ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Synthesis, Process Parameters Optimization and Characterization of Banana Peel Based Bio-plastic

By

Aster Taddele

A Thesis Submitted to the School of Chemical and Bio Engineering in Partial Fulfillment of the Requirement for the Award of **Degree of Master of Science** in Chemical and Bio Engineering (**Environmental Engineering Stream**)

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This is to certify that the thesis prepared by Aster Taddele, entitled: Synthesis, process parameters Optimization and Characterization of Banana Peel Based Bio plastic is submitted in partial fulfillment of the requirement for the degree of Master of Science in Chemical and Bio engineering complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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External Examiner: **Dr. Anteneh Marelign** Signature: ______________ Date: ____________

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Declaration

I declare that this thesis entitled "Synthesis, Optimization and Characterization of Banana Peel Based Bioplastic" has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. The work was under the guidance of Dr.Eng Abubeker Yimam instructor in Addis Ababa University, School of Chemical and Bio Engineering.

Name: **Aster Taddele**

Signature: ______________________

Date of Submission: November 2019

This thesis has been submitted for the examination with my approval as University Advisor.

Name: **Dr.Eng Abubeker Yimam**

Signature: ______________________

Date: November 2019

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List of Acronyms

ASTM – American Society for Testing and Materials

ISO – International Organization for Standardization

BaSo4- Barrium salfate

CaCO3- calcium carbonate

CEN – European Committee for Standardization

DEHP- Diethylhexyl phthalate

GM- Genetic modification

HCL- hydrochloric acid

PHB- polyhydroxybutyrate

PHA- polyhydroxyalkanoates

PHV- polyhydroxyvalerate

PHH- polyhydroxyhexanoate

PE- PolyEthylene

PP- polypropylene

PET- polyethylene terephthalate

PLA- polylactic acid

PBS- polybutylene succinate

PBAT- Polybutyleneadipate Terephythalate

BPA- Biphenol A

DEHP- Diethylhexyl phthalate

PA 11- Polyamide 11

PA 12- Polyamide 1

ABSTRACT

In this study, a small scale laboratory bioplastic was synthesized and investigated using banana peel as raw material. The effect of HCL concentrations, concentrations Glycerol, drying temperature and residence time for hydrolysis were analyzed. Design of experiment for response surface methodology (RSM) was used to analyze and optimize the simultaneous effect of HCl concentration (4%, 12%, 20% v/w), Glycerol concentration (4%, 8%, 12% v/w), drying temperature (40℃, 50℃, 60℃) and Residence time of (5, 15, 25 minutes). A four-factor and three-level Box-Behnken design was used to develop a statistical model to describe the relationship between physical and mechanical property of banana peel based bio film and the chosen independent variables and to optimize the production parameters of banana peel based bio-film. The model was statistically significant ($p < 0.0001$). A relatively good quality bioplastic with 9.348MPA of tensile strength, 13.523% Elongation at break, 62.883% water absorption and 48.388% biodegradability was synthesized at optimum parameters of 52.424℃ temperature, HCl concentration of (2.937ml HCl/25g of banana peel), glycerol concentration of (2.096ml of glycerol/25g of banana peel) and 14.50 minutes of residence time for hydrolysis with high value of combined desirability (95.1%). Validation of the statistical model showed an insignificant difference between experimental and model-predicted results. After analyzing the results of the primary synthesized bioplastic, a new modified bioplastics was produced with 27 % improved water/moisture absorption using a Calcium carbonate as filler at the optimum conditions from the earlier experiments.

Keywords: Banana peel based Bioplastic, Banana peel, Substrate, Hydrolysis

CHAPTER ONE

1. INTRODUCTION

1.1 Background

The term "plastic" is derived from the Greek word "plastikos" meaning fit for molding, and "plastos" meaning molded. It refers to the material's malleability or plasticity during manufacture that allows it to be cast, pressed, or extruded into a variety of shapes, such as films, fibers, plates, tubes, bottles, boxes, and much more. Plastic is the general common term for a wide range of synthetic or semi-synthetic materials used in a huge, and growing, range of applications. (Orezzoli et al., 2018)

Plastics are derived from organic products, the same as wood, paper or wool. The materials used in the production of plastics are natural products such as cellulose, coal, and natural gas, salt and, of course, crude oil. (Orezzoli et al., 2018)

The two major processes used to produce plastics are called polymerization and polycondensation, and they both require specific catalysts. In a polymerization reactor, monomers like ethylene and propylene are linked together to form long polymers chains. Each polymer has its own properties, structure and size depending on the various types of basic monomers used. (Gironi & Piemonte, 2011)

Due to their relatively low cost, ease of manufacture, versatility, and imperviousness to water, plastics are being used all over the world; From drinking cups and disposable silverware to parts for automobiles and motorcycles and they are continuing to rise. As a result they make up about 20% by volume waste per year currently and their lack of degradation is another environmental trepidation. But since plastics are vital to people's everyday lives, production of biodegradable plastics to make plastics more compatible with the environment is necessary. (Gironi & Piemonte, 2011)

The first known bio-based plastic, polyhydroxybutyrate (PHB) was discovered in 1926 by a French researcher, Maurice Lemoigne, His work demonstrated the biodegradability of PHB with the bacterium Bacillus megaterium. The significance of Lemoigne's discovery was overlooked for many decades, in large part because, at the time, petroleum was inexpensive and abundant. The petroleum crisis of the mid-1970s brought renewed interest in finding alternatives to petroleum-based products. (Gironi & Piemonte, 2011)

Global plastics production increased by 10 million tons (3.7%) to around 280 million tons in 2011, and continued the growth pattern that the industry has enjoyed since 1950 approximately by 9% per annum. Today, climate change and energy shortage are key global challenges. Plastics account for approximately 5% of worldwide oil consumption. The industry still continues to look for new ways to lower the amount of oil used to produce plastics, which means finding alternative raw materials to meet environmental challenges. (Orezzoli et al., 2018)

Bioplastics are not a single kind of polymer but rather a family of materials that can vary considerably from one another. There are three groups in the bioplastics family, each with its own individual characteristics. Those three groups includes bio-based or partially bio-based non-biodegradable plastics such as bio-based Polyethylene(PE), Propylene(PP), or Polyethylene terephthalate(PET); Bio-based and biodegradable Plastics both such as Polylactic acid (PLA) and Polyhydroxyalkanote(PHA) or Polybutylene succinate(PBS) and fossil based and biodegradable plastics such as Polybutylene adipate terephthalate(PBAT). (Zhou_Huijuan,2016)

Bio-based plastics are plastics derived from renewable biomass sources, such as vegetable fats and oils, cornstarch, potato starch, cassava starch, banana peel starch, pea starch, or microbiota. (Orezzoli et al., 2018) Although there are many different types of bio based plastics the starch based bioplastics are the most common types specifically corn starch. Corn is a good source of starch for bio-based plastics, however; in developing countries like Ethiopia, agro-industrial residues such as banana peel and orange peel are cheaper and more ideal sources of substrates for starch based bioplastics.

Dessert banana and plantain (Musa sp.) are the fourth most important staple food crops in the world after rice, wheat, and maize. World production of banana is about 106,541,709.00 tons. For many African, Asian and Latin American countries, banana is as well one of the most important crops for foreign exchange incomes (Woldu et al., 2015)

Dessert banana is also the major fruit crop that is most widely grown and consumed in Ethiopia. It is cultivated in several parts where the growing conditions are favorable; Especially in the south and southwestern parts of the country. In Ethiopia banana covers about 59.64% of the total fruit area, about 68.00% of the total fruits produced. Gamo-Gofa, Bench-Maji and Sheka zones are among the major banana producing zones of the SNNPRS, of which Gamo-Gofa zone alone covers over 70% of the total banana marketed across the major market outlets in Ethiopia (Woldu et al., 2015)

Despite the above-stated facts and the concerted effort being made by the government of Ethiopia to promote and diversify its agricultural outputs as well as exports at large, the attention given to banana peels in terms of research, disposal method, and overall the banana wastes value-chain management has been very limited. In most parts of the country, banana peels are disposed of simply in the street which is easily rubbishing the environment.

Figure1-1: Local Banana Peels Disposed in the Street (Israel et al., 2015)

The application of banana peel as a raw material in bioplastic production has a dual benefit for the waste management in developing countries such as Ethiopia. According to Xinhua reports from 2017 Ethiopia has a firm stand on maintaining the society’s health and environment from pollutions caused by petroleum based plastics as Deyasa Leta the then deputy director of the Chemical and Construction Industries Development Institute at the Ethiopia Ministry of Industry (MoI) said the different measures such as closing three factories when they were found to be producing less than 0.3 milligram weight of plastic bags, a measurement deemed to be toxic to Ethiopia's environment is part of Ethiopia's desire to maintain the society's health and the country's environment with the country's need to generate job and revenue for the country and in a situations like this agro-industrial residues based biodegradable plastics are highly desirable. (Yan, 2017)

Bio-based plastics have experienced fast growth in the past decade thanks to the public concerns over the environment, climate change and the depletion of fossil fuels. Bio-based plastics account for around 1% of global plastics production. They have experienced a rapid growth over the last decade. In 2011, bio-based polyethylene beverage bottles, yogurt pots and hair care packaging became widely available. This perspective provides an overview of the current global market of bio-based plastics, their material properties, technical substitution potential and future market (for 2020). Global capacity of bio-based plastics is expected to reach 3.45 million metric tons in 2020 and Starch plastics, PLA, bio-based polyethylene, Polyhydroxyalkanoates (PHA) major types of bio-based plastics in the future. (Gironi & Piemonte, 2011)

1.2 Statement of the Problem

Synthetic polymers make up about 20% by volume waste per year globally (Gironi & Piemonte, 2011) and due to their hydrocarbon chain they are not biodegradable or fully breakdown in landfills which normally takes 500 years and causes the loss of another irreplaceable resource, landfill.

On the other hand banana covers about 68.00% of the total fruits produced in Ethiopia. (Woldu et al., 2015) With the high demand and increase in daily consumption of banana there is high waste accumulation of banana peel from household, agricultural areas and industrial areas, which are normally used as animal feed, incinerated or go to landfill sites. However, incineration is an expensive disposal method and causes air pollution and using landfills for a material which has many uses such as in bioplastic production is not economically feasible. Therefore in this research it was attempt to adress this problem and produced a bioplastic using waste to waste approach from banana peels.

Many reasearches has been made on application of banana peel as a raw material for bioplastic but Some related effects of process parameters such as temprature, concentration of HCl and glycerol and hydrolysis residence time on the quality and flexibility of the bioplastic wasn't adressed enough. Mainly the drying temprature of the banana peel starch based bioplastic has been held at excessively high temprature and shorter time in most of the researches and as it can be observed from the result although a bioplastic with higher tensile strength can be produced with that approach the elasticsity of the bioplastic has been compromised and has been attempted to improve its elasticsity by application of excess plastizer which is not economically feasible and has its own effect on water absorbity of the bioplastic and relatively it exhibit a birttle characterstic. Therefore it was attempt to adress the effect of those process parameters and optimized them in a way that enables a production of good quality bioplastic.

1.3 Objective

1.3.1 General Objective

- To synthesize, characterize and optimize banana peel based bioplastic

1.3.2 Specific Objective

- To investigate the effect of process variables (drying temperature, acid concentration, concentration of glycerol and residence time for hydrolysis) during the hydrolysis of amylopectin
- To optimize operating process variable specifically acid concentration, concentration of glycerol, drying temperature and residence time for hydrolysis
- To investigate the characteristic of the synthesized bioplastics produced (FTIR test, Tensile strength, elongation at break water absorption and biodegradability of the produced bio film)
- To investigate the effects of the concentration of the added filler (calcium carbonate) on the water/moisture absorption of resynthesized bioplastics

1.4 Significance of the Study

This study has two main benefits which can be applied in practical experiments as guidance and as an input for further researches. Its practical benefit includes application of the optimized process parameters gained from this research to synthesize an improved quality of bioplastic from banana peel and it can be used as a base for scale up production of banana peel based bioplastic. The other benefit includes using this research as an input for other researches. It can be used as a base for researches focused on ways to improve the quality of bioplastic and researches that focus on the areas of bioplastic production from wastes in general.

1.5 Scope of the Study

This research generally covers lab scale synthesis of bioplastics from banana peel It includes collection of banana peels from juice house, pre-treatment of banana peel using anti-oxidant Sodium metabisulfite , synthesis of bioplastic by breaking down the branched structure of banana peel known as amylopectin through hydrolysis at different parameter values to determine the optimum values of the process. Determining the model equation and hence the optimum conditions (drying temperature, concentration of HCL acid, glycerol concentration and residence time for hydrolysis). It also covers the characterization of the synthesized biofilm using FTIR test, Tensile strength, Elongation at break, water absorption and biodegradability. This research also covers synthesis of a new modified bioplastic using $CaCO_3$ as filler in oder to improve the quality of bioplastic and the effects of the filler concentration on Water/moisture absorption of the synthesized bioplastic has also been analyzed.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Plastics

A plastic is a type of synthetic or man-made polymer; similar in many ways to natural resins found in trees and other plants. Webster's Dictionary defines plastics as: any of various complex organic compounds produced by polymerization, capable of being molded, extruded, cast into various shapes and films, or drawn into filaments and then used as textile fibers. (Patil, 2018)

2.1.1 History and Worldwide Use of Plastics

The development of plastics can be viewed into two major categories as natural plastics and man-made plastics. Humans were using natural plastics for various purposes since many years ago. Egyptians, for instance, soaked burial wrappings in natural resins to help preserve their dead for long However, many of the natural plastics were in short supply and difficult to mold. Due to these and many other drawbacks, scientists began to find more efficient ways and reliable plastic source materials than they were having. (Cucci et al., 2008)

British scientist Alexander Parkes introduced the first man-made plastic, called Parkesine in 1862 (Inventors.about.com). In the year 1909, an American chemist, Leo Hendrik Baekeland, came up with the first completely synthetic man-made plastic, which he named Bakelite (Cucci et al., 2008)

The development of plastics or polymers rose when Polypropylene was discovered in 1954 by Giulio Natta, and commercial production of the resin began in 1957. It is the single most widely used thermoplastic globally. Developmental work continued through the nineteenth century on natural/synthetic polymers producing such notables as celluloid for billiard balls, polyvinyl chloride (PVC), which is used in many applications, and viscose (rayon) for clothing.(Neal et al.,2009)

Development of modern plastics really expanded in the first 50 years of the twentieth century, with at least 15 new classes of polymers being synthesized. The success of plastics as a material has been substantial; they have proved versatile for use in a range of types and forms, including natural polymers, modified natural polymers, thermosetting plastics, thermoplastics and, more recently, biodegradable polymers (Neal et al.,2009)

The history of plastic products manufacturing in Ethiopia has a 50 years long journey, “Currently there are a total of 350 plastic manufacturing companies in Ethiopia producing 12 categories of products ranging from automotive tire to the latest wood and plastic blend home partitions and PVC made tiles and small household furniture,” said Eng. Yonas Abate, Plastic and Rubber Industries Development Director at the state-owned Ethiopian Chemical and Construction input Industries Development Institute. (Andualem., 2017)

Plastics are a vital asset for humanity, often providing functionality that cannot be easily or economically replaced by other materials. Most plastics are robust and last for hundreds of years. They have replaced metals in the components of most manufactured goods, including for such products as computers, car parts and refrigerators, and in so doing have often made the products cheaper, lighter, safer, stronger and easier to recycle. (Yates, 2013) Plastics have taken over from paper, glass and cardboard in packaging, usually reducing cost and carbon emissions while also providing better care of the items that they protect (Goodall, 2011)

About 4% of the world’s oil production is converted into plastics for use in products as varied as shopping bags and the external panels of cars. Another few percent is used in processing industries because oil-based plastics require substantial amounts of energy to manufacture. Each kilo gramme of plastic typically requires 20 kilowatt hours of energy in the manufacturing process, more than the amount needed to make steel of the same weight. Almost all this comes from fossil sources. (Goodall, 2011)

Changing lifestyles have dictated the need for foods that offer convenience to the consumer in a countless of ways, such as minimizing preparation time, easy opening of the container and single service, while also offering high quality throughout an extended shelf life. Plastic packaging has responded to these demands, and creativity with plastics has been limited only by the imagination of the designer (Orezzoli et al., 2018)

2.1.2 Problems Associated With Plastics

Despite their many uses and desirable properties, petroleum based conventional plastics have many disadvantages. The major reasons for looking at alternatives to plastics are because of the following drawbacks: (Prasad et al., 2014)

A. Production Problems

Plastics are derivatives of petroleum, natural gas or similar substances. They are transformed into a polymer resin, which is then shaped and formed into whatever object is desired. However, as a petroleum by-product, plastics contribute to oil dependency, and in the present times it is generally recognized that oil will not be available indefinitely these points to a possible raw material crisis in the future. (Janusz et al., 1994)

b. Plastic Recycling

Although many types of plastics could potentially be recycled, very little plastic actually enters the recycling production process. The most commonly recycled type of plastic is polyethylene terephthalate (PET), which is used for soft drink bottles. Approximately 15 to 27 percent of PET bottles are recycled annually. The other type of plastic which is somewhat commonly recycled is high-density polyethylene (HDPE), which is used for shampoo bottles, milk jugs and two thirds of what are called rigid plastic containers. Approximately 10 percent of HDPE plastic is recycled annually. (Prasad et al., 2014) These figures show that most of the plastics manufactured do not get recycled and as production continues unabated, this poses a serious problem.

c. Landfill Disposal

The vast majority of plastics, especially plastic bags, wind up in landfills. The fact that available landfill space is becoming increasingly scarce and plastics are non-biodegradable poses special problems for landfills.

Compounding the issue is the survey (Zero Waste America, 1988-2008) which found that 82 percent of the surveyed landfill cells had leaks, while 41 percent had a leak larger than 1 square foot.

Also these leaks are detectable only if they reach landfill monitoring wells. Both old and new landfills are usually located near large bodies of water, making detection of leaks and their cleanup difficult. All these issues point to the fact that landfill disposal of plastics is not a sustainable solution. (Prasad et al., 2014)

D. Incineration

Some industry officials have promoted the incineration of plastic as a means of disposal. A similar process of pyrolysis breaks plastics into a hydrocarbon soup which can be reused in oil and chemical refineries. However, both incineration and pyrolysis are more expensive than recycling, more energy intensive and also pose severe air pollution problems. In 2007, the EPA acknowledged that despite recent tightening of emission standards for waste incineration power plants, the waste-to-energy process still “create significant emissions, including trace amounts of hazardous air pollutants”.

Incinerators are a major source of 210 different dioxin compounds, plus mercury, cadmium, nitrous oxide, hydrogen chloride, sulphuric acid, fluorides, and particulate matter small enough to lodge permanently in the lungs. (Woody, 2007)

E. Adverse effect on Biodiversity

Plastic debris affects wildlife, human health, and the environment. Plastic pollution has directly or indirectly caused injuries and deaths in 267 species of animals (including invertebrate groups) that scientists have documented. These problems are because of various reasons which include poisoning due to consumption of plastics, suffocation due to entanglement in plastic nets etc.

The millions of tons of plastic bottles, bags, and garbage in the world's oceans are breaking down and leaching toxins posing a threat to marine life and humans. Some marine species, such as sea turtles, have been found to contain large proportions of plastics in their stomach. When this occurs, the animal typically starves, because the plastic blocks the animal's digestive tract. In some cases small bits of plastics are accidently consumed by animals. Any such animal, if eaten by another will cause the plastics to travel up the food chain. This may cause serious health hazards in a wide array of creature. (Chris, 2010)

F. The Carbon Cycle

When a plant grows, it takes in carbon dioxide, and when it biodegrades, it releases the carbon dioxide back into the earth – it's a closed loop cycle. When we extract fossil fuels from the earth, we disrupt the natural cycle, and release carbon dioxide into the atmosphere faster than natural processes can take it away. As a result, the atmosphere is getting overloaded with carbon dioxide. Additionally, fossil fuels take millions of years to form, and are therefore non-renewable resources. In other words, we are using our fossil resources faster than they can be replaced.

When we make products like plastics from fossil fuels, we are contributing to the imbalance in the environment while depleting valuable fossil resources, thereby increasing the carbon footprint of the product. Bioplastics, on the other hand, can replace nearly 100% of the fossil fuel content found in conventional plastics, and require considerably less energy for production.

