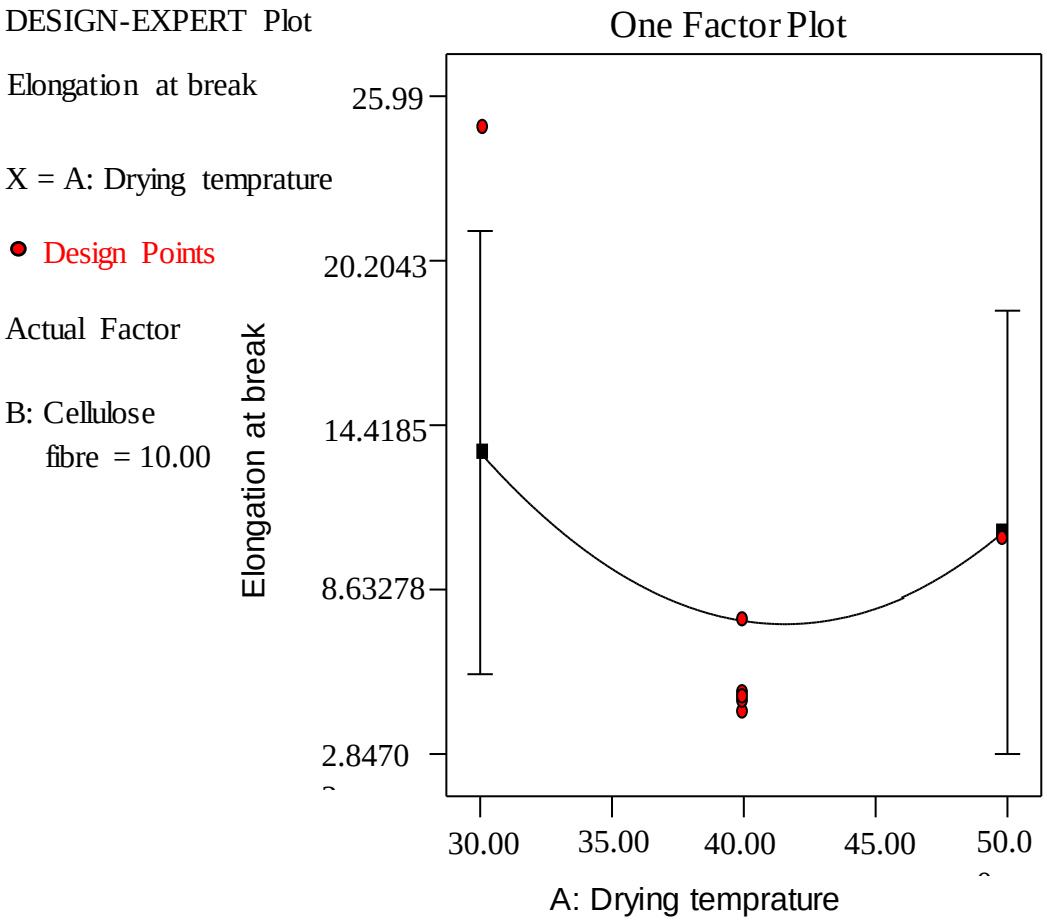


Figure 4.5 Effect oven drying temperature on elongation at break of bio-plastic

4.5.1.6 Effect of cellulose fiber on elongation at break of bioplastic

The effect of cellulose fibre content on elongation at break of developed bio-plastic was shown in figure 4.6 as shown from the figure below increasing fiber content from low level coded(-1)up to center point coded(0) decreases response elongation at break up to cellulose fibre content reaches 10% and elongation at break become increasing as cellulose fibre content further increases beyond 10% or center point. This is in agreement with other literature, the work done by Funke *et al* (1998) and Dufresne and Vignon (1998) reported that considerable improvements in product properties were achieved by adding small amounts of fibers to the starch samples with natural plasticizers. Blend systems with 2-7% fibers resulted in an increase of elongation at break, tensile strength and water resistance of these products (Funke *et al* 1998). But in this research it reaches up to 10% of fibre concentration content increases elongation at break this is may be due to treatment of sugarcane bagasse fiber by alkali to remove the lining before it mix with starch as reinforced material.

Similarly, in another work it was suggested that The fibre content in the matrix of synthetic or biological polymers increased the values of elasticity modulus and maximum resistance to the tension; and decreased the values of elongation at break (Oskman et al 2003, Alvarez et al 2004). Probably this effect is due to an interaction of the fibre with the matrix, decreasing the molecular mobility and resulting in more rigid and less flexible materials (Wu *et al.*, 2007).

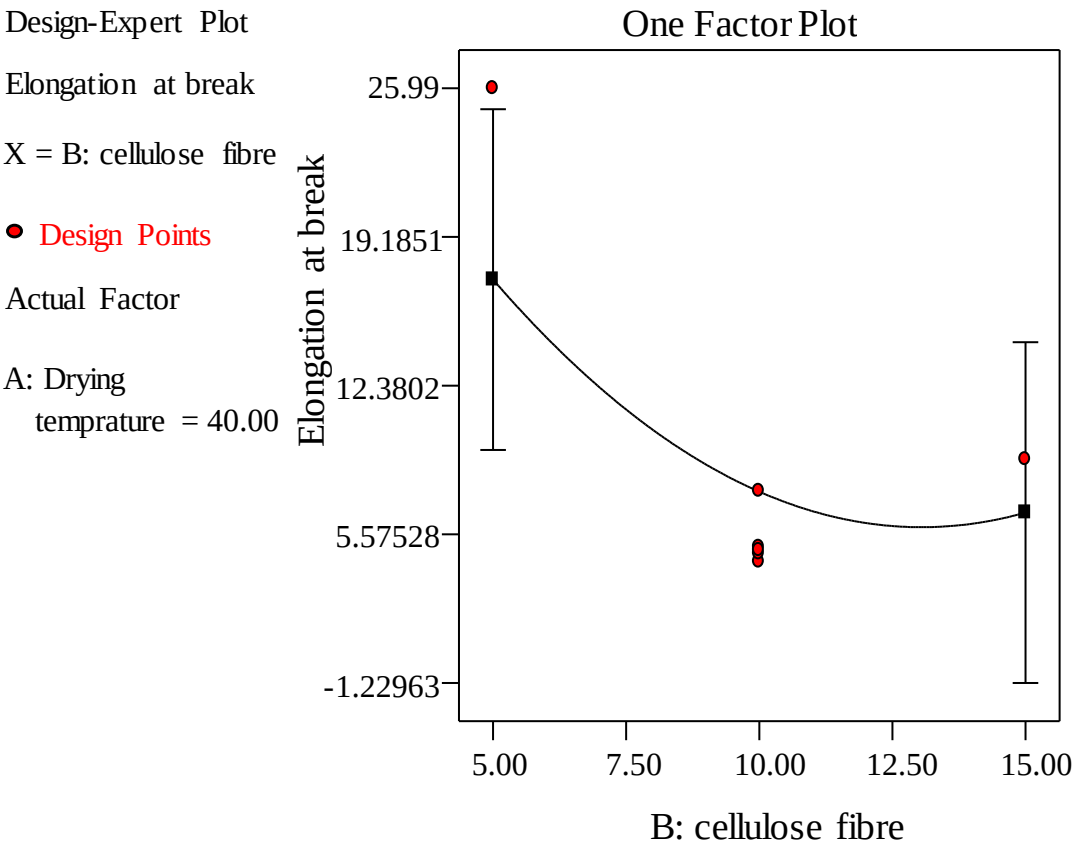


Figure 4.6 Effect of cellulose fiber on elongation at break of bioplastic

4.5.1.7 Effects of interactive parameters between process variables on tensile strength, water absorption and elongation at break

Figure 4.7 shows the effect of the interaction of drying temperature and starch-cellulose fiber ratio where the maximum values of tensile strength (26.81 MPa) were at drying temperature of 40°C and cellulose fibre (10 wt%) concentration. However, further increase in oven drying temperature above 40°C and the increase of fibre content above 10 % in the blend smoothly increase the values of water absorption and elongation at break. Low drying temperature values (30°C) and low contents of cellulose fibre (5%) showed the minimum tensile strength values (10.79 MPa) and at oven drying temperature (40°C) and cellulose fibre (10%) shows maximum tensile strength (see figure 4.10 below). In general the values of tensile strength were favored at the center values of drying temperature and cellulose fiber. The increment of oven drying temperature values decreased drastically both water absorption and elongation at break (see

figure 4.12 and 4.13 below) for water absorption and elongation at break respectively. Thus, high contents of cellulose fiber originated flexible films, however, with a low resistance to the tension as shown in assay (4) number (drying temperature 50℃ and cellulose fiber 15%) but better than low level. Jansson *et al* (2005) reported that films added to high cellulose fiber contents in blends with starch induced a drastic decrease in the tensile strength, increasing the elongation at break until 35%. However, the increasing of sugarcane bagasse cellulose up to 15% contents and at high oven drying temperature up to 50℃ increased the water absorption and elongation at break.

Similarly Funke *et al* (1998) and Dufresne and Vignon (1998) reported that considerable improvements in product properties were achieved by adding small amounts of cellulose fibers to the starch matrix with natural plasticizers. Blend systems with 2-7% cellulose fibers resulted in an increase of tensile strength and water absorption resistance of these products (Funke *et al*., 1998). This is in agreement with present work of (10% fibre contents) with insignificant difference. The minimum values of water absorption and elongation at break (19.97 and 4.32 respectively) resulted with an increasing of drying temperature (40℃) at cellulose fiber of 10wt%.

In a general way the values of Water absorption and elongation at break were increased with an increasing of and cellulose fibre and also at high values of drying temperature and cellulose fibre the value of both responses start to increase. Thus, the values of both water absorption and elongation at break were favored at 40℃ and 10% of cellulose fibre (CF) (see figure 4.12 and 4.13) below of 3D and counter surface plot. The incorporation of cellulose fibre acts as reinforcement in thermoplastic materials (Averous *et al*., 2001). This evidence was demonstrated in the assay where the absence of sugarcane bagasse cellulose fibre decreased the value of tensile strength.

According to (Stanisław *et al*., 2003) high fibre contents decreased the tensile strength forming a rigid and fragile material. The tensile strength and water absorption of the specimen determines the final quality of the bioplastic and is an indicator of the high posterior behavior of the films during thermoformed process. High cellulose fibre contents, not more than 10%, increased the tensile strength; reduce water absorption and elongation at break values at the center point of Temperatures (40℃). Thin films with low tensile strength were found at low drying temperatures

(30°C) and low fibre contents (not below 10%). Also intermediate drying temperature and cellulose fibre concentrations were showed low water absorption and elongation at break.