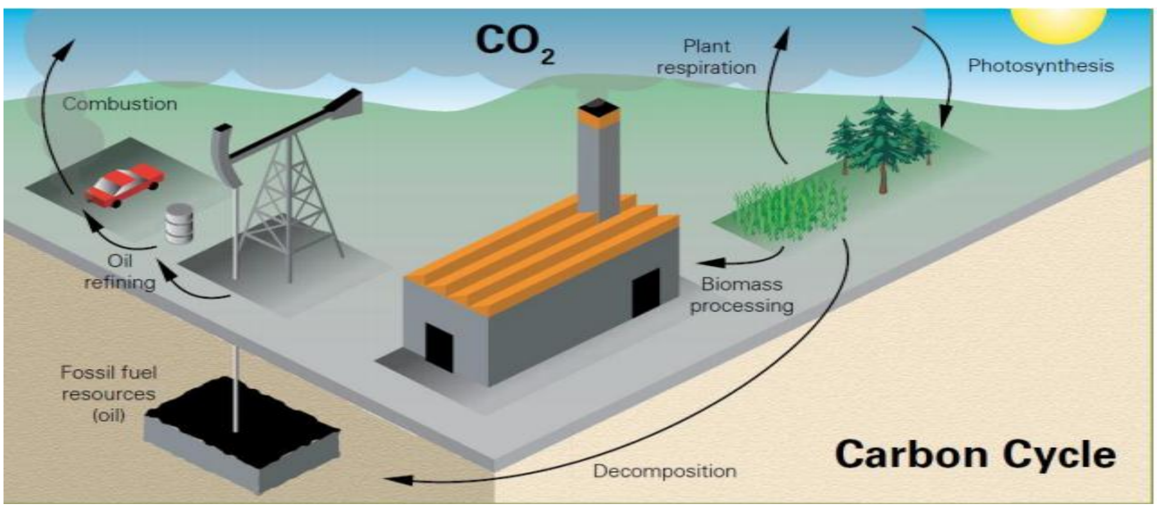


Figure 2-1: Carbon Cycle (Chris, 2010)

These problems can be overcome. All the major oil-based plastics have substitutes made from biological materials. The polyethylene in a shopping bag can be made from sugar cane and the polypropylene of food packaging can be derived from potato starch. Plastics are irreplaceable and will all eventually be made from agricultural materials. (Thompson et al., 2009) (Chris, 2010)

2.2 Bioplastic

A bioplastic is a plastic that is made partly or wholly from polymers derived from biological sources such as sugar cane, potato starch, corn starch, banana peel starch or the cellulose from trees, straw and cotton. (Chen, 2014)

Bioplastics are usually derived from sugar derivatives, including starch, cellulose, and lactic acid but can also be made from agricultural by-products and also from used plastic bottles and other containers using microorganisms. Common plastics (petro based polymers) are derived from petroleum or natural gas. Not all bioplastics are biodegradable or biodegrade more readily than commodity fossil-fuel derived plastics. (Chua et al. 1999)

Bioplastics is a broad term used to describe a range of plastic materials that are either biodegradable or derived from renewable resources or both. Some bioplastics degrade in the open air, others are made so that they compost in an industrial composting plant, aided by fungi, bacteria and enzymes. Others mimic the robustness and durability of conventional plastics such as polyethylene or PET. Bioplastics can generally be directly substituted for their oil-based equivalent. Indeed, they can generally be made to be chemically identical to the standard industrial plastics. (Buchholz, 2012)

Generally bioplastic materials can be grouped according to their properties as follows:

- **Bio-based and biodegradable bioplastics:** These are made using renewable resources, such as plant biomass, and will biodegrade under certain environmental conditions. These materials are suitable for disposable items, such as packaging, drink bottles, single-use food containers and cutlery. They are more sustainable because they save fossil fuel resources and, if disposed of appropriately, support further plant growth.
- **Bio-based and durable (non-biodegradable) bioplastics:** These are made using renewable resources but are designed to have a longer life span (for example, carpet fibers and interior car panels). Using renewable resources makes these materials more sustainable. Also, using them to replace metal components in vehicles has the advantage of reducing vehicle weight, which increases fuel efficiency.

- **Petrochemical-based and biodegradable bioplastics:** There are some petrochemical-based plastics that can be biodegraded by the microbes in the soil, compost or oceans. (Buchholz, 2012)

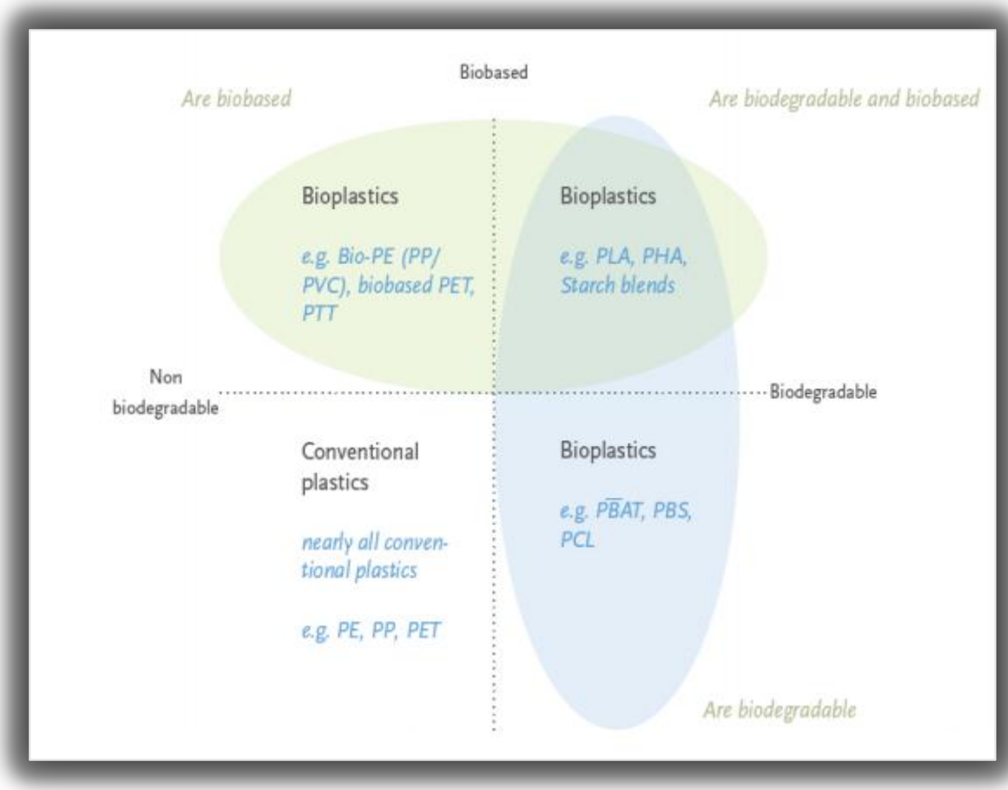


Figure 2-2: Broad categories of bioplastics (Buchholz, 2012)

2.2.1 Development of Bioplastics

The first known bio-based plastic, Galalith was created by German chemists in 1897. Galalith is a milk-based bioplastic and primarily found in buttons. After the first discovery of bioplastics by a German scientist, scientists start to create many different types of bioplastics from different raw materials and with improved heat resistance and plastic property some of the major discoveries are listed here in Table 2-1 with a brief explanation. (Jouhara et al., 2017)

The petroleum crisis of the mid-1970s brought renewed interest in finding alternatives to petroleum-based products. The rise of molecular genetics and recombinant DNA technology after that time further spurred research, so that by the beginning of the 21st century the structures, methods of production, and applications for numerous types of bio-based plastics had become established.

Bio-based plastics that were either in use or under study included PHB and polyhydroxyalkanoate (PHA), both of which are synthesized within specialized microbes, as well as polylactic acid (PLA), which is polymerized from lactic acid monomers produced by microbial fermentation of plant-derived sugars and starches. (Lackner, 2015)

Table 2-1: Development of bioplastic

Year	Bioplastic Discovery or Development	Brief Description
1862	Parkesine - Alexander Parkes	At the Great London Exhibition, Alexander Parkensine displays Parkenisine, the first plastic. Parkensine is made from nitrocellulose. (White, 1998)
1897	Galalith - German chemists	Still produced today, Galalith is a milk-based bioplastic that was created by German chemists in 1897. Galalith is primarily found in buttons. (Raschka et al., 2013)
1907	Bakelite - Leo Baekeland	Leo Baekeland invented Bakelite, which received the National Historic Chemical Landmark for its non-conductivity and heat-resistant properties. It is used in radio and telephone casings, kitchenware, firearms and many more products. (Pathak et al,2014)
1912	Cellophane - Jacques E. Brandenberger	Brandenberger invents Cellophane out of wood, cotton, or hemp cellulose. (Raschka et al., 2013)
1920s	Polylactic ACid (PLA) - Wallace Carothers	Wallace Carothers finds Polylactic Acid (PLA) plastic. PLA is incredibly expensive to produce and is not mass-produced until 1989. (Whiteclouds, 2018)
1926	Polyhydroxybutyrate (PHB) -	Maurice Lemoigne invents polyhydroxybutyrate

	Maurice Lemoigne	(PHB) which is the first bioplastic made from bacteria. (Raschka et al., 2013)
1930s	Soy bean-based bioplastic car - Henry Ford	The first bioplastic car was made from soy beans by Henry Ford. (Raschka et al., 2013)
1983	Biopal - Marlborough Biopolymers	The first bioplastics company, Marlborough Biopolymers, is started which uses a bacteria-based bioplastic called biopal.
1989	PLA from corn - Dr. Patrick R. Gruber; Matter-bi - Novamount	The further development of PLA is made by Dr. Patrick R. Gruber when he figures out how to create PLA from corn. (Whiteclouds 2018). The leading bioplastic company is created called Novamount. It uses matter-bi, a bioplastic, in multiple different applications.
1992	PHB can be produced by Arabidopsis thaliana (a small flowering plant)	It is reported in Science that PHB can be produced by the plant Arabidopsis thaliana. (Poirier et al., 1992)
2007	Mirel (100% biodegradable plastic) by Metabolic inc. is market tested	Metabolix inc. market tests its first 100% biodegradable plastic called Mirel, made from corn sugar fermentation and genetically engineered bacteria. (DiGregorio, 2009)
2012	Bioplastic is developed from seaweed	A bioplastic is developed from seaweed proving to be one of the most environmentally friendly bioplastics based on research published in the journal of pharmacy research A bioplastic is developed from seaweed proving to be one of the most environmentally friendly bioplastics based on research published in the journal of pharmacy research (Rajam & Yogindran, 2018)
2013	Bioplastic made from blood and a cross-linking agent which is used in medical procedures	A patent is put on bioplastic derived from blood and a crosslinking agent like sugars, proteins, etc. (iridoid derivatives, diimidates, diones, carbodiimides, acrylamides, dimethylsuberimidates, aldehydes, Factor XIII,

		dihomo bifunctional NHS esters, carbonyldiimide, glyoxyls, proanthocyanidin, reuterin). This invention can be applied by using the bioplastic as tissue, cartilage, tendons, ligaments, bones, and being used in stem cell delivery. (Campbell, 2004)
2014	Bioplastic made from vegetable waste	It is found in a study published in 2014 that bioplastics can be made from blending vegetable waste (parsley and spinach stems, the husks from cocoa, the hulls of rice, etc.) with TFA solutions of pure cellulose creates a bioplastic. (Bayer, et al., 2014)
2016	Car bumper made from banana peel bioplastic	An experiment finds that a car bumper that passes regulation can be made from nano-cellulose based bioplastic biomaterials using banana peels (Hossain et al., 2016)
2017	Bioplastics made from lignocellulosic resources (dry plant matter)	A new proposal for bioplastics made from Lignocellulosics resources (dry plant matter). (Brodin et al., 2017)
2018	Bioplastic furniture, bio-nylon, packaging from fruit	Many developments occur including Ikea starting industrial production of bioplastics furniture (Barret, 2018).
2019	Five different types of Chitin nanomaterials- Korea Research Institute of Chemical Technology	Five different types of Chitin nanomaterials were extracted and synthesized by the 'Korea Research Institute of Chemical Technology' to verify strong personality and antibacterial effects. When buried underground, 100% biodegradation was possible within 6 months (Tran, 2019)

2.2.2 The World Plastic Industry and the Role of Bioplastic

The annual output of the world’s plastics industry is about 300 million tonnes a year._(Weiss, 2012) This number has grown by a few per cent per year over the last decade. The bioplastics industry is much smaller, it only represents approximately 0.2% of the global polymer market, but the growth rate of bioplastics is much higher. Most sources suggest that this part of the plastics industry is growing at least 20% a year. Not even the most fervent advocates of the bioplastics suggest that they will quickly replace all oil-derived compounds though most people expect rapid growth to continue. (Andreas Künkel, 2016)

2.2.3 Market Size

Growing demand for more sustainable solutions is reflected in growing production capacities of bioplastics: in 2011 production capacities amounted to approximately 1.2 million tonnes. Market data of "European Bioplastics" forecasts the increase in the production capacities by fivefold by 2016 – to roughly 6 million tons. (Mohanty et al., 2013)
The factors driving market development are both internal and external. External factors make bioplastics the attractive choice. This is reflected in the high rate of consumer acceptance. Moreover, the extensively publicized effects of climate change, price increases of fossil materials, and the increasing dependence on fossil resources also contribute to bioplastics being viewed favorably. (Reddy et al., 2013)

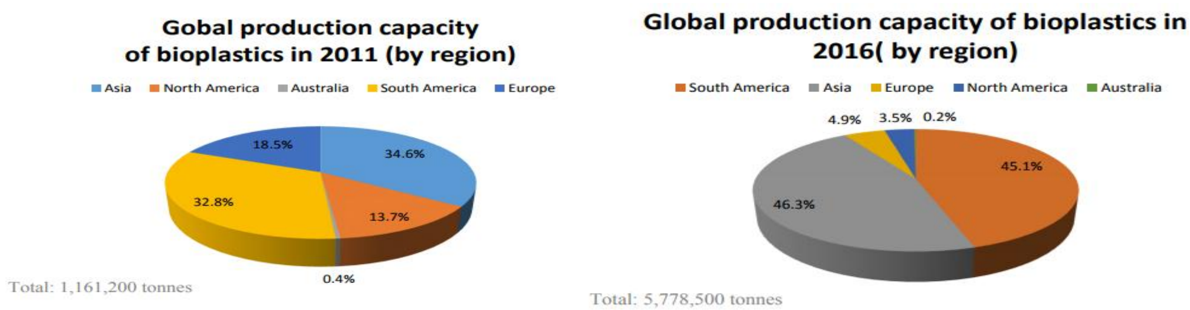


Figure 2-3: Global production of bioplastic by region (Mohanty et al., 2013)

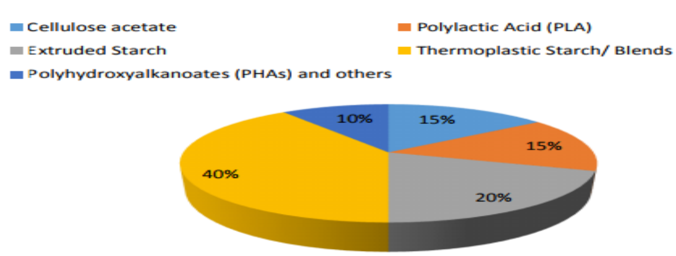


Figure 2-4: Bioplastics Market Share (Mohanty et al., 2013)

2.2.4 Advantage of Using Bioplastics

a) Major Consumer Goods Brands and Bioplastics

Over the last five years many of the world's largest consumer good companies have begun to employ bioplastics in the packaging of their products. Examples include Coca Cola's use of a mixture of a conventional plastic and bioplastic in its soft drink bottles (petroleum PET and up to 30% plant-based equivalent), Proctor and Gamble's bioplastic shampoo packaging and Nestle's adoption of a bioplastic top for his Brazilian milk products and 30 other upcoming projects and Sun Chip, a subsidiary of PepsiCo's Frito-Lay snacks unit. (Ottman, 2011)

These companies are among the biggest consumer goods companies in the world, with operations in almost every country. All of them appear to be committed to an increase in the use of bioplastic packaging for their products. Their reasons are simple: these businesses are watching the actions and attitudes of their customers who are increasingly concerned about the use of fossil fuel resources and, particularly, about indestructible litter. Bioplastics are important in helping consumer goods companies present their brands in a favorable light. Recyclable or compostable packaging made from biological materials can be used to make their products more environmentally friendly in the eyes of consumers. Although bioplastics may be more expensive per kilo of packaging, the extra cost is more than outweighed by the benefits seen by purchasers. The client lists of the major bioplastic suppliers include most of the largest and best-known consumer goods companies, ranging from the Shiseido cosmetics brand to Ecover, the Belgian cleaning products company. (Ottman, 2011)

b) The value of the reduction in landfill/expensive preparation for recycling

Some bioplastics are as robust and durable as their oil-based equivalents. Others will rapidly break down in commercial composting plants. These rapidly biodegradable plastics have high value in some circumstances such as when plastics become inevitably mixed with other streams of compostable waste and would otherwise need to be hand separated. For example, quantities of plastic material are used in greenhouse applications. A productive application for bioplastics is the ties that hold tomato vines to the support wires in commercial greenhouses. After the crop is concluded, the waste organic material, including the ties and other plant-based plastics such as the small pots in which plants are grown as seedlings, can be quickly and efficiently cleared and taken to be composted. Conventional plastics would have to be separated by hand at great expense and usually then sent to an incinerator or landfill. . (Martien van den Oever, 2017)

A bioplastic mulch that will dissolve in the soil over the winter is much better because it saves time and money but also adds to the carbon content of the soil, helping to maintain fertility. In other important agricultural uses, such as for strimmer cord (‘weedwacker’ in the US, full biodegradability means that small pieces of plastic filament do not persist in the environment. As disposal sites fill up around the world, the need either to recycle plastics or to compost them can only increase, adding further buoyancy to bioplastic sales. (Martien van den Oever, 2017)

In a similar move, municipalities around the world collecting food waste from homes are now often providing compostable plastic bags into which the food goes prior to collection. Householders benefit from easier and more hygienic storage of the waste. The municipality can collect the bag and does not have to separate it from the waste food before the composting process begins. While these bags are not as strong as the equivalent standard polyethylene bag, they perform their functions well.

C **Litter**

The best understood advantage of biodegradable bioplastics lies in the reduction of permanent litter. Plastic single use shopping bags are the most obvious example of how plastics can pollute the environment with huge and unsightly persistence. A large fraction of the litter in our oceans is of disposable plastic bags. Cities and countries around the world are taking action against the litter, sometimes by banning non-degradable plastic bags entirely. Italy has decided to block the use of non-biodegradable single use shopping bags from the beginning of 2012. The city of Portland, Oregon has just (July 2011) joined several dozen US municipalities in banning most plastic bags. These legislative changes represent a clear trend as politicians respond to the irritation over the persistence of plastic bag litter in the world's seas, rivers and rural and urban environments. (Chen, 2014)

Some places will continue to allow plastic bags that are genuinely biodegradable and meet the published standards for compensability (Bags that are oxy-degradable, and only break down in to very small pieces rather than truly biodegrading, will generally be banned). Biodegradable bioplastic bags will be allowed in Italy, providing a huge boost to the European market for these products not least because until now the country has been the largest European market for single use shopping bags. (Chen, 2014)

d. Bioplastics demand will continue to grow

Continued research and development in bioplastics is creating high quality products for a wide variety of industries. Now that the benefits of biologically sourced plastics are well-understood, their market share is likely to rise sharply. The three drivers of growth – the importance of brand image to consumer goods companies, the value of joint composting and the reduction of litter – will provide the spur for continued growth in bioplastics across the world. (Goodall, 2011)

e. The carbon footprint of plastics

Calculating the greenhouse gas reductions arising from the use of bioplastics is a complex and controversial area. But it is nevertheless important to try to quantify the benefits from making plastics from biological materials in order to encourage further debate and research.

The first point to make is that the carbon footprint of a bioplastic is crucially dependent on whether the plastic permanently stores the carbon extracted from the air by the growing plant. A plastic made from a biological source sequesters the CO_2 captured by the plant in the photosynthesis process. If the resulting bioplastic degrades back into CO2 and water, this sequestration is reversed. But a permanent bioplastic, made to be similar to polyethylene or other conventional plastics, stores the CO_2 forever. Even if the plastic is recycled many times, the CO_2 initially taken from the atmosphere remains sequestered. (Goodall, 2011)

The chart below offers illustrative figures for the greenhouse gas impact of making a kilo of bioplastic from a material such as wheat starch. (Chauhan et al., 2010)

- The first column – a negative number - estimates the CO_2 captured from the atmosphere by photosynthesis during the growth of the plant.
- The second records an estimate of the greenhouse gases emitted in the process of producing the wheat. This includes the emissions from fossil fuels used to power the tractor and other energy use in the field and in the drying of the wheat. It also measures the impact of fertilizer manufacture and the emissions of nitrous oxide, a very powerful global warming gas, as a result of the chemical breakdown of nitrogenous fertilizer in fields.
- The third column estimates the CO_2 impact of the energy used in converting the starches to a plastic. This figure will generally be much lower than the figures for oil-based plastics because biological materials need much lower temperatures and pressures in the manufacturing process. Bioplastics can generally be processed at about 140-180 degrees Celsius compared to temperatures to 300 degrees for conversion of petrochemicals to plastics.

Chart A
The greenhouse gas implications of making a simple polymer plastic from wheat
(These numbers are illustrative – kilograms of CO_2 equivalent per kilogram of plastic produced)

-1.4 CO2 sequestration by growing plant
+0.6 GHGs emitted by farming
+2.0 GHGs produced by conversion to plastic
+1.2 Net carbon footprint

Figure 2-5: greenhouse gas impact of making a kilo of bioplastics from a material such as wheat starch. (Labouze et al., 2013)

Most calculations of the energy used and greenhouse gases created in the production of conventional plastics produce much higher numbers. One estimate of the CO_2 produced per kilogram of oil-based polypropylene is 3.14 kilograms per kilogram of plastic. This compares with the 1.2 kg illustrative figure for wheat polymers in the chart above. To be clear, the implication is that those bioplastics that do not degrade might therefore have a carbon footprint of well under half the conventional equivalent. (Labouze et al., 2013) (Pierre et al., 2010)

If, on the other hand, the bioplastic is of a degradable type the advantages over conventional plastics are less pronounced. The plastic will compost back into carbon dioxide and water, returning all the sequestered carbon to the atmosphere. In the illustration given above, the savings from making the bioplastic compared to the oil-based comparator would be relatively small, but nevertheless still positive. The crucial point – not well understood by commentators or by the public – is that compostable plastics will typically have a much larger carbon footprint than ones that are manufactured to be permanent. The return of the CO_2 to the air reduces the sequestration of organic material (Labouze et al., 2013)

f. Significant technical advantages

- Improved ‘printability’, the ability to print a highly legible text or image on the plastic
- A less ‘oily’ feel. Bioplastics can be engineered to offer a much more acceptable surface feel than conventional plastics

- Less likelihood of imparting a different taste to the product contained in a plastic container. Milk, for example, will acquire a new taste in a styrene cup but the bioplastic alternative has no such effect.
- A bioplastic may have much greater water vapor permeability than a standard plastic. In some circumstances, such as sandwich packaging, this can be a disadvantage, but in the case of newly baked bread a bioplastic container will offer a significant advantage in letting out excess vapor or steam.
- A bioplastic can feel softer and more tactile. For applications such as cosmetics packaging, this can be a major perceived consumer benefit.
- Bioplastics can be made clearer and more transparent (although they are usually more opaque)

Plastics made from biological sources still need to contain additives such as plasticizers that give the product its required characteristics. But bioplastics do not contain bisphenol A, an additive thought to leak from plastics and which an endocrine disruptor is. Bisphenol A is not yet banned in most countries because the chemical is rapidly excreted by most creatures, including humans. But the high levels of continuing exposure to this worrying chemical from conventional plastics may mean that consumers will want to avoid this chemical and shift to safer bioplastic alternatives (Goodall, 2011) (Kasterine, 2012)

2.2.5 Disadvantage of bio plastic

- They are generally two or three times more expensive than the major conventional plastics such as polyethylene or PET. This disadvantage will tend to diminish as bioplastics manufacturing plants become larger and benefit from economies of scale. When the local biological feedstock is particularly cheap, as it is in Brazil, large bio-polyethylene plants may already be close to being cost-competitive with oil-based alternatives. But more generally, the crude oil for a kilo of plastic costs around €0.20 but the corn, a key source of feedstocks for bioplastics currently (August 2011) costs about twice this amount.

- Their physical characteristics are not always a perfect substitute for the equivalent polymer. Sometimes the differences are trivial, such as the biological version having a slightly different texture, but in some cases the bioplastic cannot substitute for the conventional plastic. But for the most important plastic – polythene – the product based on biological sources is identical to the plastic made from oil.
- There are a huge number of different market segments in which bioplastics can compete. In some cases, bioplastics are likely to make substantial inroads into share of traditional plastics while in others they will struggle. Novamont, the leading Italian bioplastics company, has estimated that biodegradable plastics can replace about 45% of the total sales of oil-based plastics in horticulture and 25% of those used in catering. Others regard these estimates as too low.
- Bioplastics versus food in many types of applications bioplastics offer substantial advantages over conventional products. Despite of their relatively minor current role, one serious issue does need to be addressed, both now and in the future. At the moment many bioplastics are made from sugars and starches harvested from crops that otherwise might be grown for food. As with liquid biofuels, the bioplastics industry has to deal with the vitally important question of whether the growth of bioplastics will tend to decrease the land available for food production, or increase the incentive to cut down forested areas to create more arable land. Perhaps 300,000 hectares are used to grow the crops which the industry processes into plastics. If today's entire plastics production was made from biological sources it would consume between 0.1% and 0.2% of the globe's total annual production of organic matter ('net primary production'). This is not a trivial amount but concerns about the competition for land need to be balanced by consideration of the enormous potential value of making bioplastics compared to the equivalent oil-based plastics.
- Finally, we need to consider the impact of improved recycling. We are stressing the importance of the recycling of non-biodegradable plastics, because whether from oil or from plant matter? Because the world needs to be more economical in its use of its scarce resources. Whether this is the oil used for most plastics or the starches, sugars and cellulose for biological plastics, we cannot afford to continue to throw away three quarters of the plastic we use. (Goodall, 2011) (Gironi & Piemonte, 2010)

2.2.6 Classification of Bioplastic

The Flowing diagram shows an attempt to classify the biodegradable polymers into two groups and four different families. The main groups are

(i) The agro-polymers (polysaccharides, proteins, etc.)

(ii) The bio polyesters (biodegradable polyesters) such as poly lactic acid (PLA), poly hydroxyl kanoate (PHA), aromatic and aliphatic co polyesters. (Reddy et al., 2013)

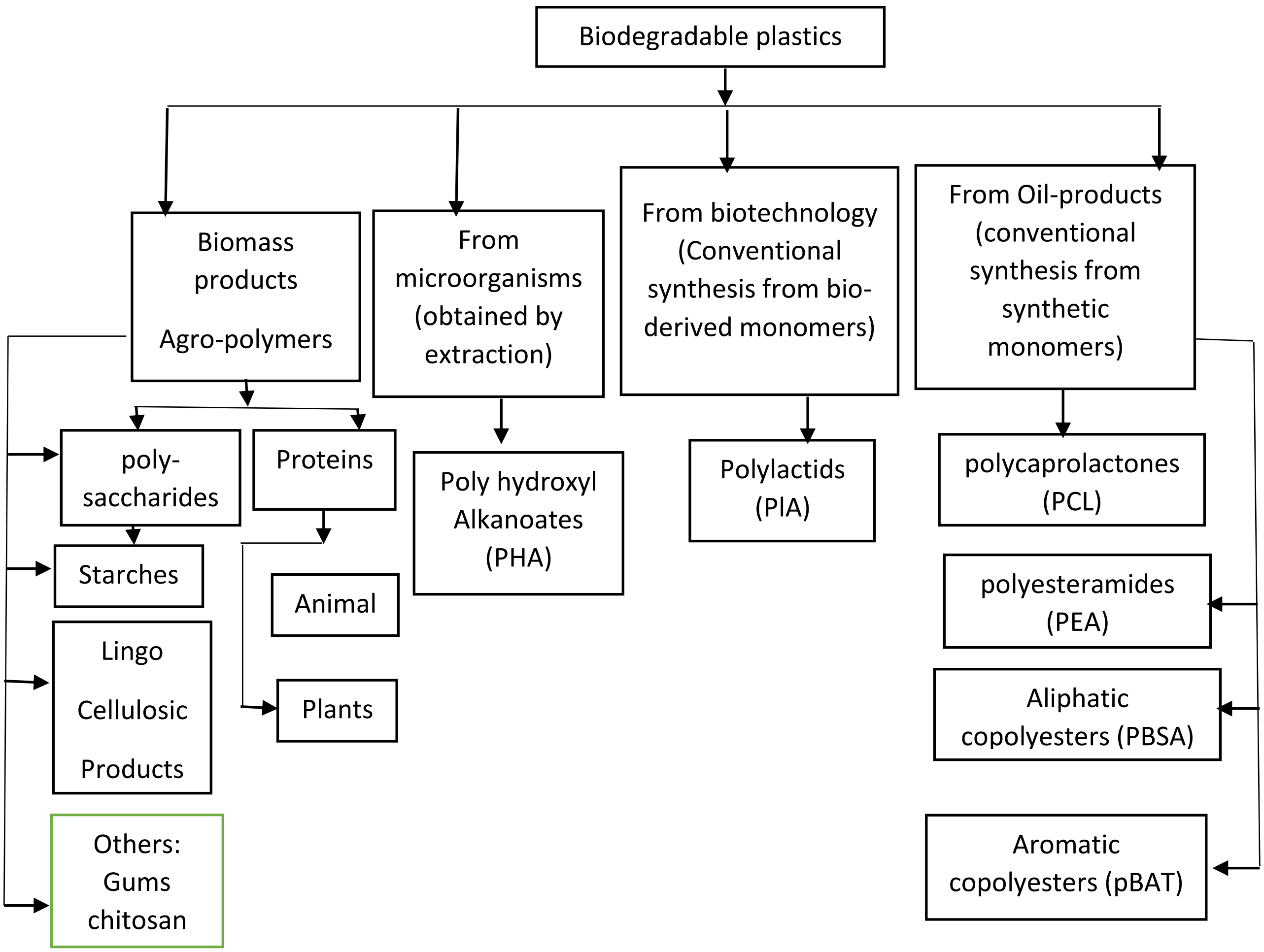


Figure 2-6: Classification of Biodegradable polymers (Reddy et al., 2013)

2.3 Types of Bioplastic

There are several types of bioplastics which are developed from different types of raw materials. Each type of bioplastic differ from one another based on the raw materials it is synthesized from, properties, strength, biodegradability, transparency etc. some of the most common bioplastics are listed below:

2.3.1 Starch-Based Plastics

Thermoplastic starch currently represents the most widely used bioplastic, constituting about 50 percent of the bioplastics market. Simple starch bioplastic can be made at home. Pure starch is able to absorb humidity, and is thus a suitable material for the production of drug capsules by the pharmaceutical sector. Flexibiliser and plasticizer such as sorbitol and glycerin can also be added so the starch can also be processed thermo-plastically. The characteristics of the resulting bioplastic (also called "thermo-plastical starch") can be tailored to specific needs by adjusting the amounts of these additives. (Mehta, Dharaiya, & Marjadi, August 2014)

Starch-based bioplastics are often blended with biodegradable polyesters to produce starch/polylactic acid, starch/polycaprolactone or starch/Ecoflex blends. These blends are used for industrial applications and are also compostable. Other producers, such as Roquette, have developed other starch/polyolefin blends. These blends are not biodegradable, but have a lower carbon footprint than petroleum-based plastics used for the same applications. (Sherman, 2008)

Due to the origin of its raw material, starch is cheap, abundant, and renewable. Starch based plastics are complex blends of starch with compostable plastics such as Polylactic acid, Polybutylene Adipate Terephthalate, Polybutylene Succinate, Polycaprolactone, and Polyhydroxyalkanoates. These complex blends improve water resistance as well as processing and mechanical properties. (Eric & Luc, 2014)

Starch-based films (mostly used for packaging purposes) are made mainly from starch blended with thermoplastic polyesters to form biodegradable and compostable products. These films are seen specifically in consumer goods packaging of magazine wrappings and bubble films. In food packaging, these films are seen as bakery or fruit and vegetable bags. Composting bags with this films are used in selective collecting of organic waste. (Eric & Luc, 2014)

Further, a new starch-based film was developed by Agricultural Research Service scientists can even be used as a paper (Peter Cate, 2016)

There are several sources of starch for the synthesis of starch based bioplastics such as corn, cassava, Banana peel, rice, avocado, sugarcane etc… almost all of them are edible materials and used as food source by the public which would make it economically unfeasible to use starch based bioplastics from those kind of sources except banana peel as it is a waste material in addition to its waste nature Banana peels consists high sources of starch, which is about 18.5%. (Erprihana, Astuti, & Ajeng, 2014)

As banana peels ripen, the glucose level increases. However, if the peels are too ripe, the starch will be converted into glucose while the least ripened peels, becomes too firm although high in starch molecules. (Firouz et al.,2010) Therefore, banana peels can be suggested as a suitable source for the manufacturing of bioplastics.

2.3.2 Cellulose-Based Plastics

Cellulose bioplastics are mainly the cellulose esters, (including cellulose acetate and nitrocellulose) and their derivatives, including celluloid. Cellulose can become thermoplastic when extensively modified. An example of this is cellulose acetate, which is expensive and therefore rarely used for packaging. However, cellulosic fibers added to starches can improve mechanical properties, permeability to gas, and water resistance due to being less hydrophilic than starch (Eric & Luc, 2014)

A group at Shanghai University was able to construct a novel green plastic based on cellulose through a method called hot pressing (Murphy et al.,2009)

2.3.3 Protein-Based Plastics

Bioplastics can be made from proteins from different sources. For example, wheat gluten and casein show promising properties as a raw material for different biodegradable polymers. (Brian & Osswald, 2008)

Additionally, soy protein is being considered as another source of bioplastic. Soy proteins have been used in non-bioplastic plastic production for over one hundred years. For example, body panels of an original Ford automobile were made of soy-based plastic (Ralston & Osswald, 2008)

There are difficulties with using soy protein-based plastics due to their water sensitivity and relatively high cost. Therefore, producing blends of soy protein with some already-available biodegradable polyesters improves the water sensitivity and cost (Zhang et al., 2006)

2.3.4 Some Aliphatic Polyesters

The aliphatic bio polyesters are mainly polyhydroxyalkanoates (PHAs) like the poly-3-hydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and polyhydroxyhexanoate (PHH).

- **Polylactic acid (PLA)**

Polylactic acid (PLA) is a transparent plastic produced from corn or dextrose. Superficially, it is similar to conventional petrochemical-based mass plastics like PS. It has the distinct advantage of degrading to nontoxic products. Unfortunately it exhibits inferior impact strength, thermal robustness, and barrier properties (blocking air transport across the membrane). PLA and PLA blends generally come in the form of granulates with various properties, and are used in the plastic processing industry for the production of films, fibers, plastic containers, cups and bottles. PLA is also the most common type of plastic filament used for home fused deposition modeling. (Andreas Künkel, 2016)

- **Poly-3-hydroxybutyrate**

The biopolymer poly-3-hydroxybutyrate (PHB) is a polyester produced by certain bacteria processing glucose, corn starch or wastewater. Its characteristics are similar to those of the petro plastic polypropylene. PHB production is increasing. The American sugar industry, for example, has decided to expand PHB production to an industrial scale. PHB is distinguished primarily by its physical characteristics. It can be processed into a transparent film with a melting point higher than 130 degrees Celsius, and is biodegradable without residue. (Knights, 2011)

- **Polyhydroxyalkanoates**

Polyhydroxyalkanoates are linear polyesters produced in nature by bacteria fermentation of sugar or lipid. They are produced by the bacteria to store carbon and energy. In industry production, the polyester is extracted and purified from the bacteria by optimizing the conditions for the fermentation of sugar. More than 150 different monomers can be combined within this family to give materials with extremely different properties. PHA is more ductile and less elastic than other plastics, and it is also biodegradable. These plastics are being widely used in the medical industry. (Justyna & Robert, 2016)

- **Polyamide 11**

PA 11 is a biopolymer derived from natural oil. It is also known under the tradename Rilsan B, commercialized by Arkema. PA 11 belongs to the technical polymers family and is not biodegradable. Its properties are similar to those of PA 12, although emissions of greenhouse gases and consumption of nonrenewable resources are reduced during its production. Its thermal resistance is also superior to that of PA 12. It is used in high-performance applications like automotive fuel lines, pneumatic airbrake tubing, electrical cable ant termite sheathing, flexible oil and gas pipes, control fluid umbilical, sports shoes, electronic device components, and catheters.

A similar plastic is Polyamide 410 (PA 410), derived 70% from castor oil, under the trade name EcoPaXX, commercialized by DSM. PA 410 is a high-performance polyamide that combines the benefits of a high melting point (approx. 250 °C), low moisture absorption and excellent resistance to various chemical substances. (Nohra et al., 2013)

- **Bio-derived polyethylene**

The basic building block (monomer) of polyethylene is ethylene. Ethylene is chemically similar to, and can be derived from ethanol, which can be produced by fermentation of agricultural feedstock such as sugar cane or corn. Bio-derived polyethylene is chemically and physically identical to traditional polyethylene – it does not biodegrade but can be recycled. The Brazilian chemicals group Braskem claims that using its method of producing polyethylene from sugar cane ethanol captures (removes from the environment) 2.15 tonnes of CO_2 per tonne of Green Polyethylene produced. (Aeschelmann & Carus, 2017)

- **Genetically modified bioplastics**

Genetic modification (GM) is also a challenge for the bioplastics industry. None of the currently available bioplastics – which can be considered first generation products – require the use of GM crops, although GM corn is the standard feedstock.

Looking further ahead, some of the second generation bioplastics manufacturing technologies under development employ the "plant factory" model, using crops or genetically modified bacteria to optimize efficiency. (Maximillian, 2015)

- **Polyhydroxyurethanes**

Recently, there have been a large emphasis on producing bio based and isocyanate-free polyurethanes. One such example utilizes a spontaneous reaction between polyamines and cyclic carbonates to produce polyhydroxurethanes. Unlike traditional cross-linked polyurethanes, cross-linked polyhydroxurethanes have been shown to be capable of recycling and reprocessing through dynamic transcarbamoylation reactions. (Fortman et al., 2015)

- **Lipid derived polymers**

A number bioplastic classes have been synthesized from plant and animal derived fats and oils. Polyurethanes, polyesters, epoxy resins and a number of other types of polymers have been developed with comparable properties to crude oil based materials. The recent development of olefin metathesis has opened a wide variety of feedstock to economic conversion into bio monomers and polymers. With the growing production of traditional vegetable oils as well as low cost microalgae derived oils, there is huge potential for growth in this area. (Metzger et al., 2007) (R.Meier., 2009)

2.3.5 Banana Peel Based Bio Plastics

One of the most common waste forms of starch is the banana peels. The waste management problem is also faced due to the disposal of tonnes of banana peels in some parts of the globe, especially in developing countries. In Malaysia, there are several industries based on banana products such as manufacturing of banana cake, banana chips, banana fritters and many more.

These industries use banana flesh as raw materials and discard the peels into the waste at end of the process. The disposal of these large amounts of wet organic waste can eventually harm the environment and lead to health problems such as respiratory disorders (Zuraidah,et al., 2012)

Banana peels consists high sources of starch, which is about 18.5% (Erprihana et al., 2014) as banana peels ripen, the glucose level increases. However, if the peels are too ripe, the starch will be converted into glucose while the least ripened peels, becomes too firm although high in starch molecules (Soltani & R.Omid, 2010). Therefore, banana peels can be suggested as a suitable source for the manufacturing of bioplastics. The study also intended to show the bioplastic film from combination of organic waste has potential to become alternative resources in plastic making industries, to reduce the amount of discarded organic wastes and to contribute to waste-to-wealth industry development in Malaysia. (Martins et al., 2013)

2.4. Raw Materials

2.4.1 Banana Peel

A banana peel, also called banana skin in British English, is the outer covering of the banana fruit. The nutritional value of banana peel depends on the stage of maturity and the cultivar; for example plantain peels contain less fiber than dessert banana peels, and lignin content increases with ripening (from 7 to 15% dry matter). On average, banana peels contain 6-9% dry matter of protein and 20-30% fiber (measured as NDF). (Happi et al., 2011)

Green plantain peels contain 40% starch that is transformed into sugars after ripening. Green banana peels contain much less starch (about 15%) when green than plantain peels, while ripe banana peels contain up to 30% free sugars. (Happi et al., 2011)

Banana peels consists of two different types of polymer chains, called amylose and amylopectin, made up of adjoined glucose molecules that are bonded together forming the plastic as shown in figure below:

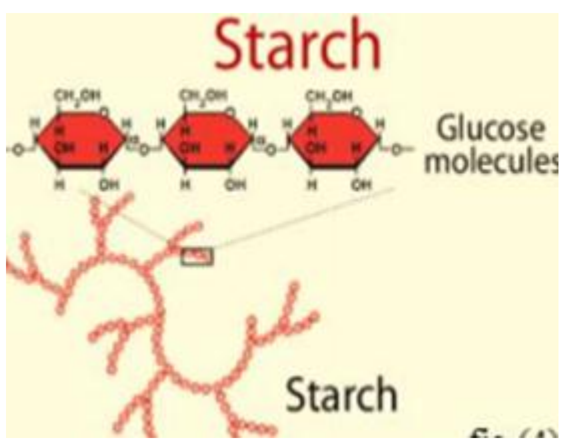


Figure 2-7: Bonded glucose molecules (Happi et al., 2011)

Table 2-2: The nutrition facts for 1 medium-sized banana peel (100 grams)

Calories: 89		
Water: 75%	**Sugar:** 12.2 grams	**Fiber:** 2.6 grams
Fat: 0.3 grams	**Protein:** 1.1 grams	**Carbs:** 22.8 grams

- **Carbs**

Bananas are a rich source of carbs, which occur mainly as starch in unripe bananas and sugars in ripe bananas. The carb composition of bananas changes drastically during ripening. The main component of unripe bananas is starch. Green bananas contain up to 80% starch measured in dry weight. During ripening, the starch is converted into sugars and ends up being less than 1% when the banana is fully ripe (Heuzé V., 2016)

The most common types of sugar in ripe bananas are sucrose, fructose, and glucose. In ripe bananas, the total sugar content can reach more than 16% of the fresh weight

- **Fibers**

A high proportion of the starch in unripe bananas is resistant starch, which passes through gut undigested. (Heuzé V., 2016)

- **Vitamins and minerals**

Bananas are a good source of several vitamins and minerals, especially potassium, vitamin B6, and vitamin C

- Potassium. Bananas are a good source of potassium. A diet high in potassium can lower blood pressure in people with elevated levels and benefits heart health (6Trusted Source).
- Vitamin B6. Bananas are high in vitamin B6. One medium-sized banana can provide up to 33% of the Daily Value (DV) of this vitamin.