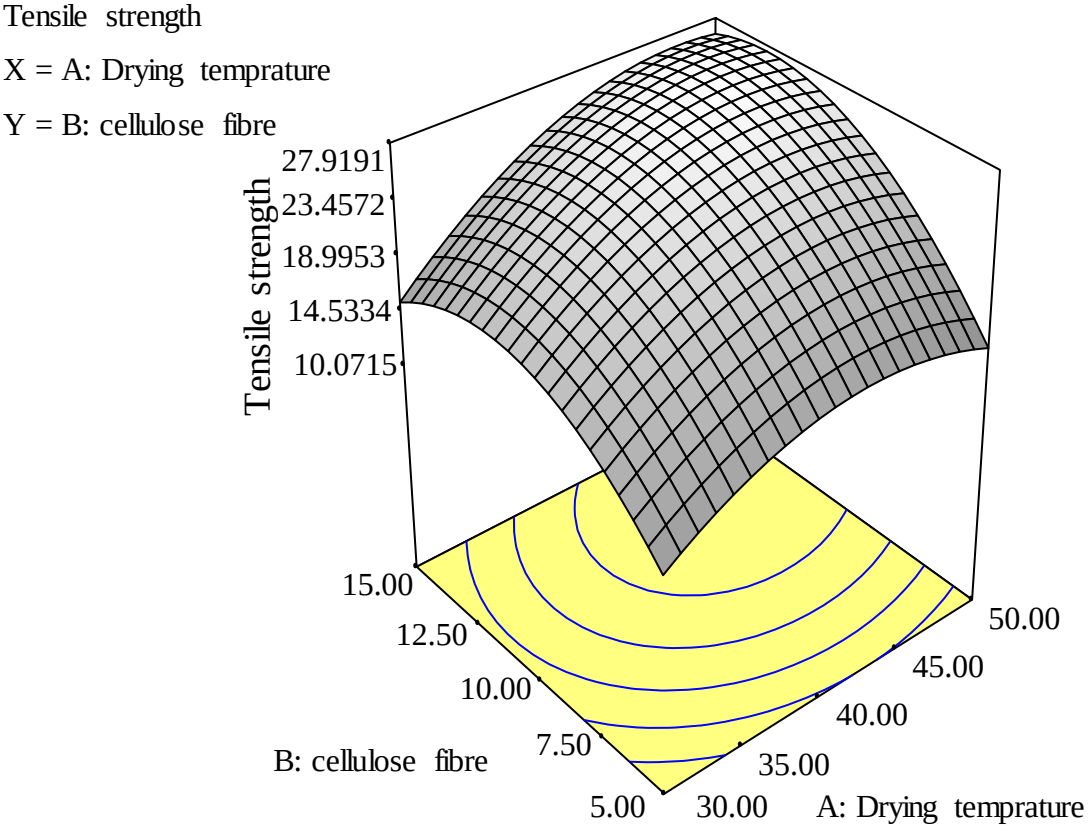


Figure 4.7 Effects of drying temperature and cellulose fibre interactive on tensile strength, water absorption and elongation at break.

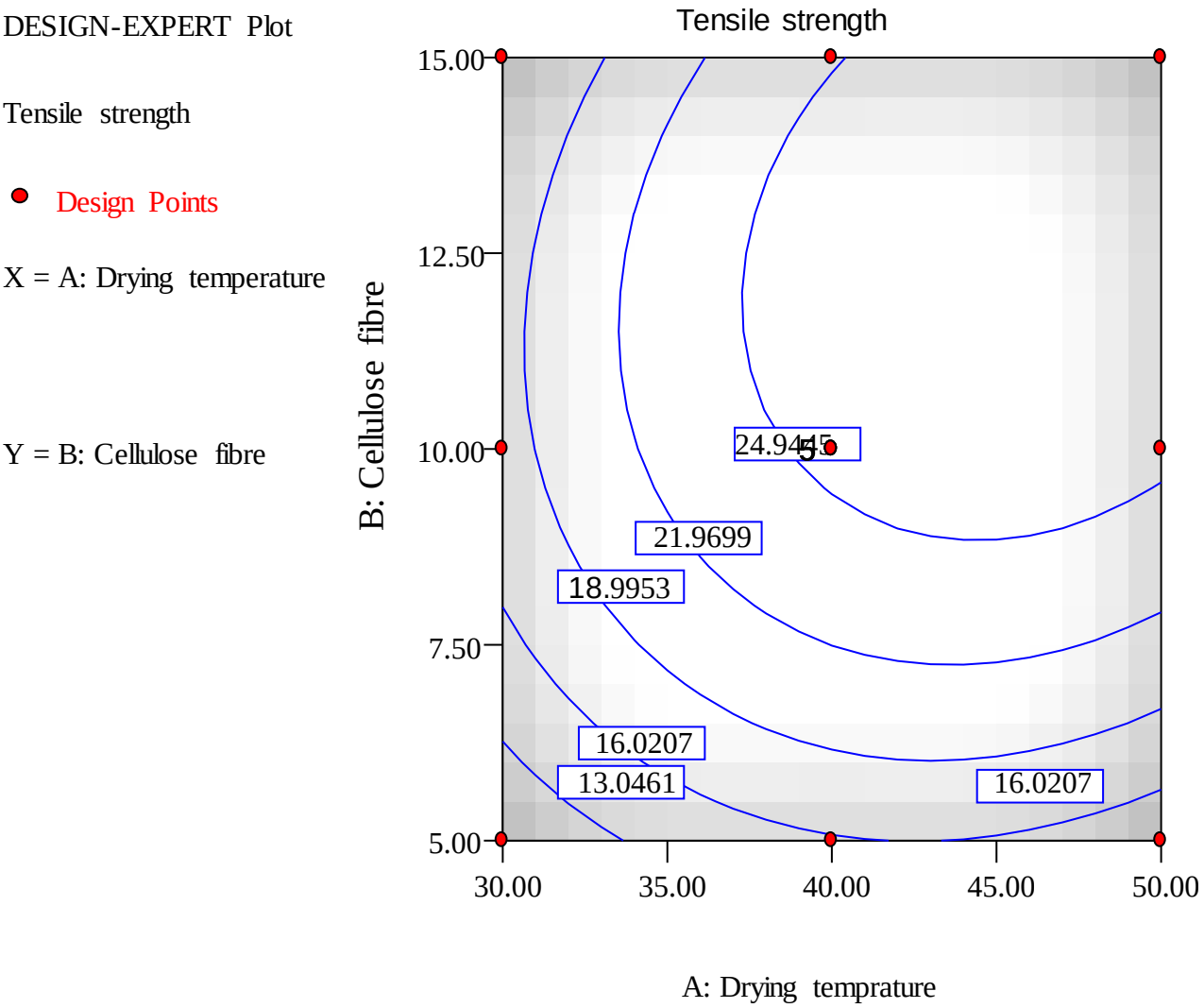


Figure 4.8 Effect of drying temperature and cellulose fibre on tensile strength contour plot bioplastic

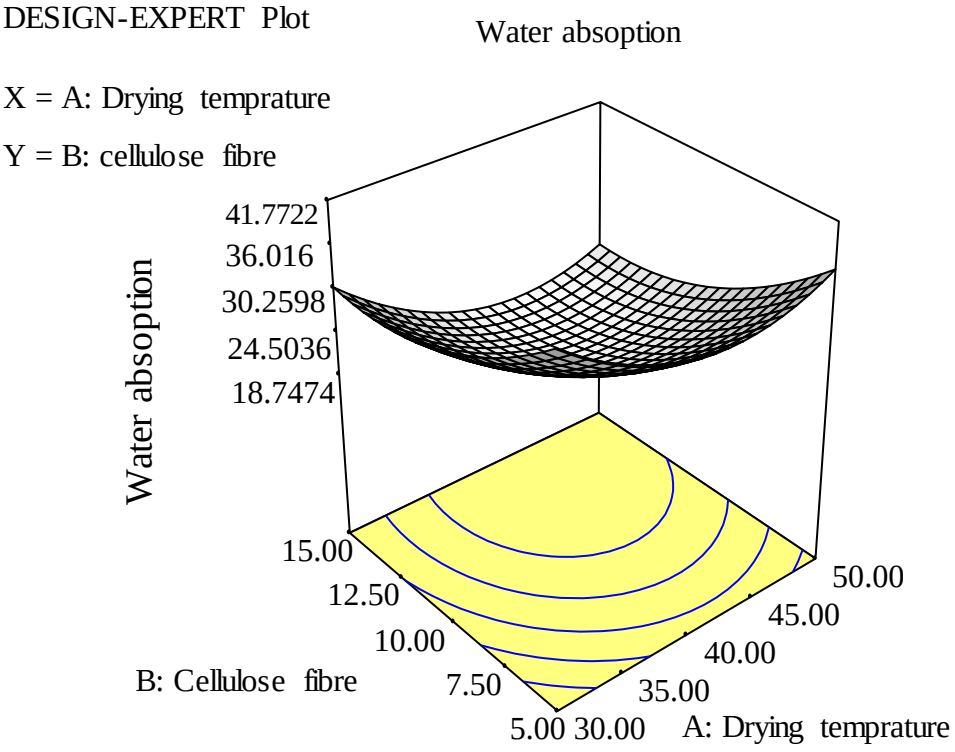


Figure 4.9 Interactive effects of drying temperature and cellulose fibre on water absorption of developed bioplastic

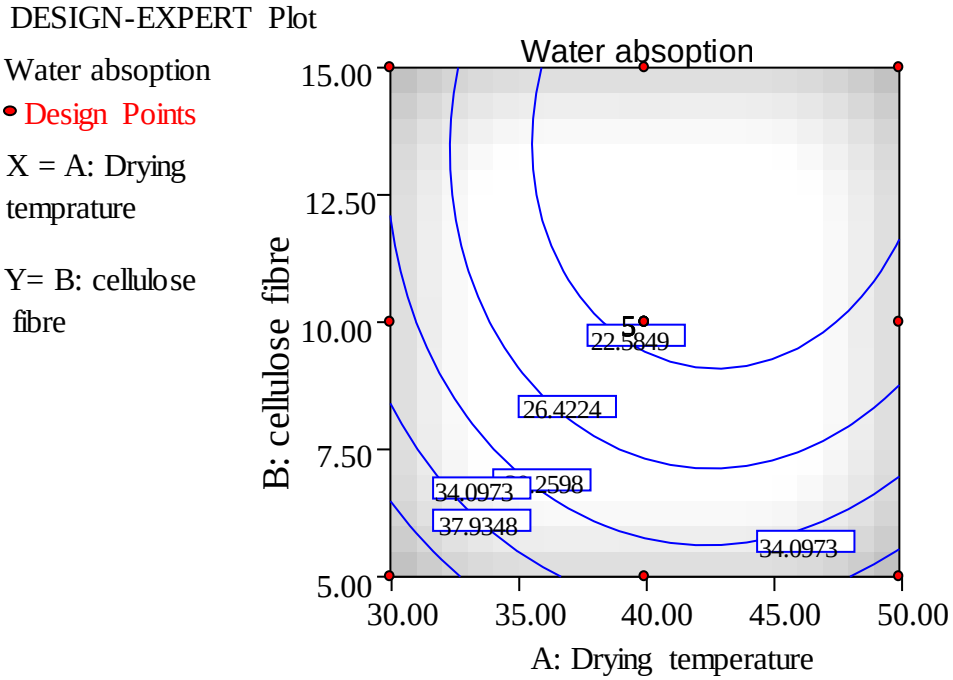


Figure 4.10 Contour effect of drying temperature and cellulose fibre on water absorption of bioplastic

DESIGN-EXPERT Plot

Elongation at break

X = A: Drying temprature

Y = B: cellulose fibre

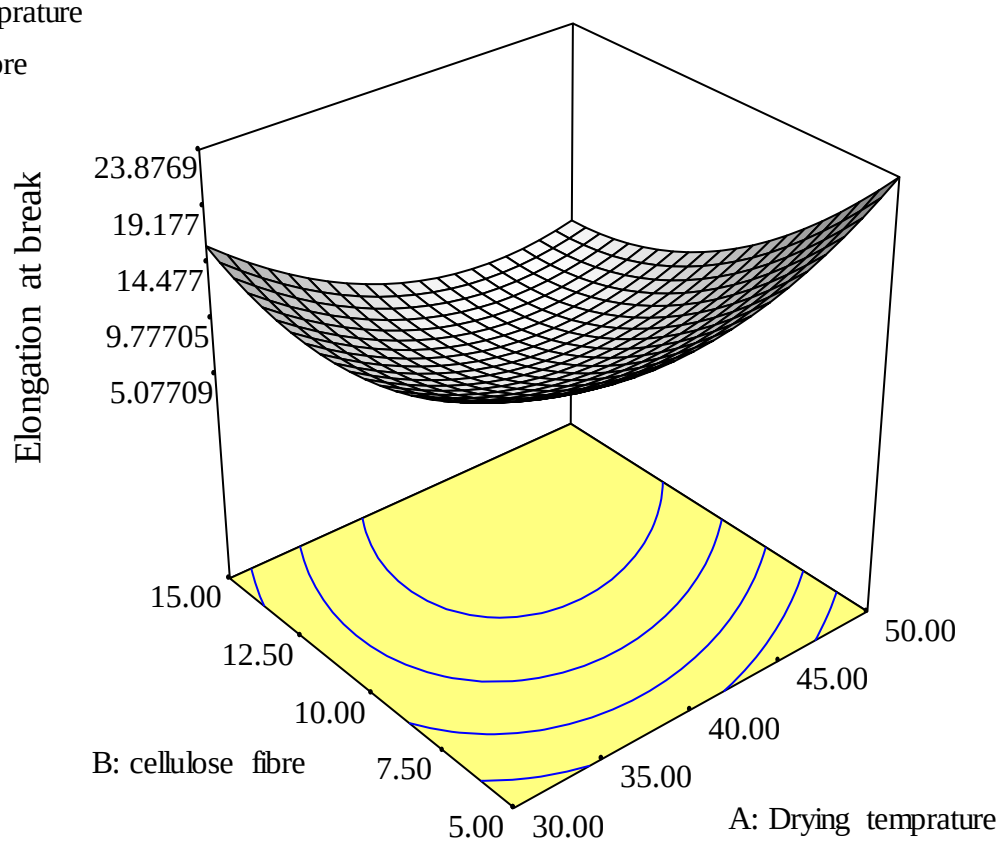


Figure 4.11 Interactive effects of drying temperature and cellulose fibre on elongation at break of bioplastc

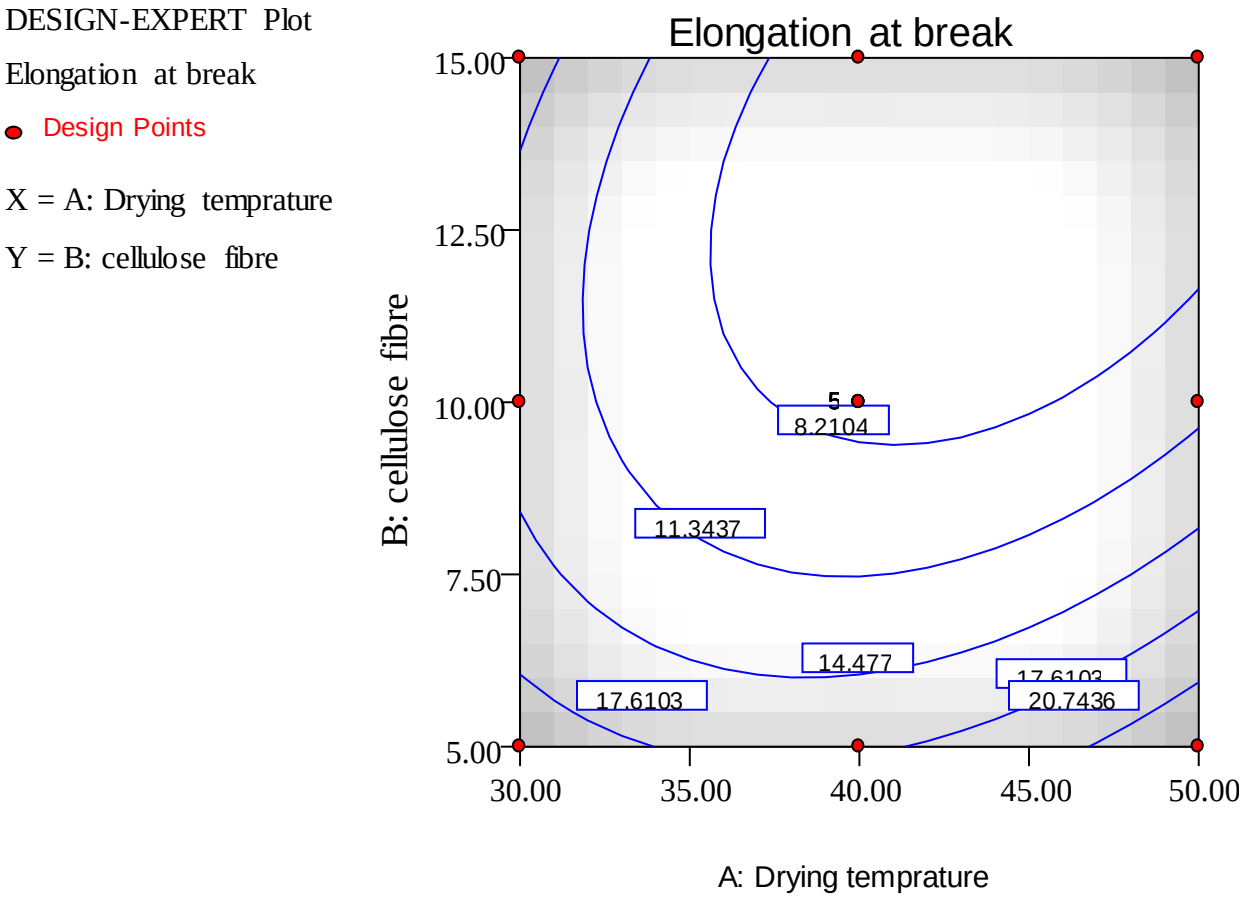


Figure 4.12 Effect of drying temperature and cellulose fibre on elongation at break contour figure

4.6 Optimization of process factors

The broad optimization objective is the maximization of quality and minimizing of oven drying costs. RSM (Response Surface Methodology) is a collection of statistical and mathematical techniques used for developing, improving, and optimizing processes in which a response of interest is influenced by several variables and the objective is to optimize the response. RSM has important application in the design, development and formulation of new products, as well as in the improvement of existing product design. It defines the effect of the independent variables, alone or in combination, on the processes. In addition to analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which describes the physical or biochemical processes (Montogomery, 2001). It consists of a group of mathematical and statistical techniques that can be used to define the relationships between the response and

the independent variables. In addition to analyzing the effects of the independent variables, this experimental methodology also generates a mathematical model. The graphical perspective of the mathematical model has led to the term Response Surface Methodology (Bas, D., and Boyaci, I.H, 2007a). Optimization studies using RSM could be separated into three stages. The first stage is the preliminary work in which the determination of the independent parameters and their levels are carried out. The second stage is the selection of the experimental design and the prediction and verification of the model equation. The last one is obtaining the response surface plot and contour plot of the response as a function of the independent parameters and determination of optimum points (Baş & Boyacı, 2007a). Optimization analyses were conducted on the data from the Central Composite Design(CCD) to relate drying temperature and sugar cane bagasse cellulose fibre concentration to Tensile strength, water absorption and elongation at break of developed specimen. The numerical optimization was generated by design expert 6.0.8 software and elucidated in a table 4.6 below as a function of two factors drying temperature and sugar cane bagasse cellulose fibre. An optimal processing conditions of the bioplastic developed from corn starch and cellulose fibre was selected for further characterization based cellulose fibre and oven drying temperature setting in the range and as well as maximizing the tensile strength and minimizing water absorption and elongation at break of the sample (see table 4.3 below). Therefore, considering those parameters the value obtained from optimum experimental for drying temperature (40.85℃), cellulose fibre (12.20%), tensile strength (27.2175), water absorption (18.3257%) and Elongation at break (4.25203%) were obtained with desirability of 1.00

Table 4.3 Optimization constraint for developed bioplastic

Constraints Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Drying temperature	Is in the range	30	50	1	1	1
Cellulose fiber	Is in the range	5	15	1	1	1
Tensile strength	Maximize	10.79	26.81	1	1	1
Water absorption	Minimize	19.97	44.54	1	1	1
Elongation at break	Minimize	4.32	27.34	1	1	1

4.7 Physicochemical characterization of developed bioplastic from starch-cellulose based fiber

4.7.1 Compound microscopy

In Fig 4.13 the compound micrographs of bio-plastics prepared with particle sizes of 80µm (a) unfilled starch matrix of control and (b) reinforced bioplastic are shown. The biocomposite samples observed in Fig.4.13 correspond to thermoplastic material prepared unfilled matrix without reinforcing cellulose particles, and the samples shown in (b) prepared with a treated sugarcane bagasse fiber (cellulose) amount of 10% contained. As can be observed in reinforced bioplastic, an even distribution of cellulose particles in the thermoplastic starch matrix is clearly evident due to the obtained transparency. Moreover, Fig.4.13b shows the compatibility of the reinforcing material with the matrix and the organization of the cellulose fiber in the bioplastic. Alexander, (1993) prepared composites of corn starch and banana fibers *via* thermo molding. In the Bourtoom, (2009) study, the authors reported the formation of air bubbles during the molding process that may have formed by the evaporation of water. In the present study, the absence of bubbles in the samples, which can produce defects in the plastic, confirmed the success of the preparation and viability of the process. In addition, the methodology applied to prepare bioplastic in the present work avoids problems such as fluidity by high viscosity in the processing of the thermoplastic starches by extrusion and injection that is determined in literature (Ma *et al.* 2005).