- Vitamin C. Like most fruit, bananas are a good source of vitamin C.
- They have been linked to various health benefits, including a reduced risk of heart disease

Banana peels are used as Banana peels are sometimes used as feedstock for cattle, goats, pigs, monkeys, poultry, fish, zebras and several other species, typically on small farms in regions where bananas are grown. (Chen. & Patel, 2012) In addition to that Banana is used in water purification and for manufacturing of several biochemical products (Heuzé V., 2016)

2.4.2 Sodium Metabisulfite

It is an inorganic compound of chemical formula $Na_2S_2O_5$. The substance is sometimes referred to as disodium metabisulfite. It is used as a disinfectant, antioxidant, and preservative agent.
sodium metabisulfite can be prepared by evaporating a solution of bisulfite saturated with sulfur dioxide: $2\ HSO_3^- \rightleftharpoons H_2O + S_2O_5^{2-}$ Which yields a residue of colorless solid $Na_2S_2O_5$ (Catherine E.Housecroft & Sharpe, 2012)
It is used as a preservative and antioxidant in food and is also known as E223. It may cause allergic reactions in those who are sensitive to sulfites, including respiratory reactions in asthmatics, anaphylaxis, and other allergic reactions in sensitive individual (Lack, 2011)
Sodium metabisulfite and potassium metabisulfite are the primary ingredients in Campden tablets, used for wine and beer making. (Milne, Sept.30 2005) The acceptable daily intake is up to 0.7 milligrams per kilogram of body weight. Sodium metabisulfite oxidizes in the liver to sulfate which is excreted in the urine. (Lack, 2011)

Chemical properties

When mixed with water, sodium metabisulfite releases sulfur dioxide (SO_2), a pungent, unpleasant smelling gas that can also cause breathing difficulties in some people. For this reason, sodium metabisulfite has fallen from common use in recent times, with agents such as hydrogen peroxide becoming more popular for effective and odorless sterilization of equipment. Released sulfur dioxide however makes the water a strong reducing agent.
Sodium metabisulfite releases sulfur dioxide in contact with strong acids:

$$Na_2S_2O_5 + 2\ HCl \rightarrow 2\ NaCl + H_2O + 2\ SO_2$$

On heating to high temperature, it releases sulfur dioxide, leaving sulfite behind (Niazi & Safaraz, 2009)

$$Na_2S_2O_5 \rightarrow Na_2SO_3 + SO_2$$

2.4.3 Plasticizer

Bio-films need to have good elasticity and flexibility, a low brittleness, a high toughness and to prevent cracking during handling and storage (Brreto, 2002) Therefore, plasticizers of low molecular weight are typically added to hydrocolloid film forming solutions to modify the flexibility of films. Plasticizers with characteristics such as small size, and high polarity impart greater plasticizing effects on a polymeric system. Indeed, plasticizers act by increasing the free volume, decreasing intermolecular attractions between adjacent polymeric chains by reducing hydrogen bonding between polymers chains. (Myllärinen et al., 2002) Plasticizers are often added to modify the mechanical properties of bio-polymeric films and these may cause significant changes in the barrier properties of the material. Glycerol is often used as plasticizer for starch based films because of its hydrophilic properties, making it miscible with water. Generally plasticizers are required for polysaccharides based bio-films. Their amount added into hydrocolloid film forming preparations varies between 10% and 60% by weight of the hydrocolloid (Gurgel et al., 2011)

Effects of Plasticizers on Properties of starch based Films Plasticizers are relatively low molecular weight compounds that can be co-polymerized with the polymer or added to it in order to reduce the intermolecular force and increase the mobility of the polymeric chains (Gurgel et al., 2011) (Sothornvit & Krochta, 2005)

Plasticizers are usually mixed with biopolymers such as starch-based materials to aid processing, improve film flexibility and lower the glass transition temperature of the polymer. The type and amount of plasticizer, its number of functional hydroxyl groups and its compatibility with the polymer may affect the properties of the resultant films (Roz et al., 2012) (Talja et al.,2009) Examples of plasticizers that are commonly used with biopolymers include polyols such as glycerol, sorbitol and mannitol, monosaccharides such as fructose, glucose and mannose, and polyethylene glycol. Water is another important plasticizer for bio-based films although moisture may affect the film properties (Van et al., 1997) Water can be added to a starch-based film in order to break its native granular structure and hydrogen bonding (Avelino et al., 2009)

When a high concentration of plasticizer is used, the mechanical strength, barrier properties and rigidity are decreased. According to (Mchugh et al., 1994) plasticizers that are added to film formulations decrease the film density and increase the free volume of the film matrix which, in turn, increases the permeability of the films to gases and vapors. For example, glycerol molecules interfere with starch packing, thus decreasing intermolecular attraction and increasing polymer mobility (Garcia et al., 2000) (Kuorwel et al., 2011)

2.4.4 Hydrochloric Acid

It is a colorless inorganic chemical system with the formula H_2O:HCl. Hydrochloric acid has a distinctive pungent smell. It is classified as strongly acidic and can attack the skin over a wide composition range, since the hydrogen chloride completely dissociates in aqueous solution. Hydrochloric acid is the simplest chlorine-based acid system containing water. It is a solution of hydrogen chloride and water, and a variety of other chemical species, including hydronium and chloride ions. It is an important chemical reagent and industrial chemical, used in the production of polyvinyl chloride for plastic. In households, diluted hydrochloric acid is often used as a descaling agent. In the food industry, hydrochloric acid is used as a food additive and in the production of gelatin. Hydrochloric acid is also used in leather processing. (Favre & powell, 2014)

Physical properties of hydrochloric acid, such as boiling and melting points, density, and pH, depend on the concentration or molarity of HCl in the aqueous solution. They range from those of water at very low concentrations approaching 0% HCl to values for fuming hydrochloric acid at over 40% HCl. (Lide, 2000) (Perry & Green, 1984)

Hydrochloric acid is used for a large number of small-scale applications, such as leather processing, purification of common salt, household cleaning, and building construction. Oil production may be stimulated by injecting hydrochloric acid into the rock formation of an oil well, dissolving a portion of the rock, and creating a large-pore structure. Oil well acidizing is a common process in the North Sea oil production industry. (McCaleb, 1971)

In this research the hydrochloric acid (HCl) is used in the hydrolysis of amylopectin, which is needed in order to aid the process of film formation since the H-bonding amongst the chains of glucose in starch restricts the film formation.

Acid hydrolysis changes the physiochemical properties of starch without changing its granule structure. A research by (Kerr, 1952) said that at the temperature below the gelatinization temperature, the amylopectin region of starch gets hydrolyzed preferentially than the amylose region. Also, if the amylopectin content is higher in the starch, the recovery of starch decreases i.e. more of the starch gets hydrolyzed.

2.4.5 Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is a compound with the formula NaOH. It is a white solid ionic compound consisting of sodium cations Na^+ and hydroxide anions $OH^−$

Sodium hydroxide is a highly caustic base and alkali that decomposes proteins at ordinary ambient temperatures and may cause severe chemical burns. It is highly soluble in water, and readily absorbs moisture and carbon dioxide from the air. It forms a series of hydrates $NaOH·nH_2O$. (Siemens & Giauque, 1969) The monohydrate $NaOH·H_2O$ crystallizes from water solutions between 12.3 and 61.8 °C. The commercially available "sodium hydroxide" is often this monohydrate, and published data may refer to it instead of the anhydrous compound. As one of the simplest hydroxides, it is frequently utilized alongside neutral water and acidic hydrochloric acid to demonstrate the pH scale to chemistry students. (Floyd, 2012)

a. Physical properties

Pure sodium hydroxide is a colorless crystalline solid that melts at 318 °C (604 °F) without decomposition, and with a boiling point of 1,388 °C (2,530 °F). It is highly soluble in water, with a lower solubility in polar solvents such as ethanol and methanol. (Warsinger et al., 2018) NaOH is insoluble in ether and other non-polar solvents.

Similar to the hydration of sulfuric acid, dissolution of solid sodium hydroxide in water is a highly exothermic reaction where a large amount of heat is liberated, posing a threat to safety through the possibility of splashing. The resulting solution is usually colorless and odorless. As with other alkaline solutions, it feels slippery with skin contact due to the process of saponification that occurs between NaOH and natural skin oils. (Beek, 2014)

b. Chemical properties

- Reaction with acids

Sodium hydroxide reacts with protic acids to produce water and the corresponding salts. For example, when sodium hydroxide reacts with hydrochloric acid, sodium chloride is formed:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

In general, such neutralization reactions are represented by one simple net ionic equation:

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

This type of reaction with a strong acid releases heat, and hence is exothermic. Such acid-base reactions can also be used for titrations. However, sodium hydroxide is not used as a primary standard because it is hygroscopic and absorbs carbon dioxide from air.

Sodium hydroxide is used in many industries: in the manufacture of pulp and paper, textiles, drinking water, soaps and detergents, and as a drain cleaner. Worldwide production in 2004 was approximately 60 million tonnes, while demand was 51 million tonnes. (Kurt & Bittner, 2002)

Sodium hydroxide in this study is simply used to neutralize the acidity of the medium. Acid hydrolysis changes the property of starch without changing its granule structure. As the amylopectin content in the starch is higher, it decreases the recovery of the starch

2.5 Reaction Mechanism

2.5.1 Hydrolysis

Banana peel starch consists of two different types of polymer chains, called amylose and amylopectin, made up of adjoined glucose molecules. The hydrochloric acid is used in the hydrolysis of amylopectin, which is needed in order to aid the process of film formation since the H-bonding amongst the chains of glucose in starch restricts the film formation.

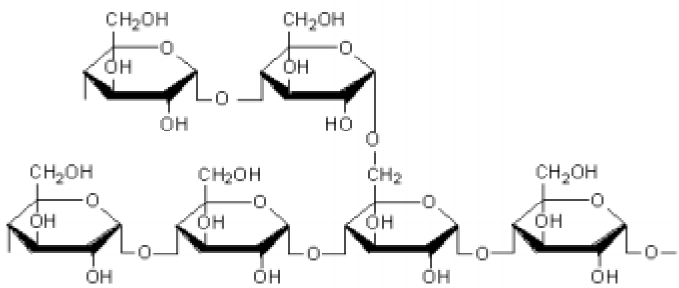


Figure 2-8: Amylopectin (Likimani, 1991)

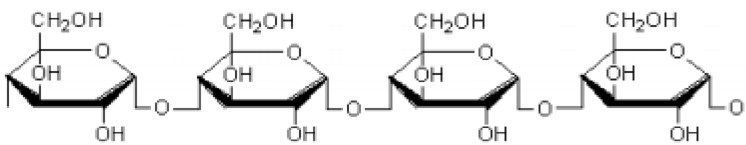


Figure 2-9: Amylose (Likimani, 1991)

2.5.2 Glycerol as a Plasticizer

Plasticizers are generally small molecules such as polyols like sorbitol, glycerol and polyethylene glycol (PEG) that intersperse and intercalate among and between polymer chains, disrupting hydrogen bonding and spreading the chains apart, which not only increases flexibility, but also water vapor and gas permeability.

Glycerol (also called glycerin) is a simple polyol (sugar alcohol) compound. It is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. It is generally accepted that plasticizers lower the number of physical cross- links between starch chains, and consequently retard the rate of retrogradation.

2.5.3 Addition of NaOH

NaOH in the experiment is simply used to neutralize the acidity of the medium. Acid hydrolysis changes the property of starch without changing its granule structure. As the amylopectin content in the starch is higher, it decreases the recovery of the starch

2.5.4 Sodium Metabisulfite

The sodium metabisulfite ($Na_2S_2O_5$) is used as an antioxidant here. It prevents the microbial growth in the peels. It is used as a disinfectant, antioxidant and microbial preservation agent.it is very soluble in ethanol and water.

2.6 Properties of Bioplastic

Plastics are organic polymers with the unique characteristic that each molecule is either a long chain or a network of repeating units. The properties of plastics are determined by the chemical and physical nature of the polymers used in their manufacture, the properties of polymers being determined by their molecular structure, molecular weight (MW), degree of crystallinity, and chemical composition. (Sun, 2012)

These factors in turn affect the density of the polymers and the temperatures at which they undergo physical transitions. Polymer chains can and do align themselves in ordered structures, and the thermodynamics of this ordered state determine such properties as melting point, glass transition temperature (Tg), and mechanical and electrical properties. However, it is the chemical nature of the polymer that determines its stability to temperature, light, water, and solvents, and hence the degree of protection it will provide to food when used as a packaging material. (Orezzoli et al., 2018)

- The most common General properties of bioplastics for packaging materials are:

1. Bursting strength—the resistance of a packaging material to a sudden rupture especially due to internal pressure.

2. Coefficient of friction—a measure of the force opposing an applied force parallel to a surface; it is dependent upon the perpendicular force between the material and another material surface.

3. Density—the mass of a material per unit volume.

4. Elongation—the change in length of a material resulting from tensile stress

5. Gauge—a unit length, 1×10^{-4} in.

6. Gloss—the ratio of light flux secularly reflected from a surface to the total reflected flux.

7. Haze—material opacity due to internal and surface reflections of incident light.

8. Light transmission—the light flux through a material over an interval of time.

9. Modulus of elasticity—a general ratio of a specific form of stress to a specific form of strain; specific examples are Young's modulus, bulk modulus, and shear modulus.

10. Opacity—the ratio of the amount of incident light reflected from a material to the amount of incident light transmitted through the material.

11. Oxygen transmission rate (OTR) —the amount of oxygen passing through a material under specified conditions of time, temperature, pressure, and relative humidity.

12. Tear strength—the force required to tear a material; tearing initiation and tearing propagation are commonly measured.

13. Tensile strength—the maximum force that a material specimen can resist under tension.

14. Tensile stress—a stretching force along an axis.

15. Water vapor transmission rate (WVTR) —the amount of water vapor that passes through a specimen in a set time period under controlled condition of time, temperature, and relative humidity.

Table 2-3: Selected package properties and their relationship to packaging functions

Properties of packaging Materials	Function
Tensile strength	Protection and containment; package, seal or seam integrity; Prevents external contamination
Water vapor transmission rate	Protection against food degradation by water
Oxygen transmission rate	Protection against food oxidation; prevents growth of micro-organisms
Burst strength	Protection and containment; seal and package integrity; Prevents external contamination
Tear strength	Protection and containment; Package integrity; Package operations, distribution

2.7 Biodegradation of Bio Plastics

Biodegradation of any plastic is a process that happens at solid/liquid interface whereby the enzymes in the liquid phase depolymerize the solid phase. Both bioplastics and conventional plastics containing additives are able to biodegrade. Bioplastics are able to biodegrade in different environments hence they are more acceptable than conventional plastics. Biodegradability of bioplastics occurs under various environmental conditions including soil, aquatic environments and compost. Both the structure and composition of biopolymer or bio-composite have an effect on the biodegradation process, hence changing the composition and structure might increase biodegradability. (Michel, 2013)

Soil and compost as environment conditions are more efficient in biodegradation due to their high microbial diversity. Composting not only biodegrades bioplastics efficiently but it also significantly reduces the emission of greenhouse gases. Biodegradability of bioplastics in compost environments can be upgraded by adding more soluble sugar and increasing temperature. Soil environments on the other hand have high diversity of microorganisms making it easier for biodegradation of bioplastics to occur. However, bioplastics in soil environments need higher temperatures and a longer time to biodegrade. Some bioplastics biodegrade more efficiently in water bodies and marine systems; however, this causes danger to marine ecosystems and freshwater. Hence it is accurate to conclude that biodegradation of bioplastics in water bodies which leads to the death of aquatic organisms and unhealthy water can be noted as one of the negative environmental impacts of bioplastics. (Emadian et al., 2017) (Gómez, 2013)

2.7.1 Mechanical Property

Mechanical properties provide an indication of the mechanical performance of the materials. The tensile properties are most frequently considered, evaluated, and used throughout the industry. Tensile testing provides tensile strength, modulus of elasticity and elongation at break. (Orezzoli et al., 2018)

2.7.2 Physio-Chemical Properties

Important properties of common packaging materials are generally mechanical, optical and barrier properties. Mechanical, optical and barrier properties of plastics are mainly based on the physical properties (crystallinity).

Crystallinity state is the state, which diffracts X ray and exhibits the first-order transition known as melting. A first-order transition normally has a discontinuity in the volume-temperature dependence, as well as a heat of transition, ΔHf, also called the enthalpy of fusion or melting. Percent crystallinity has a big influence on hardness, density, transparency and diffusion. Changes in the crystallinity of thermoplastics result in significant changes in the mechanical behavior of composites containing them. For this reason, the ability to characterize precisely the polymer crystallinity in thermoplastic composites becomes an important requirement. (Orezzoli et al., 2018) (Siracusa, 2016)

2.8 Applications

In search of new material solutions and preceding an eye on the goal of sustainable production and consumption, bioplastics have various (potential) advantages. Advances in how they are produced are allowing bioplastics with controllable physical properties to be produced enabling uses which mimic those of oil-based plastics. The properties of some bioplastics allow novel functions to be carried out. (Murphy et al, 2009)

Bioplastics can also be processed in very similar ways to petrochemical plastics such as injection molding, extrusion and thermoforming. To improve their tensile strength, bio plastic polymers can be blended with their co-polymers or with other polymers.

- The Current end-use segments of bio plastics includes the following:
  - A. **Biodegradable and short-lived products –**
    - Packaging
      - ✓ Shopping bags
      - ✓ Compostable waste collection bags
      - ✓ Trays and Punnets for vegetables, fruits, meat and eggs.
    - Disposable catering service wares
    - Medical applications
      - ✓ Implants such as screws, pins or plates

- ✓ Material for pills and capsules
- Mulch films

B. **Non-Biodegradable and durable products –**

- Automotive interiors like seats, head rests or arm rests
- Mobile phone cases

C. Emerging end-use segments of bioplastics

- 3D printing
- Metalized Biaxial oriented -PLA films for food packaging
- Baby products – Toys and Teethers
- Modified PLA for durable applications – Interiors and under the hood automotive parts

2.8.1 Packaging Bags and Wraps

Concerns over litter, the perceived waste of a single use item and the management of bio-waste have made this one of the fastest growing sectors for bioplastics in the early 21st century. Bioplastics form excellent replacements to conventional oil based materials in this sector with great performance characteristics, strength, good contact clarity and proven high speed production (Reddy et al., 2013)

2.8.2 Agriculture & Horticulture

The usually inherent property of biodegradability offers specific advantages in agriculture and horticulture.

i. Mulch film

Bioplastics can be converted into fully opaque or semi-transparent films that provide the ideal growing environment yet can be ploughed into the ground at the end of the growth cycle, providing soil nutrition for future seasons. Producing pure foods with a minimum of pesticide use is a powerful sales argument in vegetable-growing or organic farming. Ploughing-in mulching films after use instead of collecting them from the field, cleaning off the soil and returning them for recycling, is practical and improves the economics of the operation. (Kesselring & Willich, 2009)

Figure 2-10: Mulch Films made of PLA Bioplastics (Kesselring & Willich, 2009)

ii. Tree protectors and Plant supports/stakes:

Bioplastics are being developed as an answer to forest litter, providing a guard that enables young trees to get the best possible start. Protection from vermin and hostile environment is assured early in the growing cycle but the material will bio-disintegrate as the tree passes into maturity. Unsightly litter is removed and collection costs on managed woodland eliminated. Horticulturalists now choose bioplastics to make functional plant holders that are strong, water resistant, in a choice of colors and have the ability to decompose naturally into biomass. (Scarscia et al., 2012)

2.8.3 Personal Care and Hygiene

Most personal care items like toothbrushes, razors etc can be manufactured from bioplastics. Matt finishing of the bioplastics ensures that the plastic razor has good grip and gives a smooth shave. The material surface characteristics ensure good grip performance whilst providing a device that will withstand everyday use. Testing for products in this sector has demonstrated suitable thermal, moisture and fatigue performance. (Goodall, 2011)

Meanwhile bioplastics can be blown to form opaque, soft-feel bottles for the likes of shampoos and creams. Complementing bioplastic caps can be injection or compression molded. These products are one time use and throw products, if bioplastics can be used here, it can solve the problem of plastic as a gross waste to a large extent. (Murphy et al., 2009)

2.8.4 Electronics

In 2009, Japanese multinational, NEC has successfully developed and implemented a flame-retardant bio-plastic that can be used in electronic devices due to its high flame retardancy and processability. The new bioplastic includes more than 75% biomass components, and can be produced using manufacturing and molding processes that halve the CO2 emissions of conventional processes used to make petroleum-based flame-retardant plastics (PC/ABS plastics). NEC's new bioplastic is therefore one of the most environmentally friendly flame retardant plastics used for casing of electronic devices in the world.