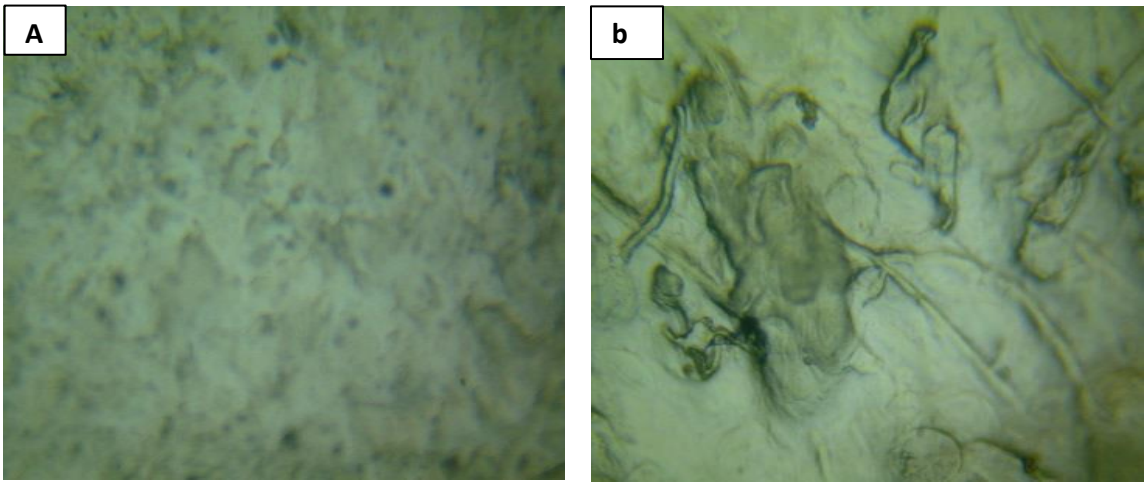


Figure 4.13 Micrographs of bioplastic developed from a) unfilled starch matrix and b) filled with 10% treated fiber.

4.7.2 FTIR spectroscopy analysis

The FTIR spectra of only starch-based bioplastic or a control (100% starch) and starch-cellulose fibre composites (10% cellulose content) were examined with respect to characterizing the chemical bonds between fibers and starch. The major observed peaks could be identified as the functional groups of starch and fiber. However, there were some slight changes in band positions and intensities. It is known that if two polymers are compatible, a distinct interaction (hydrogen bonding or dipole interaction) exists between the chains of one polymer and those of the other, causing the FTIR spectra of composites to change. It is evident in Figure 4.14 that characteristic peaks appeared at 3200 cm^{-1} to 3500 cm^{-1}, which can be attributed to C-O-H bond stretching. This behavior might be due to hydrogen bond formation occurring after the addition of fiber. In order to confirm the increase in intermolecular hydrogen bonding, it can be observed that the band at 3200 cm^{-1} to 3500 cm^{-1} was slightly broadened after the addition of sugarcane bagasse cellulose fiber. It is also worth noting that the difference in the FTIR spectra between TPS (thermoplastic starch) and TPS-CF at 1162 cm^{-1} is that the C-O stretching peak is narrower in TPS/CF, possibly due to the rearrangement of hydrogen bonds between starch and fiber. The change in the FTIR spectra indicates a distinct interaction and compatibility between the chains of polymers. Figure 4.14 shows the FTIR of the initial bio plastic from starch (100%) as a control. The starch spectrum shows the common signals for these kinds of polysaccharides, with glucopyranose rings such as OH bands at 3450 cm^{-1}, C-H stretching vibrations of aliphatic groups at 2926 cm^{-1}, adsorbed water signals at 1646 cm^{-1}, C-C and C-O stretching at 1100 cm^{-1}, and C-O-H bending vibration at 1007 cm^{-1}. It also can be seen that pure TPS bio-film exhibits FTIR main peak positions in the range of 1458 to 1150cm^{-1}, 1410-1230cm^{-1}, and 1200-1000cm^{-1}, representing C-H asymmetric stretching of -CH_2-, -CH_2- deformation, C-O-C stretching, and C-O-H stretching, respectivel. The peak position at approximately 1646 cm^{-1} is due to the bound water present in the starch (Prachayawarakorn *et al.*, 2011).

Table 4.4 Signal Assignments of Functional groups identified by Fourier transform- Infrared spectroscopy analysis of bioplastic

Wave number (cm^{-1})	Functional groups
1005-897	C-O-H stretching
1150-1005	C-C stretching
1235-1150	C-O-C stretching of Easter
1734-1631	Bounded water
3000-2826	C-H stretches
3600-3450	-OH stretching

The FTIR spectra of bio-composites with reinforced material (sugar cane bagasse cellulose fibre) content amounts (10%) and organized by particle sizes of 80µm which is keeping it at constant is depicted in Figure.4.15. In this case, different signal patterns are observed from bio-composites prepared (Fig. 4.15) as a result of their different chemical composition due to addition of fiber, the following changes in the intensity of some signals, such as those at 1764, 1660, and 1424 cm-1, can be attributed to the addition of cellulose fibre at optimal concentration. Also the FTIR results bioplastic made of 100% cornstarch are plotted in the figure. 4.14 below. In the case of the bio-plastic prepared from 100% starch-based fiber control, the signal at 1707cm^{-1} of the control specimen decreased to 1666 cm^{-1} where cellulose fibre added to the starch matrix as a reinforced material. It is known that if two polymers are compatible, a distinct interaction (hydrogen bonding or dipolar interaction) exists between the chains of one polymer and those of the other, causing the FTIR spectra of composites to change. The amount of adsorbed water seemed to have a small increase in the bio-composite that had 10% fibre content. However, this may be only an optical effect caused by the decrease of the adjacent carbonyl band (1720 cm^{-1}). In contrast, the signal at 1099 cm^{-1} for control decreased to 1050cm^{-1} when 10% of cellulose fibre was added to the starch.

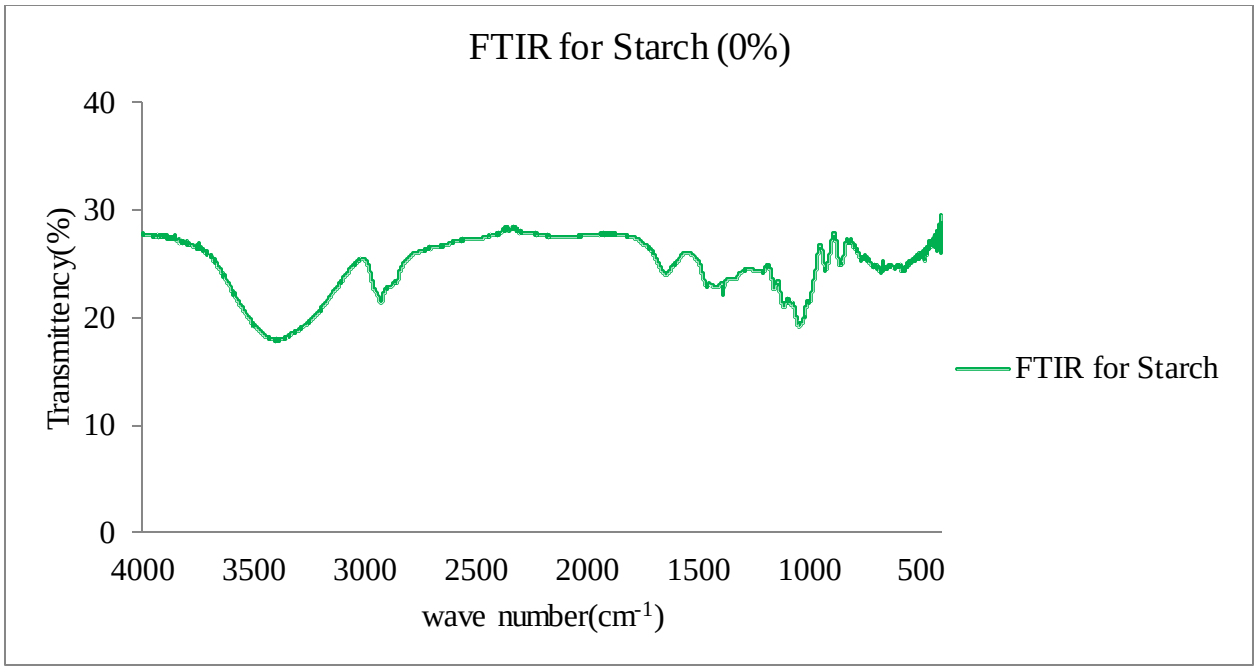


Figure 4.14 FTIR result of the starch-based bio-plastic plot

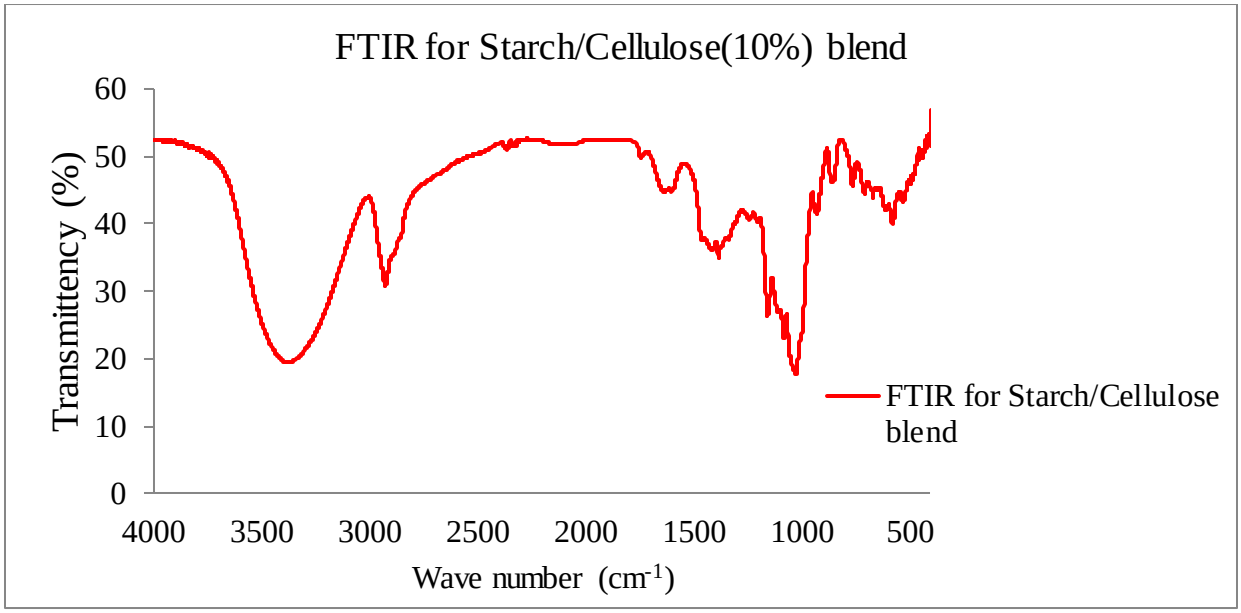


Figure 4.15 FTIR result of starch-cellulose, bio-plastic plot

Although the carbonyl signal (1720 cm^{-1}) of bio-composites prepared with particles of 80µm (Fig. 4.15) was more intense than that of the control sample bio-plastic (Fig.4.14). A possible explanation for this may be hydrogen bonding between the CH_2-OH groups from the starch and cellulose fibre (Sarifuddin Norshahida, 2012).

4.7.3 Transparency of developed bioplastic

The percentage of transmittance of corn starch film at a wavelength of 600 nm and containing optimum cellulose fiber (CF) (10% concentration) prepared by solvent casting process. The results showed (see Table 4.5) that the films were off white in color but highly translucent. Addition of cellulose increased film cloudiness for starch-based films. This was due to the cellulose being cloudier than the corn starch so the transparency decreases of 118% for starch to 113% for 10% cellulose containing bio-plastic (see Table 4.5). This was attributed to starch-cellulose films being inherently cloudier than starch-based composite films with no cellulose added. The decrease in transparency values was observed due to the cellulose incorporation. Comparing this, with the same amount of cellulose, the results pointed out those films with 100% starch based film showed higher transparency values than 10% cellulose fiber. Transparency of the films is of importance in some instances, when used as packaging materials (Assefa Z, Admassu S., 2013). Addition of cellulose fiber generally causes the films to reduce their transparency, but at less small difference compared to control. Starch composite film without cellulose was rather transparent.

4.7.4 Solubility and density of developed bioplastic

Solubility of starch-based films: Starch, being a hydrophilic polymer, shows high affinity towards water. Hence, upon hydration, starch-films absorb water and swell. The swelling behavior of the plasticized starch based film formed with cellulose fibre is shown in Table 4.5. The film with a 10% of cellulose fibre content had a lower swelling capacity than the films with only containing starch matrix. Therefore, films which had 10 % of sugarcane bagasse cellulose fibre showed a lower swelling power than only starch matrix. From the experimental result the solubility of the specimen was 10.17% for starch-cellulose based (10% cellulose fibre) bioplastic and 14.78 % for 100% starch-based bioplastic can recommend for packaging purposes. The film, which has the ability to dissolve in water may be a good candidate for edible film and packaging material development which in turn requires complete solubility upon hydration process. Films which revealed an extremely high swelling power (Control and starch-cellulose based plastic) may be desirable for development of absorbent pads such as those used in meat packages to absorb exudates from meat. As can be seen in Table 4.5 the films containing the optimal amount of cellulose fibre (10%) had a lower solubility. The control films had the highest solubility

(14.78%) than CF-starch based bioplastics. Based on the results it can be recommended that films having a low solubility are favorable for the packaging purpose. Density of film developed from 100% starch and 10% CF containing was 1.059 g/ml and 1.068g/ml, respectively (see Table 4.5), there was an increment in density in the case of CF, this is may be due to the addition of 10% of cellulose fibre.

Table 4.5 Experimental result data for measuring bioplastic transparency, solubility and density

product	Transparency (%)	Solubility (%)	Density(g/ml)
Starch (100%) as a control	118	14.78	1.059
10%SCBF containg	113	10.17	1.068

5 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this research, development of bioplastics from corn starch and cellulose fibre from sugar cane were investigated. Sugar cane bagasse fibers with an average diameter of 80μm derived from bleached or treated pulp, slightly decreased the moisture content of starch films, but doubled the tensile strength. These tensile test results are slightly higher than those obtained by wheat grass cellulose fibre composites but similar to those of flax cellulose crystals (Cao et al. 2008). As well as, in this work the strength of the cellulose fibre composite decreased at fibre loadings above 10 wt%. This may be caused by fibre agglomeration and entanglement due to the cellulose fibre having a high aspect ratio. The films formed with the mix of starch and saponins were highly flexible and resembled plastic films.

The effect of cellulose fibre to starch ratio and oven drying temperature on the tensile strength, water absorption and elongation at break were studied. The output of the experiments conducted has been analyzed by design expert 6.0.8 of three levels and two factor central composite designs and response surface methodology was employed. In the development of bioplastic the three responses were significantly depend on starch-cellulose fibre ratio and oven drying temperature. Generally, as processing condition (cellulose fibre and oven drying temperature) increase from low level to center point tensile strength increases, but, was slightly decreased at some interval as both processing conditions increased from the center to the highest level. In terms of water absorption the changed level of drying temperature and cellulose fibre ratio results water absorption decreased as drying temperature increased from low level to vicinity of middle level and increases as moved to a higher level. In terms of elongation at break of the specimen the increase oven drying temperature causes the value of elongation at break decreases until it reaches center point. As well as further increasing of drying temperature from center point the result of elongation at break increases smoothly. In both process conditions elongation at break decreases from low level to center point and increase slightly starting from the center point to high level. But, the development of bioplastic was very sensitive to oven drying temperature followed by cellulose fibre ratio in all three responses that means tensile strength, water absorption and elongation at break were mainly affected by oven drying temperature than cellulose fibre. From the design software employed the maximum tensile strength of 26.81 MPa,

water absorption of 20.52% and elongation at break of 4.32% were obtained at optimal value of the processing condition. Using numerical optimization of design expert 6.0.8 for development of bioplastic from cellulose fibre and cornstarch at operating condition for drying temperature ($44.68^{O}C$), cellulose fibre (13.99%) determined for developing bioplastic by solvent cast process.

FTIR and compound macroscopic analyses provided evidence of the strong interactions that existed between starch and bagasse fibers. The Compound micrographs revealed that the cellulose fibers are well wetted by the starch matrix, and showed that the fibers are strongly attached to the starch matrix since it pulls the matrix out of shape where the fibre is attached during tensile testing.

Results showed that the starch composites reinforced with sugar cane bagasse cellulose fibre have a potential application in biodegradable packaging and biocomposite medical science (Alvarez *et al.,* 2004). Regarding transparency, solubility and density the developed bio plastic at optimal point shows lower transparency, solubility and higher density(13%, 10.7% and 1.068g/ml) compared to control (100% starch) made bioplastic (118%, 14.7% and 1.059g/ml restively) this was due to introduction of fibre into a starch matrix which from hydrogen bond.

5.2 RECOMMENDATION

From this research it is clear that bioplastic can be produced using cornstarch and isolated cellulose from sugarcane bagasse fibre using glycerol as a plasticizer for the present study. Even though bioplastic is produced further investigations of the following points can be recommended.

- Since this study was done at the micro level to produce bioplastic the future study should focus on Nano scale production and characterization to improve quality, mechanical and physic-chemical properties of fibre reinforced based bioplastic.
- In the future the production of bioplastic reinforced with cellulose extracted from sugarcane bagasse fibre should be modified by controlling mixing temperature and using different technologies such as extrusion, injection molding, blow molding etc.

- In order to explore more effective bioplastic based on starch and cellulose fibre more wide studies should be carried out by considering other processing factors such as drying time, plasticizer, starch gelatinization temperature, fibre particle size and solvents on the quality, mechanical and physicochemical property should be investigated.
- Based on the present study developed bioplastic can be used for food packaging so in the future study focus on the feasibility of using bioplastic for food packaging.
- Since corn starch is edible food it creates problem of food security of our country as well as the world, focus should be given to non-edible based starch source.
- In addition, extensive researches are still needed on the permeability (water vapor and gas transmission rates), barrier properties, and the effect of hydrophobic plasticizers and effectiveness of these bioplastic on different application.

6. REFERENCES

Abdillahi, H., Chabrat, E., Rouilly, A. & Rigal, L. (2013). *Influence of citric acid on thermoplastic wheat flour/poly(lactic acid)blends. II. Barrier properties and water vapor sorption isotherms. .* Industrial Crops and Products, 50, 104– 111.

Abdul Khalil, I.U.H. B A. Zaidon, D. Hermawan, and Y.S. Hadi,. (2012). *Materials and Design, .* 42,353-368.

Ahmed, M.S. and Mohammad, F.A. (2014). *Theoretical Modal Analysis of Freely and Simply Supported RC Slabs. .* International Journal of Mechanical, Aerospace, Industrial and Mechatronics Engineering, 8, 2026-2030.

Alexander, A. (1993). *Biodegradable plastics based on cellulose acetate. .* Battelle- Institute E.V., Frankfurt, Germany. : J. Macromol. Sci., Pure Appl. Chem. 3 (9–10), 733–740.

Alvarez, V. A., Kenny, J. M., and Vázquez, A. (2004). *Creep behavior of biocomposites based on sisal fiber reinforced cellulose derivatives/starch blends.* Polymer Composites. 25: 281-288.

Armelin, E. (2002). *Síntesis y caracterización de nuevas poliesteramidas: estudio de sus propiedades.* Barcelona España.: Tesis Doctoral. Universidad Politécnica de Cataluña. Escuela Técnica Superior de Ingenieros Industriales de Barcelona.