In another case, Mitsubishi Plastics, Inc has already succeeded in raising the heat-resistance and strength of polylactic acid by combining it with other biodegradable plastics and filler, and the result was used to make the plastic casing of a new version of Sony Corp.'s Walkman. Mitsubishi Plastics had previously looked at bioplastic as something that would mainly be used in the manufacture of casings and wrappings, but the company now feels confident that this revolutionary material has entered a new phase in its development in which more complex applications will be found. (Syed, 2016)

2.8.5 Automobiles

Ford Motor Corp. was the first automaker in the world to use bioplastics in the manufacture of auto parts way back in the 1920s. Recently, Toyota motor corp. employed them in the cover for the spare tire in the Raum, a new model that went on sale this May. The bioplastic used here is polylactic acid (PLA) is made from plants, such as sweet potatoes and sugarcane.

A spokesperson for Toyota Motor's Biotechnology and Afforestation Business Division expresses high hopes for the future of bioplastics, saying, "The inside of a car gets very hot and is exposed to shocks while the vehicle is running. If bioplastics can be used in this tough environment, they can be used in ordinary household products or anywhere else." (Syed, 2016)

2.8.6 Food Packing

In a new study published on June 6, 2013 in the peer-reviewed scientific journal Trends in Food Science and Technology, researchers from the University of Gent review the application of bioplastics in food packaging (Peelman & Devlieghere, 2013) The main bioplastics are polylactide (PLA), starch, polyhydroxyalkanoates (PHA) and cellulose.

PLA is the most widely used bioplastics with application for fresh foods, dry foods such as pasta and potato chips, fruit drinks, yoghurt, and meat. Starch has been used as an alternative for polystyrene (PS) to package tomatoes and chocolate. Cellulose is used to package dry foods and fresh produce. While all of these materials are biodegradable, their functional limitations have so far restricted their widespread application in food packaging. As outlined by Peelman and colleagues, the main limitations of the four materials is their brittleness, thermal instability, low melt strength, difficult heat salability, high vapor and oxygen permeability, poor mechanical properties, stiffness and poor impact resistance. In their study Peelman and colleagues review three processes, which may be used to improve the properties of bioplastics, namely coating, blends and chemical/physical modifications. (Peelman & Devlieghere, 2013)

i. Coating

Coating comprises the application of a thin bio based or non-bio based layer to the bioplastics. Such coatings can lower the oxygen and vapor permeability, increase tensile strength and result in higher elastic properties. (Johansson et at., 2012)

ii. Blending

Blending bioplastics is another approach to improve functionality. Cellulose and other bio based materials may be used to create improved blends. Most bioplastics are immiscible; however the introduction of functional groups, chemical modification or esterification can enhance compatibility. Blending can reduce brittleness, increasing vapour water barrier properties, flexibility, and tensile strength. (Luzi et al., 2019)

iii. Chemical and/or physical modification

The third approach to improve functionality is chemical and/or physical modification. It can be used to enhance compatibility between two polymers or to improve the functional properties directly. Citric acid added to starch films improves water and vapor properties (WVP). Crosslinking cellulose acetate with phosphates improves tensile strength and slows water uptake and degradation. Epichlorohydrin-modified starch has an increased tensile strength and improved elongation. Partially substituting wheat gluten with hydrolyzed keratin or soaking wheat gluten film in CaCl2 and distilled water improves the water vapour and oxygen barrier properties of a wheat gluten derived film. (Jamróz & Kopel, 2019)

2.8.7 Construction

The Institute of Building Structures and Structural Design (ITKE) at the University of Stuttgart (Germany) has worked on fibre-reinforced polymers, bionics and the development of new building materials. Architect Carmen Köhler is investigating the applicability of natural fibrereinforced biopolymers in the construction industry. In contrast to fibreglass-reinforced polymers, natural fibre-reinforced polymers are considerably lighter, emission stable and breathable. "Construction material that is breathable at the same time as preventing moisture from penetrating, is also of major interest in architectural terms," (Kasapoglu, 2008)

The global biodegradable plastics market accounts for less than 1% of the overall plastics market, however, it is expected to grow at a fast pace over the next 5 years. The market growth is driven by continuous R&D activities, increased environmental awareness, and implementation of stringent environmental regulations. However, the high cost of biodegradable plastics has been a major barrier in the growth of the market

The growth of biodegradable plastics is driven by the following factors:

a) Consumer preference toward environmental-friendly products
b) Use of renewable and bio-based raw material
c) Biodegradability
d) Government policies toward green procurement (Tsang & Jeon, 2019)

2. 9 Disposal Options for Bioplastics

With the expected increase in bioplastic products, it's important we understand the different categories of bioplastic and how best to dispose of each type – otherwise, they can contaminate waste systems. (Alaerts et al., 2018)

- **Recycling:** Many plastics can be successfully recycled into new plastic materials at the end of their life. However, if plastics are not sorted into different categories, mixing some degradable plastics with other recycled plastics can reduce the performance and life span of the recycled product.

- **Composting:** Not all biodegradable products are suitable for composting. Products labeled 'compostable' must meet recognized international standards, which specify the composting conditions such as time, temperature and the environmental effects of the final compost. Also, industrial and home composting conditions are different. Where industrial facilities are not locally available, which is generally the case in New Zealand, compostable products are likely to contaminate other waste streams. (Alaerts et al., 2018) (Gómez, 2013)
- **Landfill:** Biodegradable and compostable plastics take a long time to degrade in the

CHAPTER THREE

3. MATERIALS AND METHODS

The experimental work was held in Environmental, Food, and Research laboratories of Addis Ababa institute of Technology, School of Chemical and Bio-Engineering and the characterization of the product was held in college of natural science of Addis Ababa University School of Chemistry department and Ethiopian Conformity Assessment Enterprise.

3.1 Chemicals and Analytic Reagents

Different equipment and chemicals were used in the primary stage which was banana peel preparation. Those includes plastic bags to collect and transport samples from local market to the laboratory**,** after the sample has arrived at the laboratory mass balances and stainless steel knifes were used to measure the weight of the sample and to cut the banana peel in to pieces respectively for the simplicity and better exposure of the peels for proceeding processes. In the preparation stage, Sodium Solution of Metabisulphate was used as antioxidant to prevent microbial growth in the peels as the banana peel is a raw material which can easily be exposed to microorganisms due to its high sugar content. Beakers at different volume and acid resistance were used in every stage of the bioplastics preparation and synthesis process; they have been used as container to hold samples, chemicals, Hydrochloric acid and glycerol. After the banana peel preparation process the synthesis of bioplastics from banana peel trough acid hydrolysis of amylopectin proceeds and in this stage is where HCl and glycerol were used as hydrolyzing agent and plasticizer and after the hydrolysis process NaOH was used as neutralizing chemical to neutralize the PH of medium. During synthesis of biolistic additional equipment has been used to assist the process such as peel spreading papers, blender and oven for the purpose of drying the banana peels in an open air, forming a uniform banana peel paste and drying the hydrolyzed banana peel respectively and finally plastic bags were used to mold the bioplastics as it dried up in the oven.

3.2 Experimental procedures

3.2.1 Preparation of Banana Skin

The banana peel bio-plastic films were prepared by the procedure adapted from the method describe by (Vikas Mishra, 2015) 3kg of unripe and similarly sized bananas with no injury or bruises on the skin was purchased from local markets in order to ensure the effectiveness of the experiment. The collected Banana peels was washed using distilled water and it was remove using stainless steel knife and cut in to pieces then soaked in sodium meta bisulphite (0.2M) solution for 45 minutes, sodium meta bisulphite was used as preservative in this process although it can also increase biodegradation period of the biofilm, it helped to inhibit microbial growth on the banana peel throughout the experiment which took longer than expected. 200 g of banana peel was boiled in 400ml of distilled water for about 30 minutes in 100^{o}c Stove after the water is decanted the pieces of the banana peel were left to dry on filter paper for 15 hrs. Then the dried peels were placed in a beaker and were purred using blender until uniform paste was formed.

3.3.2 Production of BioPlastic

25g of banana paste from earlier experiment was placed in a beaker then HCl with the volume of (1ml, 3ml, and 5ml) was added to the paste and stirred using glass rode. Similarly 1ml, 2ml, 3ml (4%, 8% and 12%V/W) of plasticizer (Glycerol) with purity of 99.9% was added and stirred for a desired residence time of (5minutes,15 minutes and 25 minutes) and after the desired residence time of hydrolysis 0.5 N NaOH was added according to the volume of HCl added to neutralize the mixture. The mixture was spread on plastic plate and then put in to oven at (40, 50, 60)^{0}C for 24 hrs. After it is baked the film was scrap off the surface and placed at a room temperature. This process is summarized in Figure 3-1 and Figure 3-2.

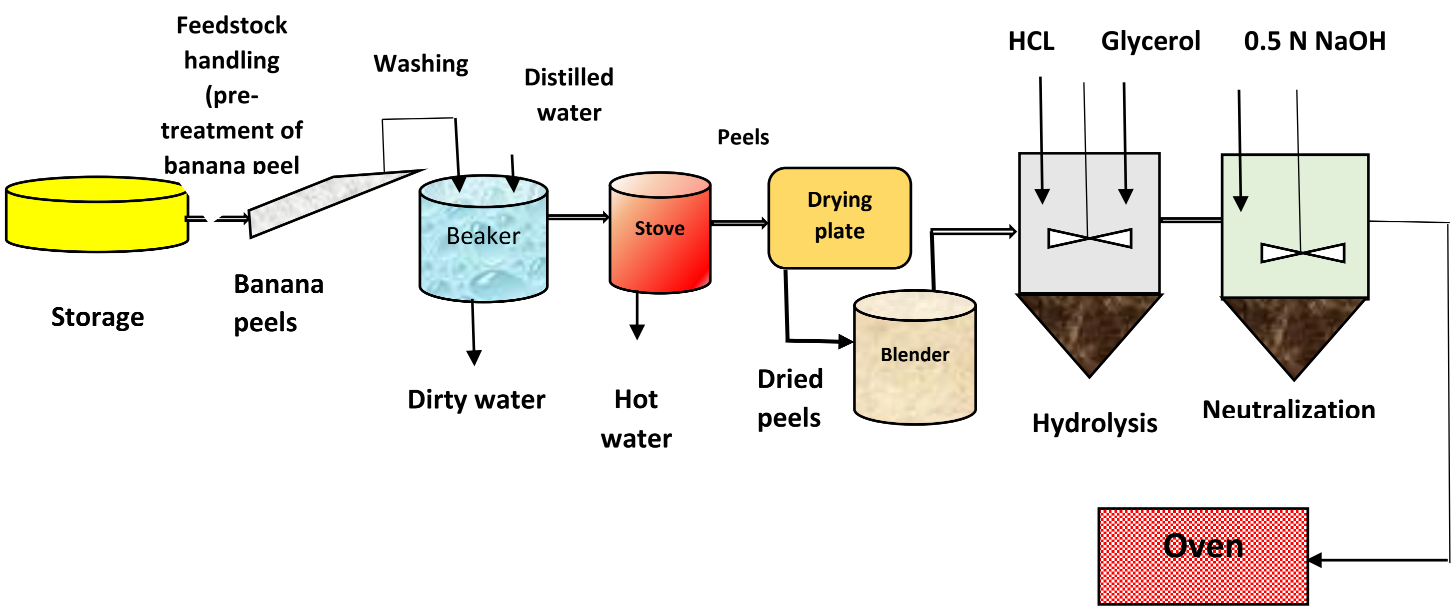


Figure 3-1: General frame work of the experiment

3.4 Synthesis of a Modified Bioplastics Using $CaCO_3$ as a Filler

The bioplastics produced in prior process was observed to obtain a good quality in terms of mechanical property such as tensile strength and elongation at break in addition to the fact that it is waste based bioplastics; However, the water absorption was relatively higher compared to conventional plastic or to any other non- starch raw material based bioplastics .This is due to the starch nature of banana peel which is hydrophilic and absorbs water from the atmosphere in storage.

Since water absorption is very important property for bioplastics especially in food packaging application of the synthesized bioplastics it is necessary to look for means to improve this quality. For that reason a method adopted from (Han et al., 2010) was used with some modifications to improve water absorption of the synthesized bioplastics.

According to (Han et al., 2010) The thermal stability and mechanical and physical properties such as tensile strength and water absorption of bio composites can also be improved by adding an inorganic filler such as Calcium Carbonate as it increases tensile strength, modulus, flexural strength and heat deformation in polypropylene (PP). $CaCO_3$ may also increase fracture resistance in PP.

Similar principles were applied to lower the water absorption of the synthesized bioplastics starting from re-collection banana peel from local market and following similar banana peels preparation techniques as the prior experiments. After purring uniform banana peel paste was formed, 25g of banana peel paste was placed in a beaker then $CaCO_3$ with the concentration of (0%, 2%, 4%, 6%, 8%, 10% w/w of banana peel) was added in to 6 beakers consecutively. Following that procedure HCL acid with the optimum concentrations of *(*11.748% V/W) approximately volume of 2.9ml was added to the paste and stirred using glass rode and similarly the optimum concentration of (8.384V/W) approximately volume of 2.1 ml plasticizer (Glycerol) with purity of 99.9% was added and stirred for a residence time of 14 minutes and 30 seconds. After the optimum residence time of hydrolysis 0.5 N NaOH was added proportional to the volume of HCl added to neutralize the mixture. Then the mixture was spread on plastic plate and put in to oven at optimum temperature of 52 ^{0}C for 24 hrs. After it is baked the film was scrap off the surface and placed at a room temperature.

Figure 3-2: Banana peel based bio plastic synthesizing procedure

3.5 Experimental Design

Response surface methodology (RSM) was used 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. Four factors (three levels of each) Boxen-Behnken experimental design was employed. The factors were (drying temperature, glycerol concentration, and hydrochloric acid concentration and Residence time for acid hydrolysis) and their levels were chosen based on the literature and preliminary experiment. According to the information gained from literature the components used for the banana-based packaging films were: unripen banana peel since they have higher starch content (40% starch) and this desired type of banana peel can be obtained from wastes of banana flour, banana Chips, banana juice factories specifically in Ethiopia there is a banana flour factory in Ariba Minch known as Anjonus fruit and vegetable processing factory. They produced banana flour from green Cavendish banana the waste i.e banana peel can be used to produce bioplastic. glycerol at the concentration of (24 v/w of banana peel paste) and HCl acid at the concentration of (29 % v/w of banana peel paste), drying temperature (130^{o}C) and Residence time for hydrolysis (5,15,25 minutes); However, The result obtained based on the levels from literature wasn't satisfactory as it can be observed from their resulting data the product lose elasticity, it appear to be somehow rigid and brittle and the fact that they used higher volume of glycerol to manage its brittleness increased the water absorption therefore some modification has been made to the levels of the factors based on the Preliminary experiment and the experiment was held with the concentration of Glycerol (4%, 8%, and 12% v/w of banana peel paste), concentration of HCL (4%, 12% and 20% v/w of banana peel paste), drying temperature at (40, 50, 60 ^{o}C) and Residence time for hydrolysis was taken as it is (5,15,25 minutes) in expectations of getting a bioplastic that exhibit good elasticity characteristics and less brittleness without using excess glycerol. The Responses were Tensile strength, Elongation at break, water absorption and biodegradability.

The 4 factors has been analyzed for the different combinations of their test levels the optimum combination of the operational factors was determined.

3.6 Characterization experiment

3.6.1 Water Absorption Test/Swelling Measurements/

The water uptake of films was measured according to (Kuorwel M. K.-S., 2011) by directly immersing film pieces into glycerol-water mixtures. In the immersion tests, film pieces were cut in smaller piece of bio plastic 4 cm × 4 cm size and directly immersed into a beaker containing mixtures of 50% water and 50% glycerol (%v/v) and kept at a temperature of 20 ± 1°C for 5 min. Samples were then removed from the beaker and wiped dry and measured the weight as:

$$\textbf{Water absorption} = \frac{W_f - W_o}{W_o} * 100\% \qquad \text{Equation 3-1}$$

Where, Wf= represents final weight of the film after 5 minute

Wo= initial weight of the film

3.6.2 Tensile strength

The mechanical properties of the developed bio-plastic films are the most important properties and they were characterized in terms of tensile strength (TS) and elongation at break (EB). Accordingly, The TS and EB values of the as prepared bio plastic films were investigated in the Ethiopian Conformity Assessment Enterprise by calibrated Universal Tensile Testing Machine (UTM, made in Thailand). The lab room condition was 45% relative humidity (RH) and 24.5^{o}C temperature. The test parameters i.e. (thickness, width and length of the test samples) were feed to the tensile strength tester with the gauge length and the crosshead of 20 mm and 100 mm/min, respectively. And the pre-prepared sample Films were cut into strips with 2 cm length and 2 cm width in dumbbell shape. Finally, the test results were generated, that is, the mean of tensile strength at break in Mpa, elongation at break in %.

3.6.3 Fourier Transform Infrared Spectroscopy (FT IR) Characterization

The packaging bio-film FTIR sample preparation was done by KBr pellet method from Science faculty in Chemistry department (AAU): ~ 1 mg of solid bio-film 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 (400-4000-cm) versus absorbance (%) was plotted using Microcal origin software and identified the functional groups.

3.6.4 Biodegradability Test

Biodegradable behavior of bioplastics was determined r using soil burial degradation test, i.e. bioplastics were buried in the soil, so that it would be degraded completely. Degradation testing serves to determine the extent of damage of bioplastics. The damage can be seen from the mass reduction of respective specimens buried in the ground. Bioplastics were cut into 2 cm x 2 cm. Then, they were buried into the ground at 15-cm depth; the burial duration varied (15, 20 , 25, and 30 days). Prior to burial, the initial mass (mass before degradation) was determined. The final mass (mass after degradation) of the bioplastics was measured afterwards. Any changes in mechanical properties due to degradation process were observed and when the bioplastics were completely degraded, the biodegradability was measured

$$\text{Microbial resistance (\%)} = \frac{\text{Initial mass} - \text{final mass}}{\text{Initial mass}} * 100\% \qquad \text{Equation 3-2}$$

Figure 3-3: Biodegradability analyzing method

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1 Statistical Analysis Using Design Expert 11

4.1.1 Factors and Responses

Table 4-1 shows the result of the 29 experimental runs carried out according to the box Behnken design (BBD). Box Behnken design is the commonly used experimental design model for three-level three-factor experiments and always has three levels for each factor and is purpose-built to fit a quadratic model. The box Behnken design does not have runs at the extreme combinations of all the factors but compensates by having better prediction precision in the center of the factor space. While a run or two can be botched in these designs the accuracy of the observations in the remaining runs is critical to the dependability of the model. In this study, Design-Expert Software 11.1.0.1 was used in the least squares regression ANOVA.

The statistical software program was used to generate the model equation, interaction effects of the four independent variables (Temperature, concentration of HCL and Glycerol and residence time) on the corresponding quality of the bioplastic and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variables constant.

Table 4-1: Number of experimental runs versus responses

Std	Run	Factor A Temperature (^{0}c)	Factor B [HCL] (ml)	Factor C [Glycerol] (ml)	Factor D Residence time (minute)	Response 1 Tensile strength (MPA)	Response 2 Elongation at break (%)	Response 3 Water Absorption (%)	Response 4 Bio-degradability (%)
1	6	40	1	2	15	7.021	9.52	70.05	46.2
2	18	60	1	2	15	7.751	11.95	64.57	40.8
3	2	40	5	2	15	7.112	11.39	68.37	39.3
4	13	60	5	2	15	7.527	10.51	62.76	41.7
5	14	50	3	1	5	8.074	10.72	65.98	36.7

6	26	50	3	3	5	7.213	9.92	64.71	22.5
7	3	50	3	1	25	8.078	9.36	68.46	22.5
8	10	50	3	3	25	7.328	11.93	62.32	37.8
9	21	40	3	2	5	7.652	9.84	69.65	40.9
10	23	60	3	2	5	7.557	12.45	63.27	40.3
11	12	40	3	2	25	7.028	11.56	68.81	42.5
12	29	60	3	2	25	8.018	10.61	63.36	38.7
13	28	50	1	1	15	7.812	9.92	69.52	29.6
14	16	50	5	1	15	8.033	9.45	65.47	26.5
15	15	50	1	3	15	7.106	10.41	63.78	30.5
16	8	50	5	3	15	7.118	11.37	62.85	26.4
17	19	40	3	1	15	9.516	7.05	72.57	26.7
18	7	60	3	1	15	8.021	9.61	64.22	28.5
19	5	40	3	3	15	7.048	9.52	65.75	29.6
20	20	60	3	3	15	9.103	9.18	63.89	27.8
21	1	50	1	2	5	7.087	11.44	65.45	45.9
22	4	50	5	2	5	6.085	13.54	64.33	35.6
23	17	50	1	2	25	6.113	13.48	66.83	39.5
24	11	50	5	2	25	7.018	11.58	62.65	42.8
25	24	50	3	2	15	9.409	13.52	63.34	49.2
26	27	50	3	2	15	9.327	13.95	64.04	47.5
27	22	50	3	2	15	9.278	13.25	62.97	46.5
28	25	50	3	2	15	9.423	13.55	63.39	48.3
29	9	50	3	2	15	9.325	13.34	63.65	49.6

4.1.2 Analysis of Variances (ANOVA)

A. Analysis of variance for tensile strength (MPA)

The analysis of variance of the quadratic regression model was a significant model, from evidence of Fisher's "F" test with a very low probability value [(P-model> F) < 0.0001]. From Table 4-2 it was observed that the values of "Prob > F" less than 0.0500 indicate model terms were significant. In this case A, C, AC, AD, BD A^2, B^2, C^2, and D2 were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. The independent variables (concentration of Glycerol, residence time, interaction between concentration of HCL and concentration of Glycerol and interaction between concentration of Glycerol and Residence time) are insignificant terms which means they have no effect on the dependent variable (tensile strength) or their effects is statistically equal to zero. The reason for this elaborated under section 4.2.1 and 4.3.1 for independent variable factors and interaction of factors respectively.