Ashok Pandey, Carlos R. Soccol, Poonam Nigam, Vanete T. Soccol. (2000). *Biotechnological potential of agroindustrial residues. .* I: sugarcane bagasse. Bioresource Technology 74 , 69 – 80.

Assefa Z, Admassu S. (2013). *Development and Characterization of Antimicrobial Packaging Films.* J Food Process Technol 4, 235.doi:10.4172/2157-7110.1000235.

ASTM. (2008). *ASTM D638-08 Standard Test Method for Tensile Properties of Plastics. .* West Conshohocken, PA, USA: ASTM International.

Aulton, ME, Abdul-Razzak MH and Hogan JE. (1981). *The mechanical properties of hydroxyl propylmethylcellulose films derived from aqueous systems. Part 1: The infuluence of plastcizers.* Drug Development and Industrial Pharmacy, 7(6): 649-68.

Averous L, Boquillon N. (2004). *Biocomposites based on plasticized starch: thermal and mechanical behaviours.* Carbohydrate Polymers 56 (2): 111-122.

Averous L, Halley PJ. (2009). *Biocomposites based on plasticised starch. .* Biofuels, Bioproducts and Biorefining 3, 329–343.

Aydinli, M. and Tutas M. . (2000). *Water sorption and water vapour permeability properties of polysaccharide(Locust Bean Gum) based edible films.* Lebensm Wiss. Technology,33: 63-72.

Bas, D., and Boyaci, I.H. (2007a). *Modeling and optimization I: Usability of response surface methodology.* Journal of Food Engineering, 78(3) , 836-845.

Berhanu, T. K. (December 2014.). *Mechanical Behaviour of Jute Fibre Reinforced Polypropylene Composites.* 5th International & 26th All India Manufacturing Technology, Design and Research Conference (AIMTDR 2014), Guwahati, 12-14 .

Billmeyer, F. W. (1984). *Textbook of polymer science. Ed. John Wiley.* Singapore. .

Boundy, J. A., Turner, J. E., Wall, J. S., and Dimler, R. J. (1967). *Influence of commercial processing on composition and properties of corn zein.* Cereal Chem. 44:281-287.

Bourtoom, T. ((2009).). *Edible protein films.* properties enhancement international food research jornal.

Cao, Y., Wu, J., Meng, T., Zhang, J., He, J.S., Li, H.Q. . (2007). *Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). .* Carbohyd. Polym. 69, 665-672.

Carr, M. E., and Cunninghan, R. L. 1989. (n.d.). *Glycol glucosidea from starch by continuous twinscrew extruder processing. .* Cereal Chem. 66:238-243.

Cha, D. S., and Chinnan, M. (2012). *Biopolymers-Based Antimicrobial packaging:.* a review. Crit. Rev. Food Sci. Nutr. 44: 223-237.

Chen Y, Liu C, Chang PR, Cao X, Anderson DP. (2009). *Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolysed from pea hull fibre: Effect of hydrolysis time. .* Carbohydrate Polymers 76, 607–615.

Cosimo, C. (.-E. (2013). *Biodegradable plastic material based on cellulose acetate and relative end-products.* EP 2599827 A1. Also published as CN103131052A, US20130133549.

Cox, David L. Nelson, Michael M. (2008). *Lehninger principles of biochemistry (5th ed.).* New York:: W.H. Freeman. ISBN 978-0-7167-7108-1.

Curvelo, A.A.S., Carvalho, A.J.F.D. and Angelli, J.A.M. . (n.d.). *Thermoplastic starch-cellulosic fibers composites: preliminary results. .* 2001: Carbohydrate Polymers. 45, 183- 188.

Cyras, V. P., Commisso, M. S., Mauri, A. N., & Vázquez, A. (2007). *Biodegradable double-layer films based on biological resources: Polyhydroxybutyrate and cellulose. .* Journal of Applied Polymer Science, 106, 749–756.

Dufresne A, V. M. (1998). *Improvement of Starch Film Performances Using Cellulose Microfibrils.* Macromolecules 31 (8): 2693-2696.

Endres, H.-J., & Siebert-Raths, A. (2009). *Technische Biopolymere, Carl Hanser Verlag, .* N. N.: DIN EN ISO 14855-1.

Eraricar, Salleh, Ida Idayu Muhamad, and Nozieanna Khairuddin. (2009). *Structural characterization and physical properties of antimicrobial starch based films.* World Acadamy of Science, Engineering and Technology,55:432-440.

FAO. (2007). *Food and Agriculture Organization of the Unites Nations. .* http://www.fao.org/page/boletin.htp.

Fengel, D., and Wegener, G. (1984). *Wood. Chemistry, ultrastructure and reactions. .* Walter de.

Forssell, P.M., Mikkila, J.M., Moates, G.K. and Parker, R. (1997). *Phase and glass transition behavior of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch.* Carbohydrate Polymers. 34, 275-282.

Funke, U., Bergthaller, W., Lindhaueur, M. G. (1998). *Processing and characterization of biodegradable products based on starch.* Polym. Degrad. Stab. 59(1-3):293-6.

Galicia-Garcia, T. M.-B.-A.-G.-M.-D. (2011). *Thermal and microstructural characterization of biodegradable films prepared by extrusion-calendering process.* Carbohydrate polymers. 83, 354-361.

Gilfillan WN, N. D. (2012). *Preparation andPreparation and characterisation of composites from starch and sugar cane fibre.* Industrial Crops and Products 40 (0): 45-54.

Gontard . (1993). *Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten films.* Journal of Food Science, 58, 206–211.

Gracida, J., Alb, A. J., Cardoso, J., and Pérez-Guevara, F. (2004). *Studies of biodegradation of binary blends of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBHV) with poly(2 hydroxyethylmetacrilate) (PHEMA). .* Polymer Degradation and Stability, 83, 247–2.

Guilbert, S., Cuq, B., & Gontard, N. (1997). *Recent innovations in edible and/or biodegradable packaging materials.* Food Additives and Contaminants, 14, 741–751.

Halley, P. R. (2001). *Developing biodegradable mulch films from starch-based polymers. .* Starch/Stärke, 53(8), 362–367.

Hattallia S., Benaboura A., Ham-Pichavant F., Nourmamode A., Castellan A. (2002). *Adding value to alfa grass (Stipa tenacissima L.) soda lignin as phenolic resins.* 1. Lignin characterization. Polymer Degradation and Stability ; 76 : 259–64.

Jacob, M. T. (2004). *Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites. .* Composites Science and Technology. 64, 955-965.

Jahn, A. (2002). *Characterization of alkali treated flax fibers by means of FT raman spectroscopy and environmental scanning electron microscopy. Spectrochimica Acta.* Part A: Molecular and Biomolecular Spectroscopy. 58, 2271-2279.

Janssen and L. Moscicki. (2009). *Thermoplastic starch: a green material for various industries, .* Wiley, Weinheim, .

John, J. K., Sunitha, V. R., Raja, K. C. M., and Moorthy, S. N. (1999). *Physicochemical and enzyme susceptibility characteristics of starch extracted from chemically pretreated Xanthosoma sagitifolium roots.* . Starch 51:86-89.

Kaushik, A. S. (2010). *Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw.* Carbohydrate Polymers. 82, 337-345.

Kebbede. (2004). *Living with urban environmental health risks.* The case of Ethiopia.

Khoathane et al, M. C. (2008). *Hemp Fiber-Reinforced 1-Pentene/Polypropylene Copolymer: The Effect of Fiber Loading on the Mechanical and Thermal Characteristics of the Composites,.* Journal of Reinforced Plastics and Composites, Vol. 27.

Kim, J., Kim, W. and Shin, M.A. (1997). *Comparative study on the retrogradation of rice starch gels by DSC, X-ray and á-amylose methods.* . Starch/Starke. 49, 71-75.

Kuorwel. (2011). *Incorporation of natural antimicrobial agents in to starch based material for food packaging.* . Journal of food science, 76.

Lafargue D, Pontoire B, Buléon A, Doublier JL, Lourdin D. (2007). *Stracture and mechanical properties of hydroxypropylated starch films.* Biomacromolecules 8,3950-3958.

Lem Ethiopia. (2006). *Study on total waste management of Jimma southern Ethiopia.*

Li, X. (2008). *Development of flax fiber-reinforced polyethylene biocomposites by injection molding.* Ph.D. dissertation, University of Saskatchewan, Canada.

Liu, J. a. (2013). *Biodegradable composites from rice straw and cornstarch adhesives.* . Advance Journal of Food Science and Technology. 5, 41-45.

Luc Avérous, Eric Pollet,. (2012). *Environmental silicate nano-biocomposites.* . London: Springer.: ISBN 978-1-4471-4108-2.

Ma, X., Yu, J. and Kennedy, J.F. (2005). *Studies on the properties of natural fibers-reinforced thermoplastic starch composites.* Carbohydrate Polymers. 62, 19-24.

MARIATTI, M. J. (2008). *"Properties of banana and pandanus woven fabric reinforced unsaturated polyester composites",* . Journal of Composite Materials, v. 42, pp. 931 – 941, May. .

McHugh, TH, Krochta JM. . (1994). *Milk-protien-based edible films and coatings.* Food Technol, 48: 97-103.

Mo, X. Z. (2010). *Studies on the properties of banana fibers-reinforced thermoplastic cassava starch composites: preliminary results.* Advanced Materials Research. 87-88, 439-444.

Moad, G. (2011). *Chemical modification of starch by reactive extrusion.* Progress in Polymer Science, 36, 218–237.

Montogomery, D. (2001). *Design and analysis of experiments. .* New York Wiley, 416-419.

Muller, C. L. (2009). *Effect of cellulose fibers on the crystallinity and mechanical properties of starch-based films at different relative humidity values.* Carbohydrate Polymers. 77, 293-299.

Nishino. (2013). *Acetylation of plant cellulose fibre in supercritical carbon dioxide.* Polymer 52, 830–836.

Obara, S. McGinity JW. . (1995). *Influence of processing variables on the properties of free films prepared from aqoues polymeric dispersions by a spray technique.* He International Journal of Pharmaceutics, 37:849-853.

Oskman, K., Skrifvars, M., and Selin, J. F. (2003). *Natural fibres as reinforcement in polylactic acid (PLA) composites. .* Composites Science and Technology. 63:1317–1324.

Park, H., Li, X., Jin, C., Park, C.-Y., & Cho, W.-J. (2002). *Preparation and properties of biodegradable thermoplastic starch/clay hybrids. .* Macromolecular Materials and Engineering, 287, 553–558.

Patrycja, Wojciechowska. (2012). *The Effect of Concentration and Type of Plasticizer on the Mechanical Properties of Cellulose Acetat Butyrate Organic-Inorganic Hybrids, Recent Advances in Plasticizers, Intech,.*

Prachayawarakorn, J., Ruttanabus, P. and Boonsom, P. . (2011). *Effect of cotton fiber contents and lengths on properties of thermoplastic starch composites prepared from rice and waxy rice starches. .* Journal of Polymers and the Environment. 19(1), 274-282.

Rasal, R. M. (2010). *Poly(lactic acid) modifications. .* Progress in Polymer Science, 35, 338–356.

RASIDI, M.S., HUSSEINSYAH, S., LENG, T.P.,. (2014). *"Chemical modification of Nypa fruticans filled polylactic acid/recycled low-density polyethylene biocomposites", .* BioResources, v. 9, n. 2, pp. 2033-2050,.

Rhim, J. W. (2009). *Tensile, water vapour barrier and antimicrobial properties of PLA/nanoclay composite films. .* Food Science and Technology, 42, 612–617.

Sarifuddin Norshahida, H. I. (2012). *"TPSS/kenaf biocomposites,".* BioResources 7(3), 4294-4306. .

SGRICCIA, N. H. (2008). *"Characterization of natural fiber surfaces and natural fiber composites", .* Composites: Part A, v. 39, pp: 1632–1637.

Teixeira, E. P. (2009). *Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. .* Carbohydrate Polymers. 78, 422-431.

Torres F. Arroyo O. and Gomez C. (2007). *Processing and mechanical properties of natural fibre reinforced thermoplastic starch biocomposites. .* Journal of Thermoplastic Composite Materials, 20: 207-223.

Vallejos ME, C. A. (2011). *Composite materials of thermoplastic starch and fibers from the ethanol–water fractionation of bagasse.* Industrial Crops and Products 33 (3): 739-746.

Wattanakornsiri, A. (2012). *Thermoplastic starch reinforced with recycled paper cellulose fibers.* Ph.D. dissertation, Burapha University, Thailand.

Whistler R. L., B. J. (2005). *Starch: chemistry and technology.* Cambridge: Academic Press.

White, P. J. (2005). *Intra- and interpopulation variability of thermal properties of maize starch.* Cereal Chem. 67:70-73.

Wikipedia, N. N.:. (2017). *Internet access during January-March.*

Willett, J.L. and Doane, W.M. (2002). *Effect of moisture content on the tensile properties of starch/poly (hydroxyester ether) composite materials.* Polymer. 43, 4413-4420.

Wu, Q., Henriksson, M., Liu, X., & Berglund, L. A. . (2007). *A high strength nanocomposite based on microcrystalline cellulose and polyurethane. .* Biomacromolecules, 8, 3687–3692.

Wurzburg. (1986). *Introduction, in Modified Starches: Properties and Uses.* CRC Press, Inc., Boca Raton, USA.

Xiaoyun, Q. S. (2013). *''Smart'' materials based on cellulose: a review of the preparations, properties, and applications.* Materials 6, 738–781.

Yu L, Dean K, Li L. (2006). *Polymer blends and composites from renewable resources.* progress in polymer science 31,576-602.

Zepnik, S., Kesselring, A., Kopitzky, R., & Michels, C. . (2010). *Basics of cellulosics. .* Bioplastics Magazine, 1, 44–47.

APPENDICES

Appendix A: Vital pictures during the research work

I. Photograph of the experimental delignification and isolation of cellulose from sugarcane bagasse fiber

a) Air dried fiber

b) Grinded fiber

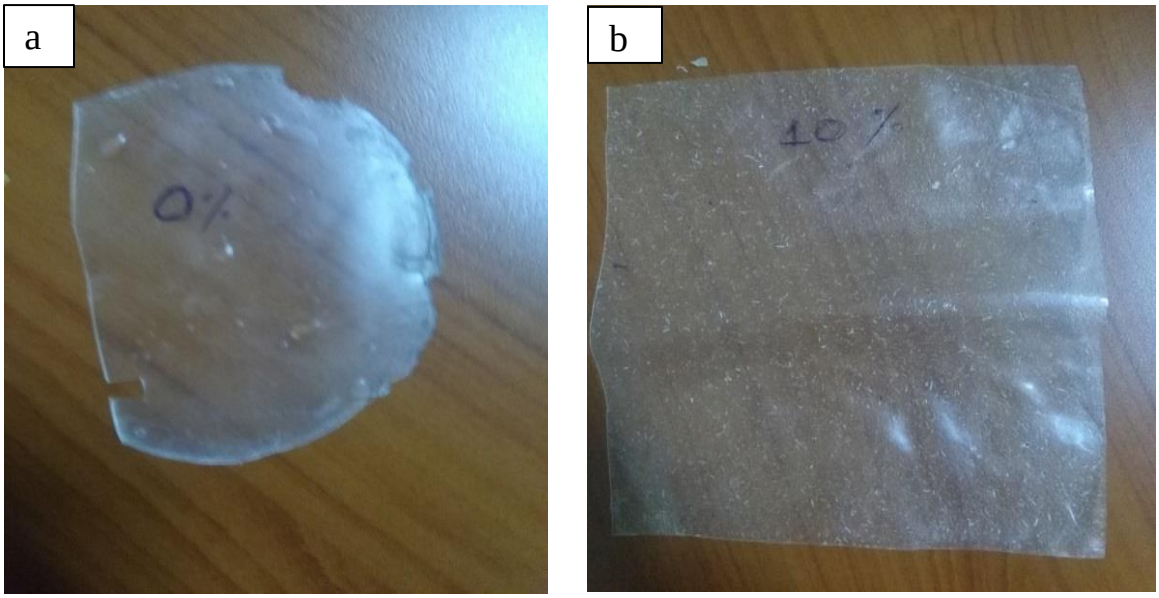
c) Sieving

d) Alkali treatment of $NaClO_2$

e) Vacume pump filtration

f) Dried cellulose

II. Photo graph of produced bioplastics from a) corn starch only b) starch reinforced by cellulose fiber



III. Equipment used during experimental process

a) Centrifugation

b) magnetic stirrer

c) Universal tensile testing machine

Appendix B: ANOVA for the two responses (pulp yield and kappa number)

Response 1: Tensile strength

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	379.03	5	75.81	318.56	< 0.0001	significant
A	79.28	1	79.28	333.16	< 0.0001	
B	94.01	1	94.01	395.07	< 0.0001	
A2	55.45	1	55.45	233.00	< 0.0001	
B2	67.41	1	67.41	283.30	< 0.0001	
AB	7.54	1	7.54	31.66	0.0008	
Residual	1.67	7	0.24			
Lack of Fit	1.12	3	0.37	2.76	0.1759	not significant
Pure Error	0.54	4	0.14			
Cor Total	380.70	12				

The Model F-value of 318.56 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, A^2, B^2, AB 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.

The "Lack of Fit F-value" of 2.76 implies the Lack of Fit is not significant relative to the pure error. There is a 17.59% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	0.49	R-Squared	0.9956	
Mean	21.81	Adj R-Squared		0.9925
C.V.	2.24	Pred R-Squared		0.9733
PRESS	10.16	Adeq Precision		47.199

The "Pred R-Squared" of 0.9733 is in reasonable agreement with the "Adj R-Squared" of 0.9925.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 47.199 indicates an adequate signal. This model can be used to navigate the design space.

Coefficient Factor	Standard Estimate	95% CI DF	95% CI Error	Low	High	VIF
Intercept	26.16	1	0.20	25.68	26.63	
A-Drying temperature		1	0.20	3.16	4.11	1.00
B-Cellulose fiber		1	0.20	3.49	4.43	1.00
A2	-4.48	1	0.29	-5.17	-3.79	1.17
B2	-4.94	1	0.29	-5.63	-4.25	1.17
AB	1.37	1	0.24	0.80	1.95	1.00

Response 2: Water absorption

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	844.65	5	168.93	433.18	< 0.0001	significant
A	90.79	1	90.79	232.82	< 0.0001	
B	352.51	1	352.51	903.94	< 0.0001	
A2	81.67	1	81.67	209.43	< 0.0001	
B2	171.19	1	171.19	438.98	< 0.0001	
AB	0.17	1	0.17	0.43	0.5325	
Residual	2.73	7	0.39			
Lack of Fit	2.13	3	0.71	4.70	0.0846	not significant
Pure Error	0.60	4	0.15			
Cor Total	847.38	12				

The Model F-value of 433.18 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, 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.

The "Lack of Fit F-value" of 4.70 implies there is a 8.46% chance that a "Lack of Fit F-value" this large could occur due to noise. Lack of fit is bad -- we want the model to fit.

Std. Dev.	0.62	R-Squared	0.9968	
Mean	26.62	Adj R-Squared		0.9945
C.V.	2.35	Pred R-Squared		0.9769
PRESS	19.58	Adeq Precision		58.128

The "Pred R-Squared" of 0.9769 is in reasonable agreement with the "Adj R-Squared" of 0.9945.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 58.128 indicates an adequate signal. This model can be used to navigate the design space.

Coefficient Factor	Standard Estimate	95% CI DF	95% CI Error	Low	High	VIF
Intercept	20.47	1	0.26	19.86	21.09	
A	-3.89	1	0.25	-4.49	-3.29	1.00
B	-7.67	1	0.25	-8.27	-7.06	1.00
A2	5.44	1	0.38	4.55	6.33	1.17
B2	7.87	1	0.38	6.98	8.76	1.17
AB	-0.20	1	0.31	-0.94	0.53	1.00

Response 3: Elongation at break

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	772.52	5	154.50	51.54	< 0.0001	significant
A	39.68	1	39.68	13.24	0.0083	
B	293.86	1	293.86	98.03	< 0.0001	
A2	74.56	1	74.56	24.87	0.0016	
B2	201.70	1	201.70	67.29	< 0.0001	
AB	6.53	1	6.53	2.18	0.1835	
Residual	20.98	7	3.00			
Lack of Fit	14.26	3	4.75	2.83	0.1703	not significant
Pure Error	6.72	4	1.68			
Cor Total	793.50	12				

The Model F-value of 51.54 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, 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.