Table 4-2: Analysis of variance for tensile strength (MPA)

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	27.69	14	1.98	264.90	< 0.0001	significant
A-Temperature	0.5633	1	0.5633	75.44	< 0.0001	
B-Concentration of HCl	7.500E-07	1	7.500E-07	0.0001	0.9921	
C-Concentration of Glycerol	1.78	1	1.78	237.99	< 0.0001	
D-Residence time	0.0006	1	0.0006	0.0806	0.7806	
AB	0.0248	1	0.0248	3.32	0.0898	
AC	3.15	1	3.15	421.92	< 0.0001	
AD	0.2943	1	0.2943	39.41	< 0.0001	
BC	0.0109	1	0.0109	1.46	0.2466	
BD	0.9092	1	0.9092	121.75	< 0.0001	
CD	0.0031	1	0.0031	0.4125	0.5311	
A^2	1.78	1	1.78	238.88	< 0.0001	
B^2	14.03	1	14.03	1879.05	< 0.0001	
C^2	0.9735	1	0.9735	130.37	< 0.0001	
D^2	10.75	1	10.75	1439.43	< 0.0001	
Residual	0.1045	14	0.0075			
Lack of Fit	0.0894	10	0.0089	2.37	0.2110	not significant
Pure Error	0.0151	4	0.0038			
Cor Total	27.80	28				

The Model F-value of 264.90 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, C, AC, AD, BD A^2, B^2, C^2, and D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant The Lack of Fit F-value of 2.37 implies the Lack of Fit is not significant relative to the pure error. There is a 21.10% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good which implies the little errors in the experimental data are due to noise and that they are negligible.

B. Analysis of Variance Elongation at break

The analysis of variance of the quadratic regression model was a significant model, from evident of Fisher's "F" test with a very low probability value [(P-model> F) < 0.0001]. From Table 4-3 it was observed that the values of "Prob > F" less than 0.0500 indicate model terms were significant. In this case A, C, AB, AC, AD, BC, BD, CD, A2, B2, C2 and D^2 were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. This indicates that the independent variable (residence time) is insignificant terms which means it has no effect on the elongation at break or its effect is statistically equal to zero. The reason for this elaborated under section 4.2.2 and 4.3.2 for independent variable factors and interaction of factors respectively.

Table 4-3: Analysis of Variance Elongation at break (%)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	78.64	14	5.62	175.12	< 0.0001	significant
A-Temperature	2.46	1	2.46	76.61	< 0.0001	
B-Concentration of HCl	0.1045	1	0.1045	3.26	0.0926	
C-Concentration of Glycerol	3.22	1	3.22	100.52	< 0.0001	
D-Residence time	0.0310	1	0.0310	0.9668	0.3422	
AB	2.74	1	2.74	85.40	< 0.0001	
AC	2.10	1	2.10	65.55	< 0.0001	
AD	3.17	1	3.17	98.78	< 0.0001	
BC	0.5112	1	0.5112	15.94	0.0013	

BD	4.00	1	4.00	124.71	< 0.0001	
CD	2.84	1	2.84	88.52	< 0.0001	
A^2	24.46	1	24.46	762.57	< 0.0001	
B^2	1.76	1	1.76	54.81	< 0.0001	
C^2	41.70	1	41.70	1300.20	< 0.0001	
D^2	0.5337	1	0.5337	16.64	0.0011	
Residual	0.4490	14	0.0321			
Lack of Fit	0.2140	10	0.0214	0.3641	0.9112	not significant
Pure Error	0.2351	4	0.0588			
Cor Total	79.09	28				

The Model F-value of 175.12 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, C, AB, AC, AD, BC, BD, CD, A2, B^2, C^2 and D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant The Lack of Fit F-value of 0.3641implies the Lack of Fit is not significant relative to the pure error. There is a 91.12 % chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good. The following second order polynomial model was derived to explain the effect of the four process factors on the Elongation at break of the biofilm.

C. Analysis of variance for water absorption (%)

The analysis of variance of the quadratic regression model was a significant model, from evident of Fisher's "F" test with a very low probability value [(P-model> F) < 0.0001]. From Table 4-4 it was observed that the values of "Prob > F" less than 0.0500 indicate model terms were significant. In this case A, B, C, D AB, AC, AD, BC, CD, A^2, B^2, C^2, D^2 were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. This indicates that the interaction between concentration of HCL and Residence time is the insignificant terms for the water absorption of the bio plastic. The reason for this elaborated under section 4.2.3 and 4.3.3 for independent variable factors and interaction of factors respectively.

Table 4-4: Analysis of variance for water absorption (%)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	181.45	14	12.96	223.29	< 0.0001	significant
A-Temperature	60.12	1	60.12	1035.79	< 0.0001	
B-Concentration of HCl	2.18	1	2.18	37.64	< 0.0001	
C-Concentration of Glycerol	14.06	1	14.06	242.26	< 0.0001	
D-Residence time	4.21	1	4.21	72.58	< 0.0001	
AB	0.8742	1	0.8742	15.06	0.0017	
AC	24.11	1	24.11	415.34	< 0.0001	
AD	1.01	1	1.01	17.40	0.0009	
BC	2.43	1	2.43	41.93	< 0.0001	
BD	0.0342	1	0.0342	0.5896	0.4553	
CD	24.26	1	24.26	417.88	< 0.0001	
A^2	22.81	1	22.81	392.94	< 0.0001	
B^2	21.79	1	21.79	375.33	< 0.0001	
C^2	20.24	1	20.24	348.69	< 0.0001	
D^2	0.8240	1	0.8240	14.20	0.0021	
Residual	0.8126	14	0.0580			
Lack of Fit	0.5063	10	0.0506	0.6613	0.7291	not significant
Pure Error	0.3063	4	0.0766			
Cor Total	182.26	28				

The Model F-value of 223.29 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D AB, AC, AD, BC, CD, A2, B2, C2 and D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant The Lack of Fit F-value of 0.6613 implies the Lack of Fit is not significant relative to the pure error. There is a 72.91% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

D. Analysis of variance for Biodegradability (%)

The analysis of variance of the quadratic regression model was a significant model, from evident of Fisher's "F" test with a very low probability value [(P-model> F) < 0.0001]. From Table 4-5 it was observed that the values of "Prob > F" less than 0.0500 indicate model terms were significant. In this case A, B, C, AB, AC, BD, CD, A^2, B^2, C^2 and D^2 were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. This indicates that the Residence time, interaction between Temperature and Residence time, interaction between Concentration of HCl and Concentration of Glycerol are the insignificant terms for the water absorption of the bio plastic. The reason for this elaborated under section 4.2.4 and 4.3.4 for independent variable factors and interaction of factors respectively

Table 4-5: Analysis of variance for Biodegradability (%)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1262.15	14	90.15	159.29	< 0.0001	significant
A-Temperature	9.01	1	9.01	15.92	0.0013	
B-Concentration of HCl	37.45	1	37.45	66.17	< 0.0001	
C-Concentration of Glycerol	433.20	1	433.20	765.39	< 0.0001	
D-Residence time	0.3675	1	0.3675	0.6493	0.4338	
AB	15.21	1	15.21	26.87	< 0.0001	
AC	22.09	1	22.09	39.03	< 0.0001	
AD	2.56	1	2.56	4.52	0.0517	
BC	1.0000	1	1.0000	1.77	0.2050	
BD	46.24	1	46.24	81.70	< 0.0001	
CD	115.56	1	115.56	204.18	< 0.0001	
A^2	71.96	1	71.96	127.15	< 0.0001	
B^2	52.90	1	52.90	93.47	< 0.0001	
C^2	518.81	1	518.81	916.64	< 0.0001	
D^2	123.78	1	123.78	218.69	< 0.0001	
Residual	7.92	14	0.5660			
Lack of Fit	5.98	10	0.5976	1.23	0.4562	not significant

Pure Error	1.95	4	0.4870			
Cor Total	1270.07	28				

4.1.3 Model adequacy check

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R^2 (0.9962, 0.9943, 0.9955 , 0.9938), adjusted R^2 (0.9925, 0.9886, 0.9911, 0.9875) and predicted R^2 (0.9806, 0.9798, 0.9814, 0.9705) for Tensile strength, Elongation at break, Water absorption and biodegradability, respectively. The quality of the model developed could be evaluated from their coefficients of correlation and the value of R-squared for the developed correlation. Since R^2 value for all responses was closer to 1.0, it indicates the model's accuracy was relatively good. Accordingly 99.62% of the total variation in the percentage of conversion is attributed to the experimental variables studied or in another term only 0.38 % of the total variance was left unexplained by the developed regression model in case of tensile strength. Similarly the R^2 for other responses like Elongation at break, water absorption, and bio degradability is 99.43%, 99.55%, 99.38%, respectively. The adequacy of the model was further checked with ANOVA, based on a 95% confidence level, F-value is a test for comparing model variance with residual (error) variance. If the variances are close to be the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P-value less than 0.05. It was calculated by model mean square divided by residual Mean square.

The effectiveness of the model could also be measured so as to assure its approximation to the true value. Thus, regression coefficient, R^2, could be used for checking its adequacy. The regression value is between 0 and 1, and as it approaches to 1 it fits well to the experimental data otherwise it indicates failure of approximation. In this case, R^2 of all parameters obtained was close to one and the value Adj.R^2 for Tensile strength, elongation at break, water absorption and biodegradability was 0.9925, 0.9886, 0.9911, 0.9875 and it is in a reasonable agreement with R^2 which means the difference b/n R^2 and mean is less than 0.2

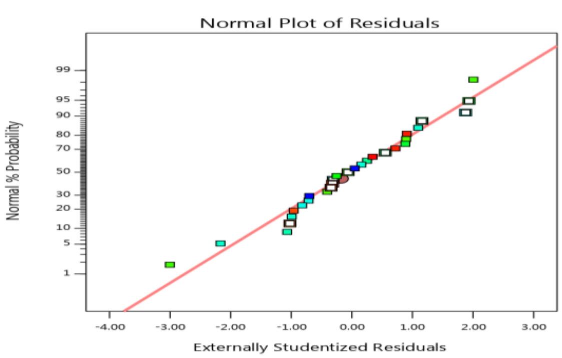
Table 4-6: the model fit summary statistics

P		Responses		
	Tensile	Elongation at	Water	Biodegradability

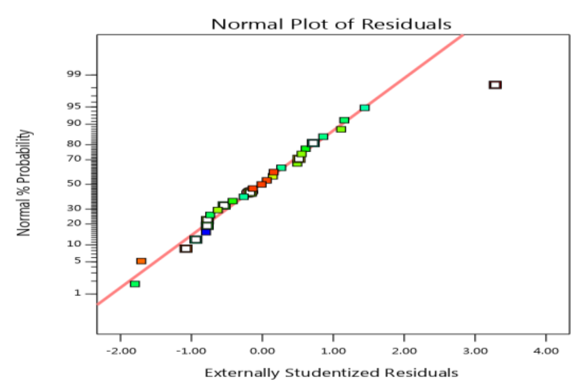
	strength	break	absorption	
Std. Dev.	0.0864	0.1791	0.2409	0.7523
Mean	7.83	11.14	65.69	40.15
C.V. %	1.10	1.61	0.36	1.87
R^2	0.9962	0.9943	0.9955	0.9938
Adjusted R^2	0.9925	0.9886	0.9911	0.9875
Predicted R^2	0.9806	0.9798	0.9814	0.9705
Adeq Precision	54.4824	49.7532	59.1389	45.9648
Press	0.5387	1.60	3.40	37.46

Figure 4-1 shows the data followed a normal distribution with mean and variance, then a plot of the theoretical percentiles of the normal distribution versus the observed sample percentiles was approximately linear. Figure 4-1: (I), (I), (III), (IV) represents the normality of the error terms of tensile strength, Elongation at break, Water absorption and biodegradability respectively, which create a normal probability plot of the residuals. The resulting plot is approximately linear, so the error terms are normally distributed.

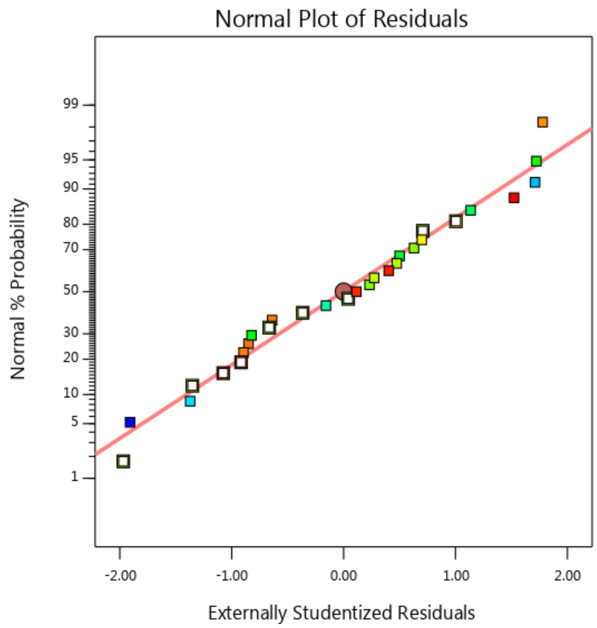
Similarly, Adequacy of the model is further shown from the predicted versus actual plots as shown in Figure 4-2. It can be seen from Figure 4-2: (I), (I), (III), (IV) that the data points on the plot of the responses (TS, Elongation at break, Water absorption and biodegradability) were reasonably distributed near to the straight line, indicating a good relationship between the experimental and predicted values of the response, and that the underlying assumptions of the above analysis were appropriate.



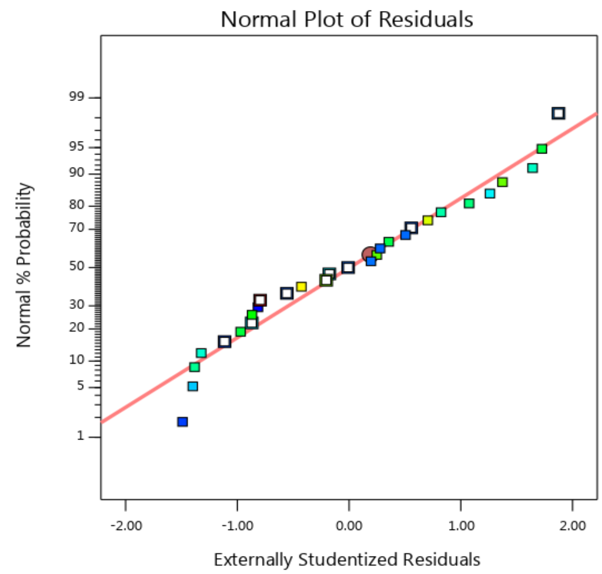
(I)



(II)

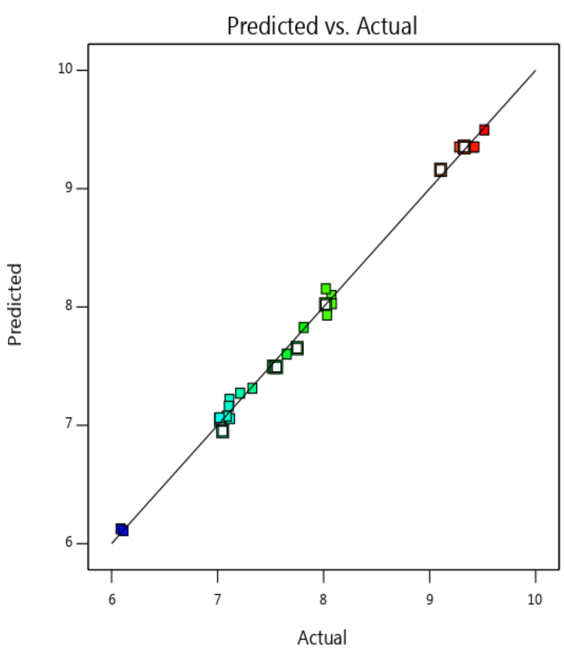


(III)

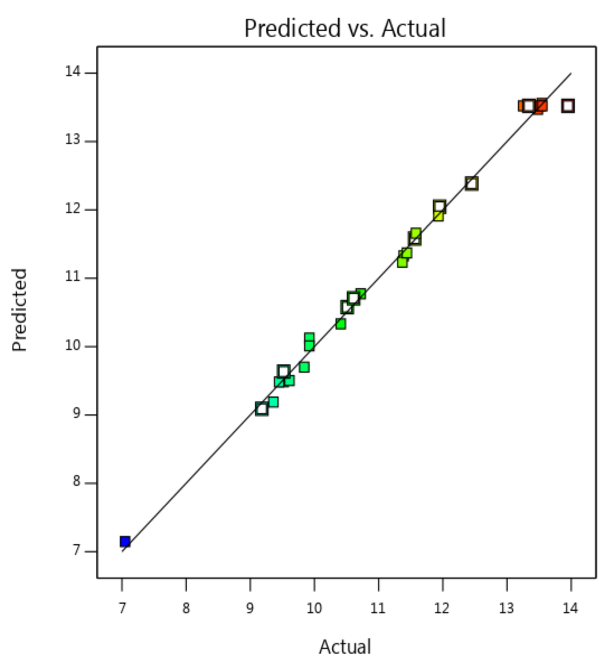


(IV)

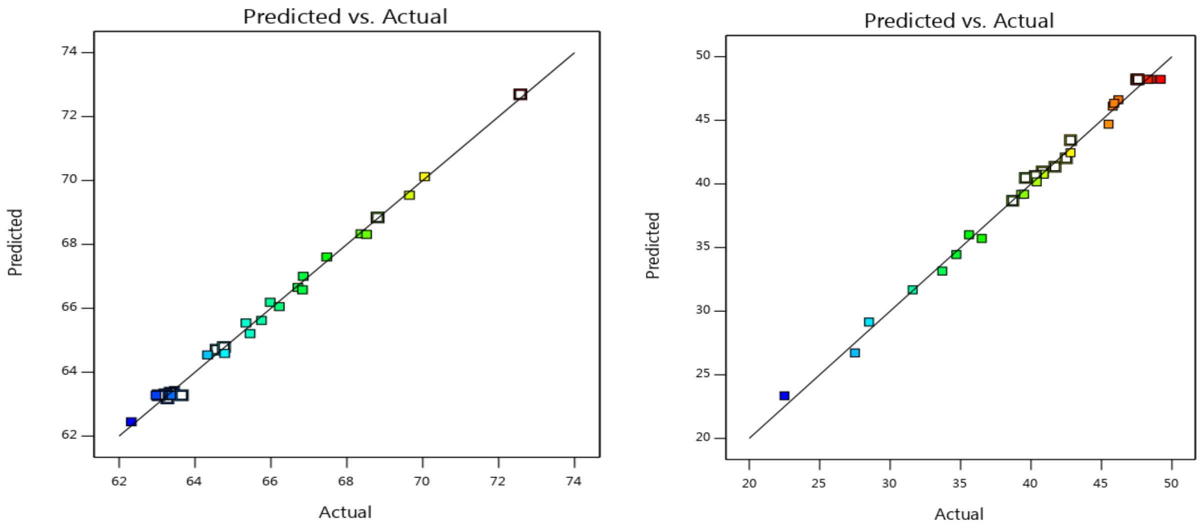
Figure 4-1: Extremly studentized residual versus normal % probability plot for (I): TS, (II): Elongation at break, (III): water absorption, (IV): Biodegradability



(I)



(II)



(III) **(IV)**

Figure 4-2: Predicted versus actual experimental values for (I): TS, (II): Elongation at break, (III): water absorption, (IV): Biodegradability

4.1.4 Final Equation in Terms of Actual Factors

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

Based on regression analysis the quadratic model equations for the four responses: Tensile strength, water absorption and biodegradability in terms of actual values can be written by considering all the terms as follows:

Tensile strength = (-0.498571)+(0.339700***T**)+(2.09786***[HCl]**)–(3.23595***[Glycerol]**)+ (0.172789* **RT**) -(0.003938* **T** * **[HCl]**) + (0.088750 **T*[Glycerol]**) + (0.002713***T*****RT**) - (-0.026125 **[HCl]** * **[Glycerol]**) – (0.023837 **[HCl]** * **RT**) + (0.002775 **[Glycerol]** * **RT**) – (0.005244* **T** ^{2}**)** – (0.367696 **[HCl]**^{2}) + (0.387408***[Glycerol]**^{2}) –(0.012873**RT**^{2}**)** Eq. 4-1

Elongation at break = (-69.47952)+(2.38971***T**)+(3.28879***[HCl]**)+(12.48567***[Glycerol]**)+ (0.517633***RT**) - (0.041375* **T* [HCl]**) - (0.072500 **T*[Glycerol]**) - (0.008900***T*RT**) + (0.178750 **[HCl]** * **[Glycerol]**) – (0.05000 **[HCl] * RT**) + (0.084250 **[Glycerol] * RT**) – (0.019418***T** ^{2}) Eq. 4-2

Water Absorption = (+115.63306)-(1.60275***T**) - (4.84171* **[HCl]**) + 1.42808***[Glycerol]**) – (0.275050***RT**) + (0.023375***T* [HCl]**) – (0.245500 **T *[Glycerol]**) – (0.005025 **T*RT**) + (0.39***[HCl] * [Glycerol]**)-(0.004625* **[HCl] * RT**)+(0.24625* **[Glycerol] * RT**) +(0.018752***T²**)+ (0.458167***[HCl]²**) + (1.76642* **[Glycerol]²**) + (0.003564***RT²**)	Eq. 4-3
Biodegradability = (-37.44938)+ (2.60167***T**) - (3.52458* **[HCl]**) + 22.71917***[Glycerol]**) – (0.108***RT**) + (0.0975***T* [HCl]**) + (0.235T ***[Glycerol]**) – (0.008 **T*RS**) - (0.2500***[HCl] * [Glycerol]**)+(0.1700* **[HCl] * RT**)+ (0.537500***[Glycerol] * RT**) - (0.033308***T²**)- (0.713958***[HCl]²**) - (8.94333* **[Glycerol]²**) - (0.043683***RT²**)	Eq. 4-4

Where,

T= Temperature

[HCL]= concentration of hydro chloric acid

[Glycerol]= concentration of Glycerol

RT = Residence time

Eq=Equation

4.1.5 Final Equation in Terms of Coded Factors

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Tensile strength = +9.35 +0.2167*A + 0.0002*B - 0.3848*C - 0.0071*D- 0.0787*AB + 0.8875*AC + 0.27*AD - 0.0522*BC + 0.4767*BD +0.0277*CD - 0.5244*A² - 1.47*B² -0.3874*C² - 1.29*D²	Eq. 4.5
Elongation at break = +13.52+0.4525*A +0.0933*B +0.5183*C +0.0508*D - 0.8275*AB - 0.7250*AC - 0.7250 *AD +0.3575 *BC -1.0000*BD +0.8425*CD- 2.04*A²-0.6206*B²-2.64*C² -0.3868*D²	Eq. 4.6
Water Absorption = +115.63306 - 1.60275*A - 4.84171*B + 1.42808*C - 0.275050*D +0.023375*AB -0.24550*AC - 0.005025*AD + 0.390*BC - 0.004625*BD + 0.246250 *CD + 0.018752*A² + 0.458167*B² + 1.76642*C² + 0.003564*D²	Eq. 4.7

$$\textbf{Biodegradability} = 48.22 - 0.8667*A - 1.77*B + 6.01*C - 0.1750*D + 1.95*AB + 2.35*AC - 0.8*AD - 0.50*BC + 3.4*BD + 5.37*CD - 3.33*A^2 - 2.86*B^2 - 8.94*C^2 - 4.37*D^2 \qquad \text{Eq. 4.7}$$

Where;

A= Temperature

B= concentration of hydrochloric acid

C= concentration of Glycerol

D= Residence time

4.2. Effect of the independent variables on Tensile strength (TS), Elongation at break (EB), water Absorption and biodegradability of banana peel based bio-films

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, coefficients of the independent variables show the effect of each independent variable on physical as well as mechanical properties of the packaging bio-film. Negative coefficient is to mean that the variable has a negative effect and positive coefficient has a positive effect in the product responses on the basis of the constraint. The limits are minimum water absorption, and possible maximum Tensile strength, Elongation at break and biodegradability.

4.2.1 Effect of independent factors on tensile strength

The effect of drying temperature is very important factor in determining the physical and mechanical property of bio film. In fact in this study temperature had to be modified so many times to get the appropriate range of levels and it has a significant impact on the quality of biofilm produced. Its effect is more visible on the tensile strength and elasticity of the synthesized bio plastic. As it is shown in the figure 4-3 (a) the obtained tensile strength is low for lower temperatures as it the drying temperature rises the tensile strength increases as well in addition to this graphical representation, from the actual model equation 4.1, the coefficient of drying temperature is positive which indicates the TS of the bio-film increase as the drying temperature increases. From the preliminary experiment it has been observed that at higher temperature (130^{o}c for 30 minutes) a bio plastic with higher tensile strength was produced except the product lacked elasticity and ductile property of plastics. Even though temperature increase the tensile strength until it reaches to the extent of brittle-ductile transition temperature (glass transition temperature), it’s preferable to use the optimum temperature due to the economic factors and in order to avoid its side effects such as Brittle and ductile fracture which is characterized by low strain and fracture at the highest stress and large degree of plastic deformation and fracture not necessarily occurs at the highest stress respectively. Brittle-ductile transition temperature highly depends on the Entanglements and molecular weight of the polymer due to the fact that the raw material in this case is banana peel which has fibrous nature the crosslink (entanglements) between starch molecules is higher than that of corn starch therefore it obviously requires more drying temperature to be a plastic but applying excessively high temperature above the glass transition to gain that result in short time either drives off volatiles in the plastic, making it more sensitive to processing, or degrades the material by reducing the molecular weight which results decrease in tensile strength eventually. Therefore, the end result could be obtained by lowering the temperature and increasing the drying time.

Plasticizers are generally small molecules such as polyols like sorbitol, glycerol and polyethylene glycol (PEG) that intersperse and intercalate among and between polymer chains, disrupting hydrogen bonding and spreading the chains apart, which not only increases flexibility, but also water vapor and gas permeability and decreases the mechanical property such as tensile strength Glycerol as it segregate the polymer chains. And the result represented in Figure 4-3 (c) supports this fact. As concentration of glycerol increases the tensile strength was observed decreasing. Adding optimum amount of plasticizer assist to obtain both flexible and relatively better tensile strength of the bio plastic as plasticizers are organic liquids or solids that are incorporated by melt processing or diffusion into a compatible polymer to reduce intermolecular interactions between starch molecules and improve molecular mobility. Therefore increasing the volume of glycerol reduces the intermolecular interaction between the starch molecules in the banana peel which results in tensile strength reduction.

The data in Figure 4-3 (d) shows that the tensile strength for sample keeps increasing when the residence time increased from 5 minutes to 15 minutes and reaches a maximum at 15 minutes and then starts decreasing when the time is increased to 20 minutes. This suggests that the optimum hydrolysis time is around 15 minutes for this sample set. According to (Emaga et al., 2011) the amylose content increased during the initial stages of hydrolysis; however, if the hydrolysis time was increased further, the amylose content decreased slightly.

Therefore based on (Emaga et al., 2011) explanation if this hydrolysis time was continued uninterrupted for long durations, there would be significant drop in the amylopectin and amylose content of starch. This was because once the amylopectin is hydrolyzed to amylase, further hydrolysis leads to formation of glucose monomers which do not aid in polymer formation.

Similarly the hydrochloric acid is used in the hydrolysis of amylopectin, which is needed in order to aid the process of film formation due to the H-bonding amongst the chains of glucose in starch, since amylopectin restricts the film formation. At lower concentration the synthesized bioplastic relatively had lower tensile strength and increase as hydrolyzed amount of amylopectin increases and turn in to linear chains of amylose but as the hydrolyzing acid increases further the amylose content decrease in similar manner as in the hydrolysis retention time.

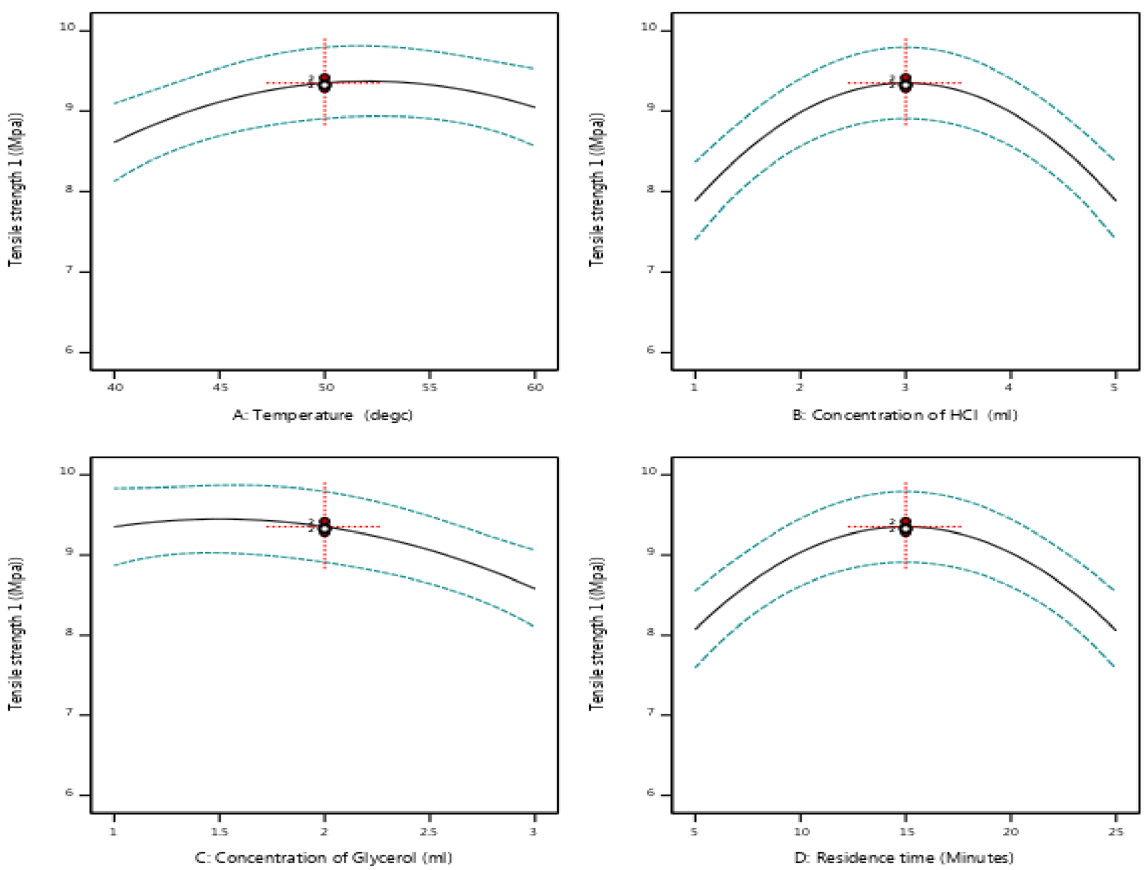


Figure 4-3: Effect of independent parameters on tensile strength

4.2.2 Effect of independent factors on Elongation at break

Elongation at break also known as fracture strain or tensile elongation at break, it is the ratio between increased length and initial length after breakage of the tested specimen at a controlled temperature. In addition to temperature, concentration of glycerol, concentration of HCL and residence time, it also depends on the nature of bioplastics source in this case the fibrous nature (presence of stiffening materials) of banana peel decreases the elasticity of the bioplastic than the other starch based bioplastic because the presences of those stiffening groups in banana peel such as amide which was discovered from the FTIR result in Figure 4-4. The presence of this component decreases the flexibility of the chain which makes the bioplastic to tear up with smaller or no change in its elongation length of the bioplastic as external force or stress is applied. As it can be observed from Figure 4-4, the major effect of the parameter was observed in the temperature and Glycerol concentration. Elongation at break increases with the increases in temperature until it reaches around 52.2 ^{0}C then observed to decrease after the optimum value. Plasticizers in general has a huge effect on elongation at break as it increases the elasticity or decrease its toughness which gives its non-brittle plastic nature leading to increase of elongation at break but as the plasticizer in this case glycerol increases beyond the optimum value, it weakens the intermolecular force in the starch component in the bioplastic which makes it easily affected by external force and tear up easily. The science behind this is as the mobility and flexibility (ease of the chain segment to rotate along the chain backbone) increases with the increase in volume of glycerol, the polymeric chain can move easily. Then the glassy state can be converted to rubbery state. But as the volume of the plasticizer exceeds the rubbery state it gives a liquidity nature to the bioplastic rather than elasticity and that lowers the elongation length at which the plastic tear up as a stress or an external force is applied. The effect of concentration of HCL and residence time is almost constant and both factors have a direct relationship with its elongation at break until they reach around 3ml and 15 minutes, respectively.

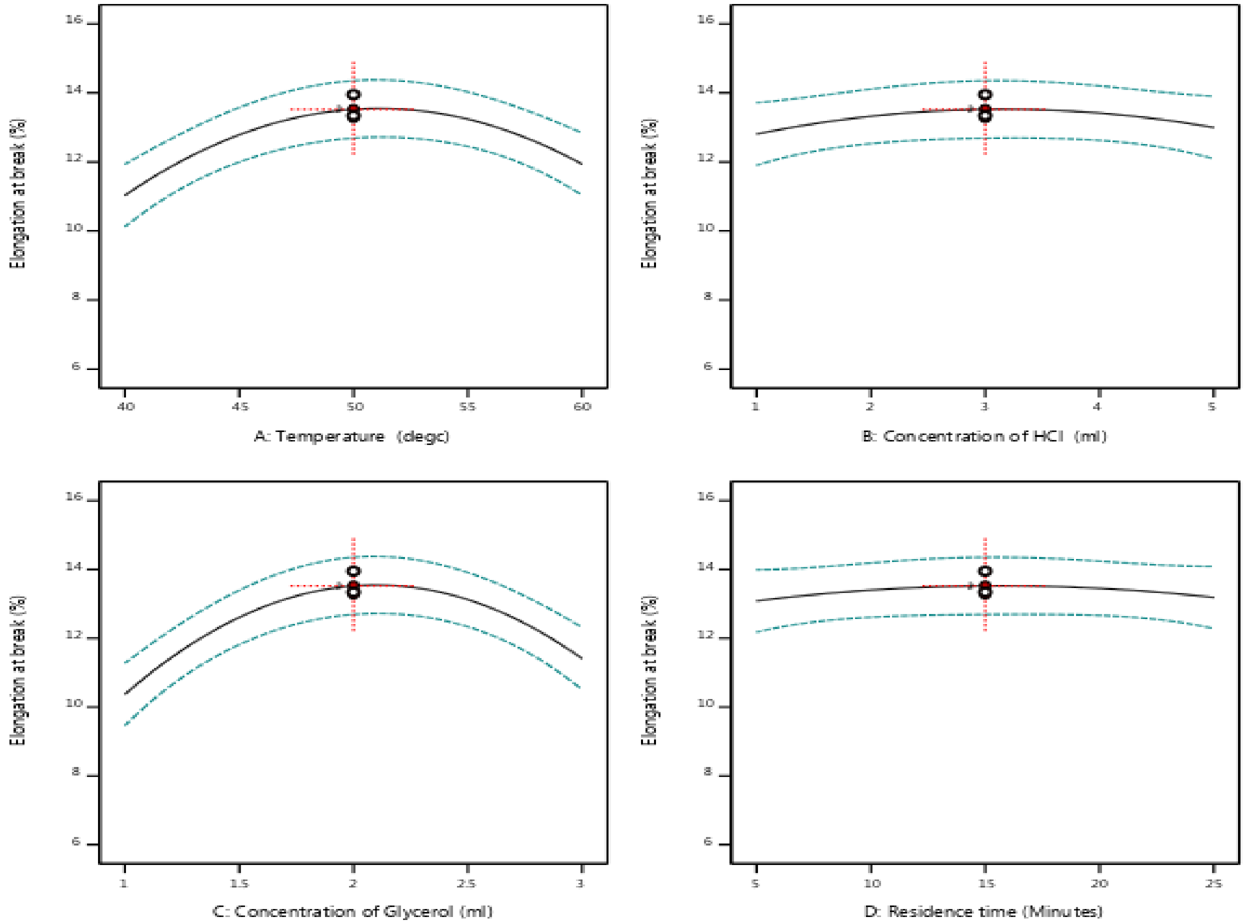


Figure 4-4: Effect of independent parameters on Elongation at break

4.2.3 Effect of independent factors on Water absorption

From the figure 4-5 it is obvious to state, water absorption of the bio-film increases with glycerol concentration. This is due to the hydrophilic behavior of glycerol. As glycerol concentration increases, O-H bonds on the films matrix will be increased. This will in turn increase molecules that interact with water. Similar results were reported by (Assefa, 2013) (Asgar, 2012).

The main factors that affect water absorptions are morphology, fiber fraction and length of exposure As drying temperature increases, the exposure of bioplastic to heat increases and usually results in a rigid, cross-linked starch molecules, with stronger tensile strength and narrow free volume spaces in which the water molecules would have been diffused in to. Therefore the diffusion of the water molecules in to micro voids free volume space of the bioplastic was inhibited by the rigid structure created at higher temperature. A bioplastic with lower water absorption is desired for effective protection against external contamination and degradation of wrapped material by water

Similarly concentration of hydrochloric acid and residence time of hydrolysis affect water absorption of bioplastic. From figure 4-5 and the water absorption decreases with an increase in HCl concentration; this is because of the direct association of the starch swelling capacity (moisture absorption) with amylopectin content due the fact that amylose act as a dilute and inhibitor of swelling (Rantnayake et al., 2002). Therefore more amylopectin converts in to amylose as the concentration of HCl and residence time increases which lead to decrease in water absorption but further hydrolysis decrease the amylose content as it is turned in to glucose and water absorption rises again as there is no amylose content left to inhibit swelling.

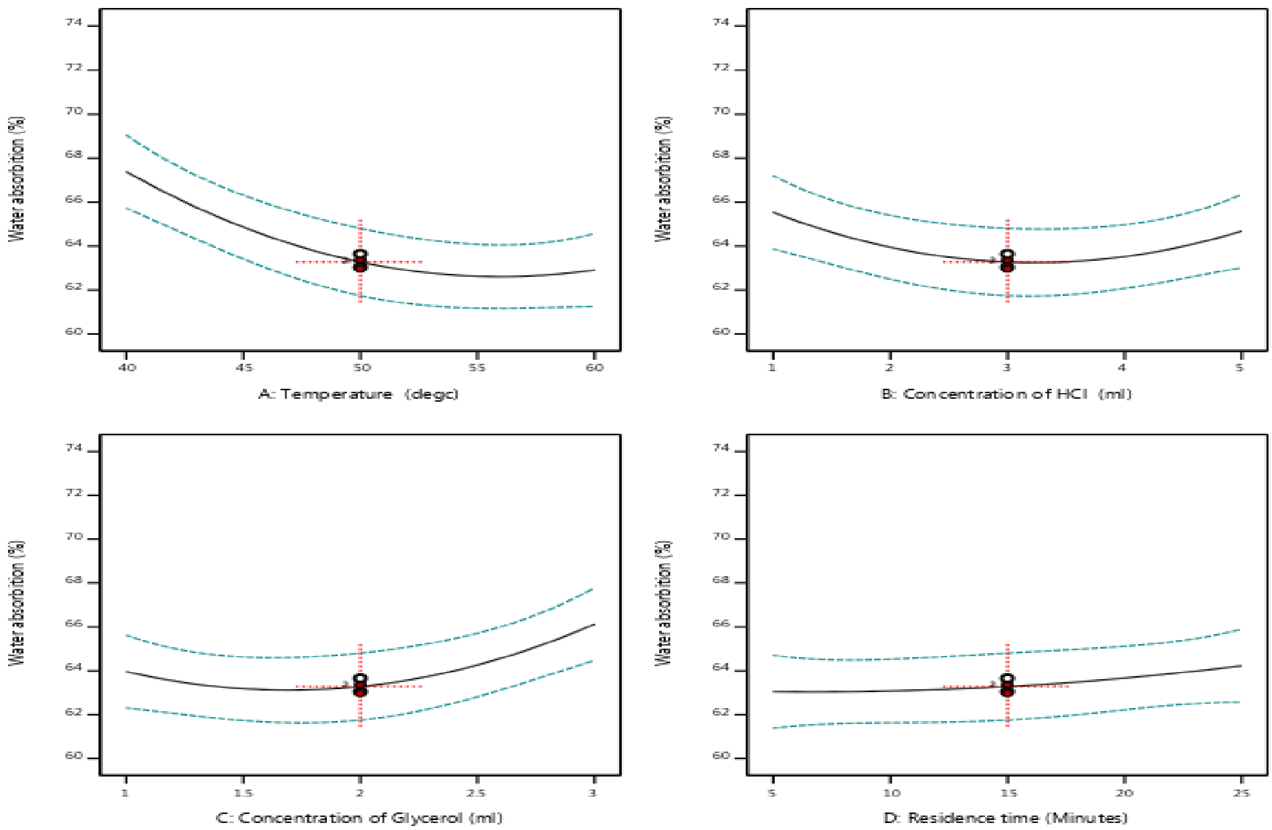


Figure 4-5: Effect of independent parameters on water absorption

4.2.4 Effect of independent factors on Biodegradability

Percent of biodegradability slightly increases as temperature rises from 40^0c to around 50^0c and observed decreasing with slow pace as the temperature increases. In addition to that the effect of temperature on biodegradability is positive as it is described earlier in equation 4.3 therefore biodegradability slightly increase with the temperature until it reaches its optimum point or to the point in which the bioplastic reached its rubbery stage. Then after the optimum temperature the biodegradability decreases due the fact that temperature increases the cross-link and intermolecular force between starch molecules of banana peel.