The "Lack of Fit F-value" of 2.83 implies the Lack of Fit is not significant relative to the pure error. There is a 17.03% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	1.73	R-Squared	0.9736
Mean	12.25	Adj R-Squared	0.9547
C.V.	14.14	Pred R-Squared	0.8636
PRESS	108.21	Adeq Precision	18.733

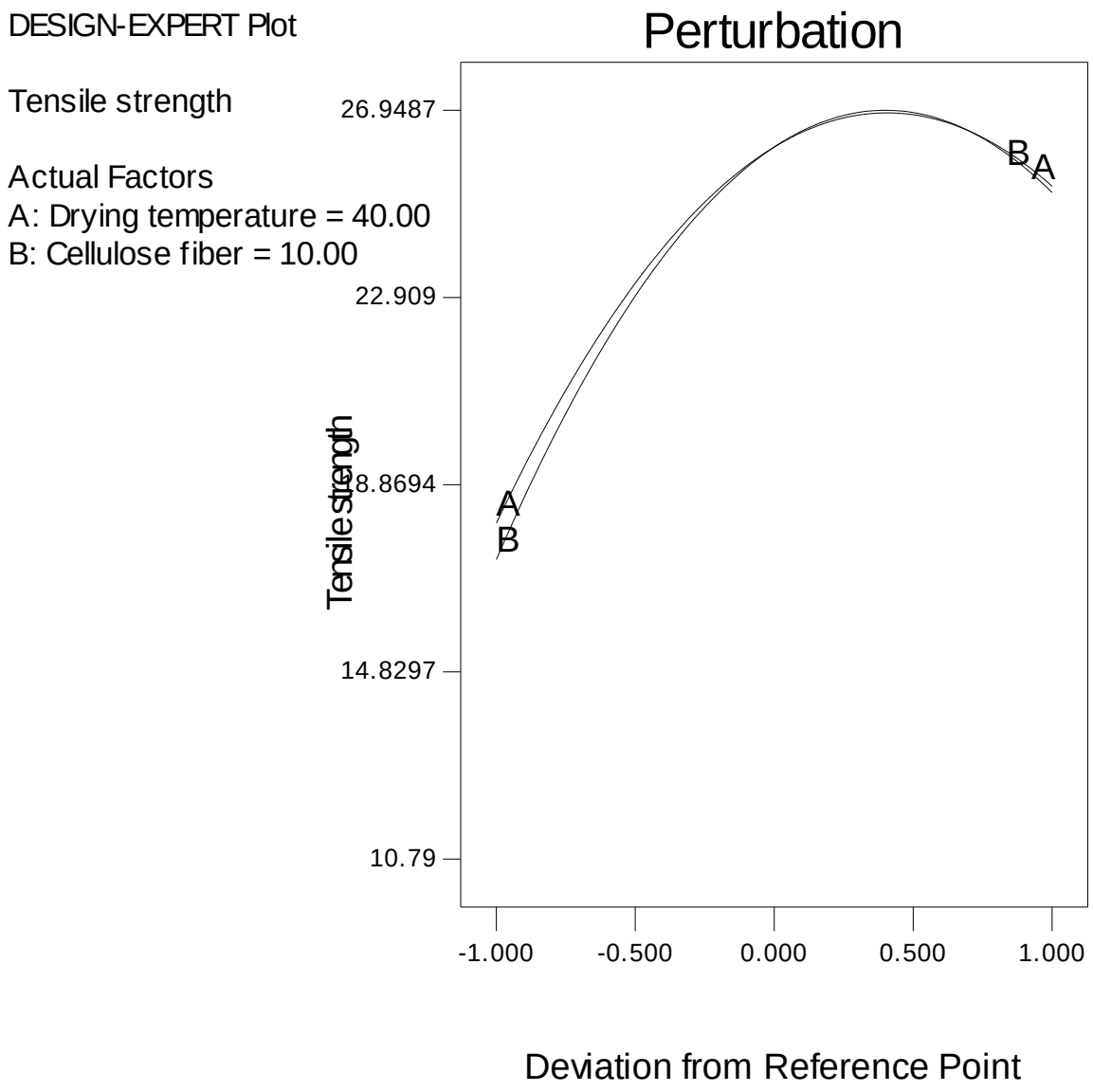
The "Pred R-Squared" of 0.8636 is in reasonable agreement with the "Adj R-Squared" of 0.9547.

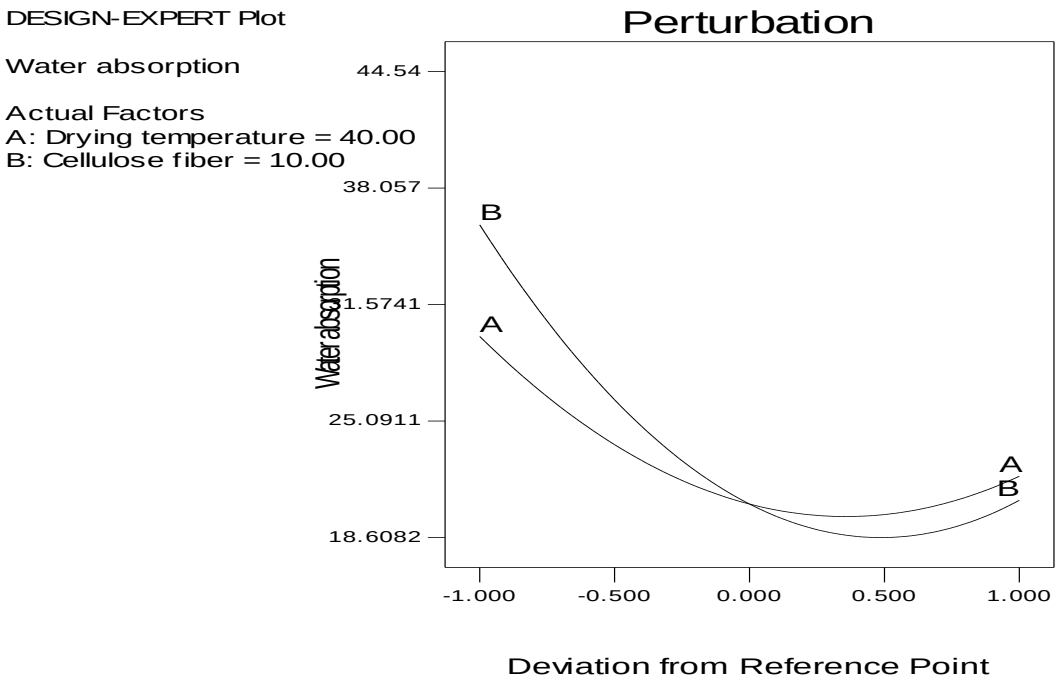
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 18.733 indicates an adequate signal. This model can be used to navigate the design space.

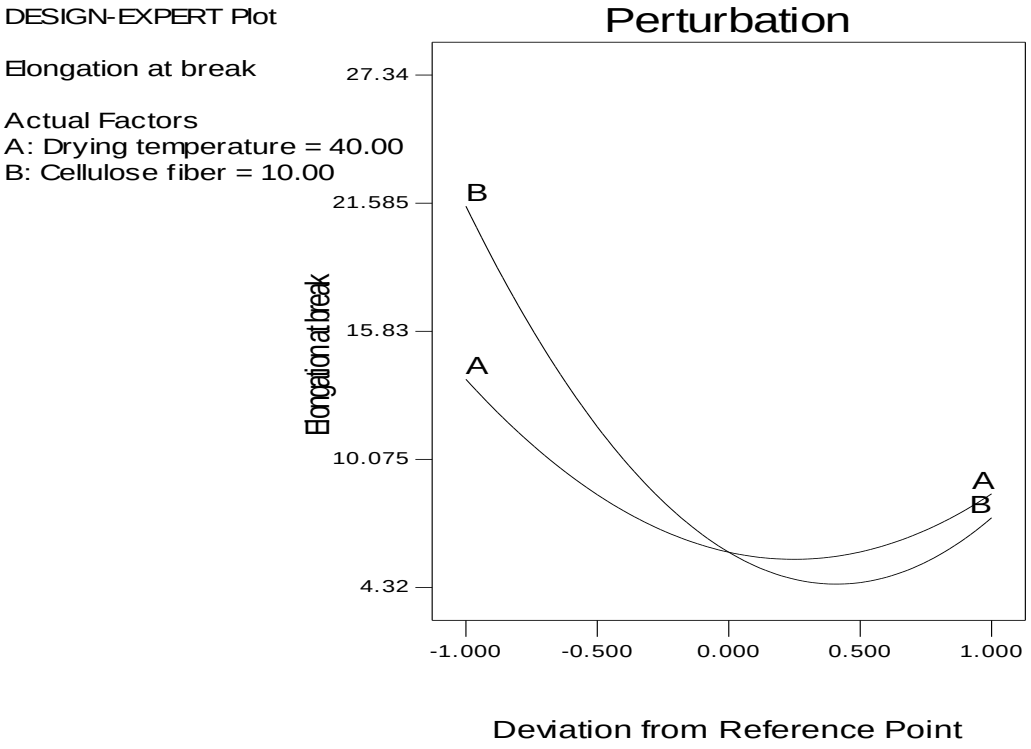
Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	5.91	1	0.72	4.21	7.61	
A-Drying temperature	-2.57	1	0.71	-4.24	-0.90	1.00
B-Cellulose fiber	-7.00	1	0.71	-8.67	-5.33	1.00
A^2	5.20	1	1.04	2.73	7.66	1.17
B^2	8.55	1	1.04	6.08	11.01	1.17
AB	-1.28	1	0.87	-3.32	0.77	1.00

Appendix C: Perturbation plot

I. Perturbation graphs showing the interaction factors




DESIGN-EXPERT Plot
Water absorption
Actual Factors
A: Drying temperature = 40.00
B: Cellulose fiber = 10.00
Perturbation
44.54
38.057
31.5741
25.0911
18.6082
Water absorption
B
A
A
B
-1.000
-0.500
0.000
0.500
1.000
Deviation from Reference Point


DESIGN-EXPERT Plot
Elongation at break
Actual Factors
A: Drying temperature = 40.00
B: Cellulose fiber = 10.00
Perturbation
27.34
21.585
15.83
10.075
4.32
Elongation at break
B
A
A
B
-1.000
-0.500
0.000
0.500
1.000
Deviation from Reference Point

DECLARATION

I declare that the thesis for the M.Sc. degree at the university of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, that all resources of materials used for this thesis have been duly acknowledged.

Name: Gadissa Mosisa

Signature: _____

Date of submission: _____

This thesis has been submitted for examination with my approval as a university advisor.

Name: Professor Belay Woldeyes

Signature:_____

Date: _____