The effect of glycerol on biodegradability is similar to the other responses as glycerol decrease intermolecular-forces soften the rigidity of the film's structure and increase polymer mobility. This creates a vulnerable material is in agreement with those reported in the literature that show a decrease of Tensile strength values with the presence and increasing concentrations of glycerol plasticizer (Lawton & Fanta, 1993) (Nevena &Vladislava, 2010) (Assefa, 2013) (Asgar & Mahsa, 2012).

As it is shown in figure 4-6 maximum biodegradability is achieved at optimum acid concentration (HCL) residence time where a branched amylopectin is fully hydrolyzed in to a straight chain amylose which is makes it is easier for both film formation and biodegradation of the bioplastics.

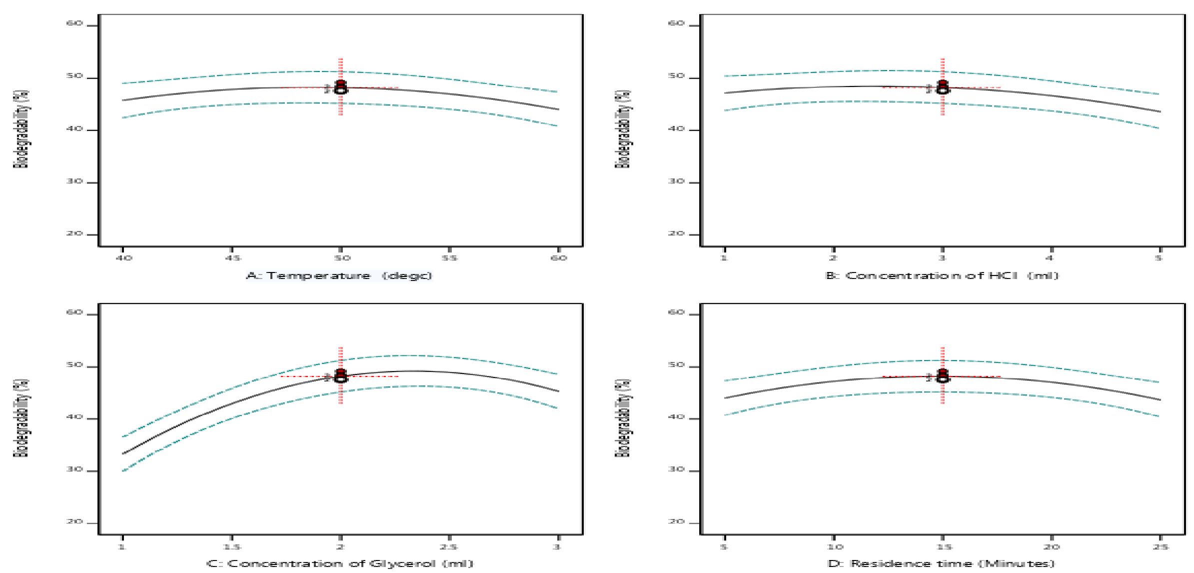


Figure 4-6: Effect of independent parameters on biodegradability

4.3 Interaction effects of factors on Tensile strength, Elongation at break, water absorption and biodegradability

An interaction occurs when the response is different depending on the settings of two factors. They will appear with two non-parallel lines, indicating that the effect of one factor depends on the level of the other.

The interaction response was also significantly affected by two interactive variables at fixed third variable. Three-dimensional (3D) response surface plots (plotted in order to understand the interaction between the variables and the optimum level of each variable).

The significance of the interaction between the corresponding variables was indicated by saddle nature of the contour plots. An interaction occurs when the response was different depending on the setting of two factors. Plots make it easy to interpret two factors interact. They would appear with two non-parallel lines, indicating that the effect of one factor depends on the level of other. If the plotted points fall outside of the range, the differences are unlikely to be caused by error alone and can be attributed to the factor. Therefore, in this study six interaction factors were analyzed by the model equation.

Factors interaction on Tensile strength, elongation at break, water absorption and biodegradability

AB= Temperature * Concentration of HCl

AC= Temperature * Concentration of Glycerol

AD= Temperature * Residence time

BC= Concentration of HCl * Concentration of Glycerol

BD=Concentration of HCl * Residence time

CD=Concentration of Glycerol * Residence time

From figure 4-9 AC (temperature*concentration of Glycerol) was the most significant factor for tensile strength of the produced bioplastic as a response among these six interaction factors, because it has the highest coefficient (+0.8875) of the rest. Therefore, the interaction factors with positive sign have positive effect on tensile strength (as interaction factors increase tensile strength also increase). Whereas, interaction factors with negative signs have a negative effect on tensile strength (as the interaction factors increase the tensile strength of the biofilm decrease).

Similarly as it can be shown in figure 4-17, figure 4-23 and figure 4-29 among the six interaction factors CD (concentration of Glycerol * residence time) has the maximum interaction effect on elongation at break, water absorption and biodegradability of the synthesized bio-film with coefficients of CD (+0.8425), CD (+2.46) and CD (+5.37) respectively.

Interaction factors AB and BC affect tensile strength negatively as it can be observed in figure 4-8 and figure 4-11 And similarly according to figure 4-14, figure 4-20, figure 4-21, figure 4-24, figure 4-16 and figure 4-18 AC (temperature*concentration of Glycerol), AD (Temperature * Residence time), BD (Concentration of HCl * Residence time) has a negative influence on Elongation at break and water absorption in common and AB (temperature*concentration of HCL) has an extra negative effect on Elongation at break. Biodegradability is affected negatively by AD (Temperature * Residence time) and BC Concentration of HCl * Concentration of Glycerol

4.3.1 Interaction effects of the factors on Tensile strength

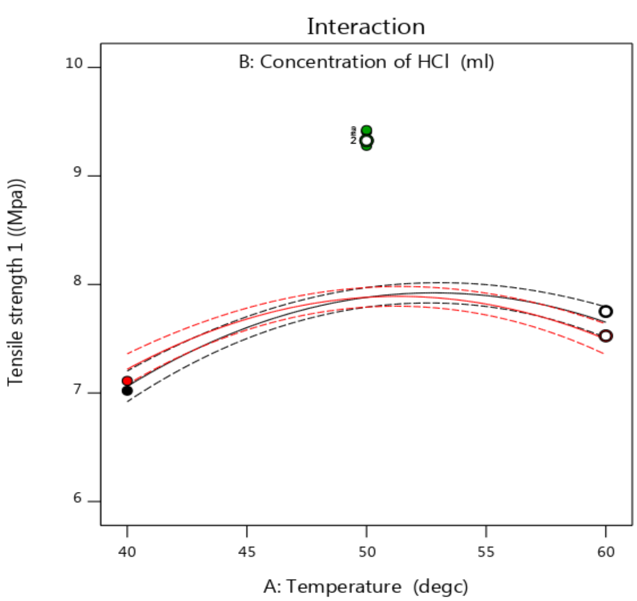


Figure 4-7: interaction effect of AB (Temperature and concentration of HCL acid) on tensile strength

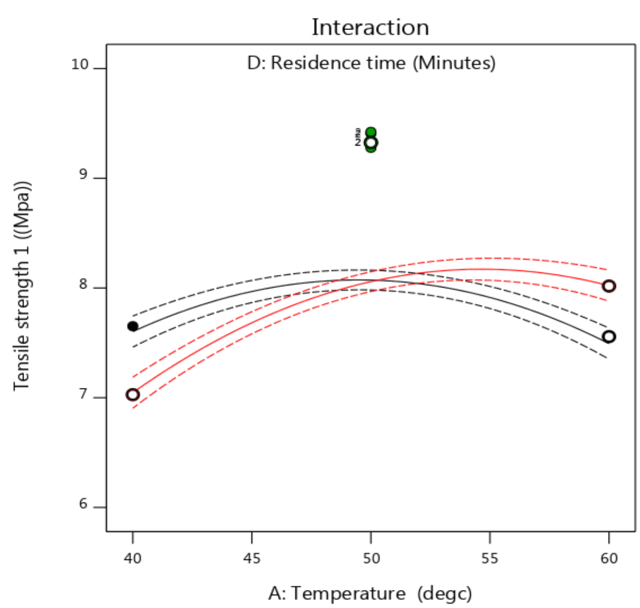


Figure 4-8: Interaction effect of AD (Temperature and Residence time) on tensile strength

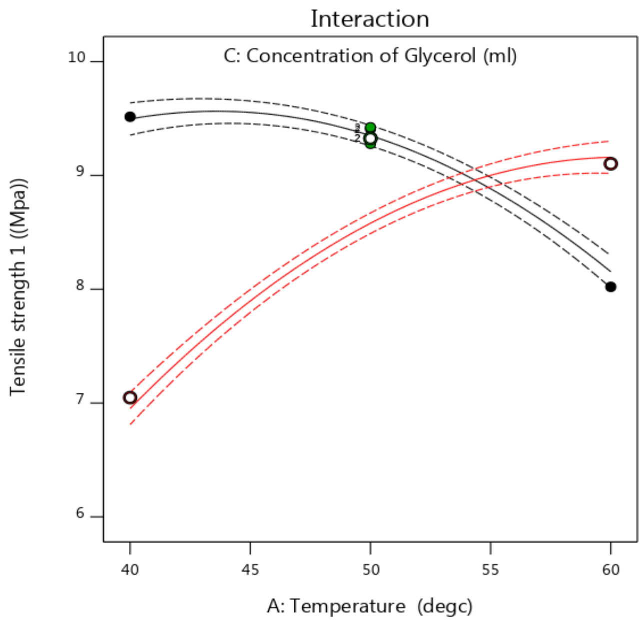


Figure 4-9: Interaction effect of AC (Temperature and concentration of Glycerol) on tensile strength

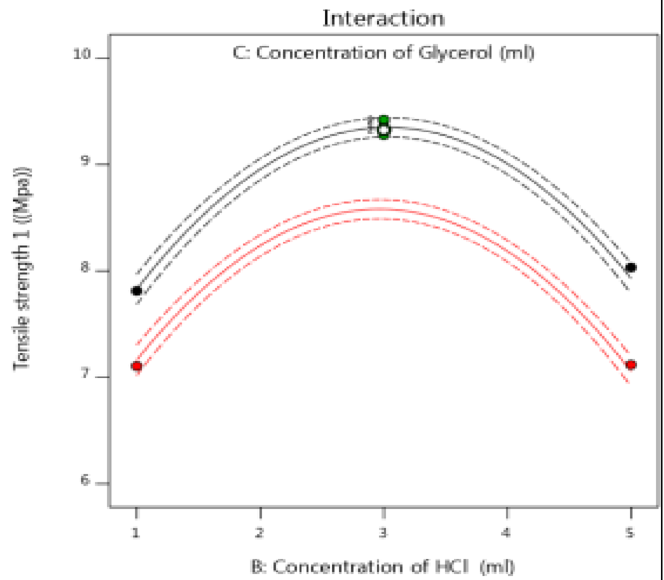


Figure 4-10: Interaction effect of BC (Concentration of HCL and concentration of Glycerol) on tensile strength

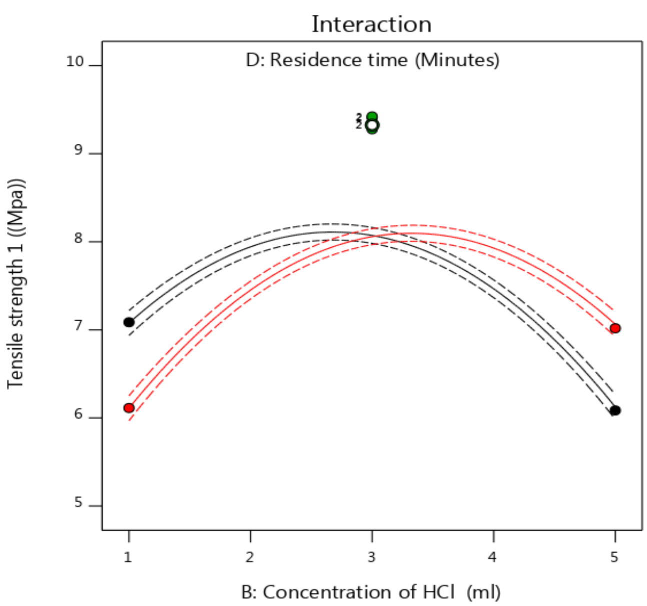


Figure 4-11: Interaction effect of CD (concentration of Glycerol and Residence time) on tensile strength

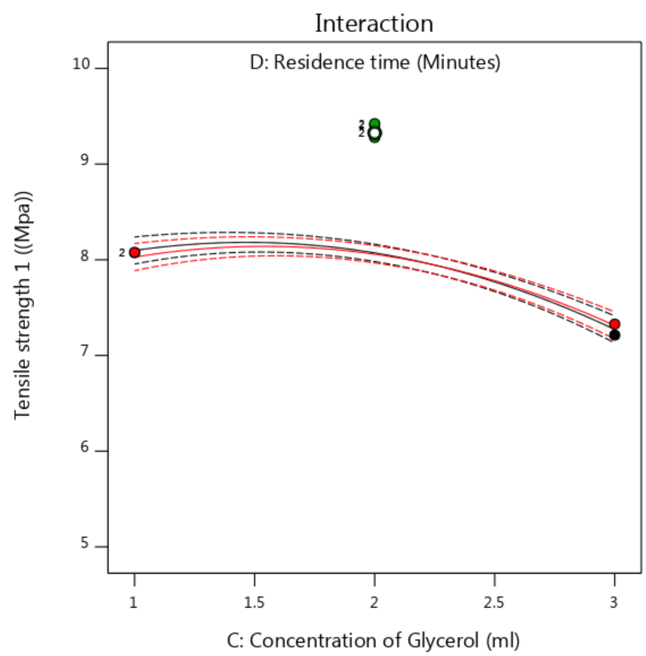


Figure 4-12: Interaction effect of BD (Concentration of HCL and Resistance time) on tensile strength

4.3.2 Interaction effects of the factors on Elongation at break

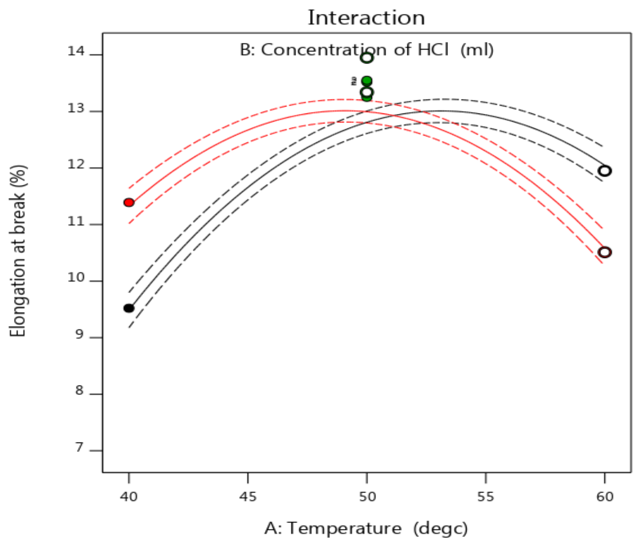


Figure 4-13: Interaction effect of AB (Temperature and concentration of HCL acid) on EB

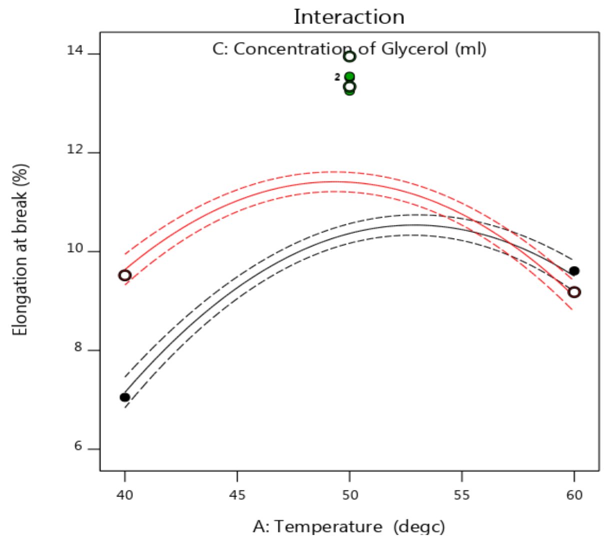


Figure 4-14: Interaction effect of AC (Temperature and concentration of Glycerol) on EB

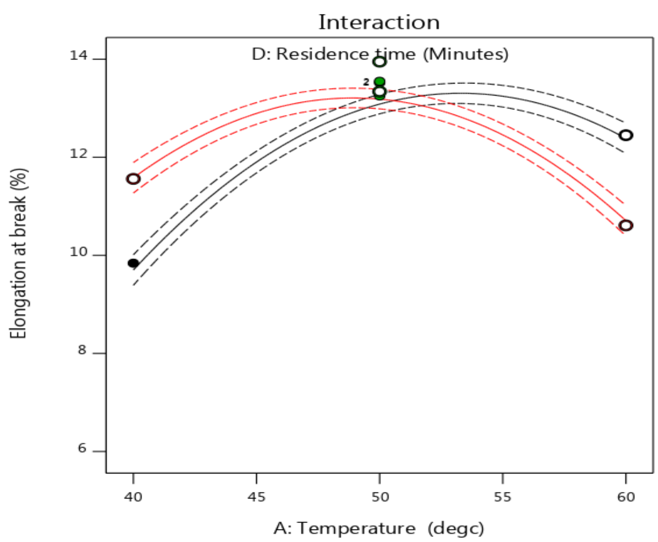


Figure 4-16: Interaction effect of AD (Temperature and Residence time) on EB

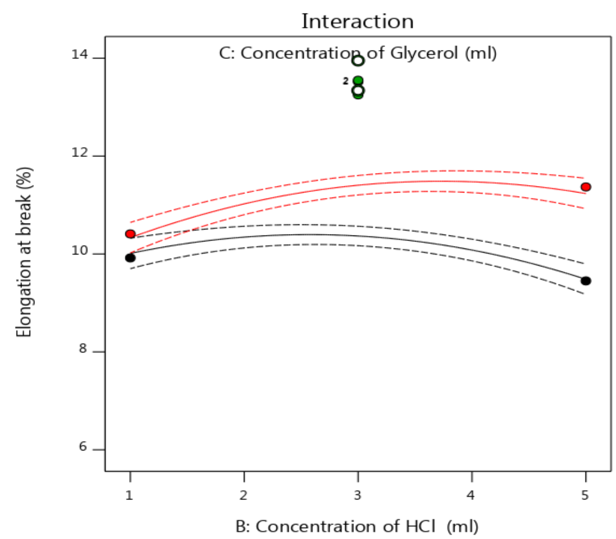


Figure 4-15: Interaction effect of BC (concentration of HCL and concentration of glycerol) on EB

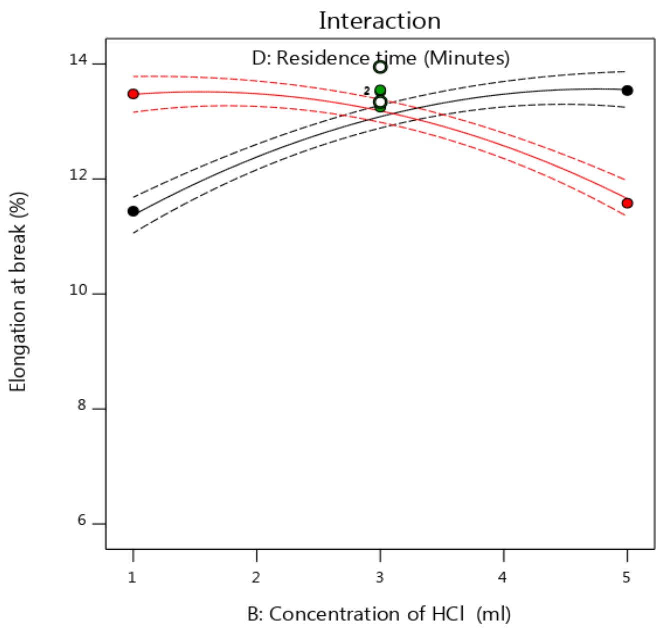


Figure 4-18: Interaction effect of BD (concentration of HCL and Residence time) on EB

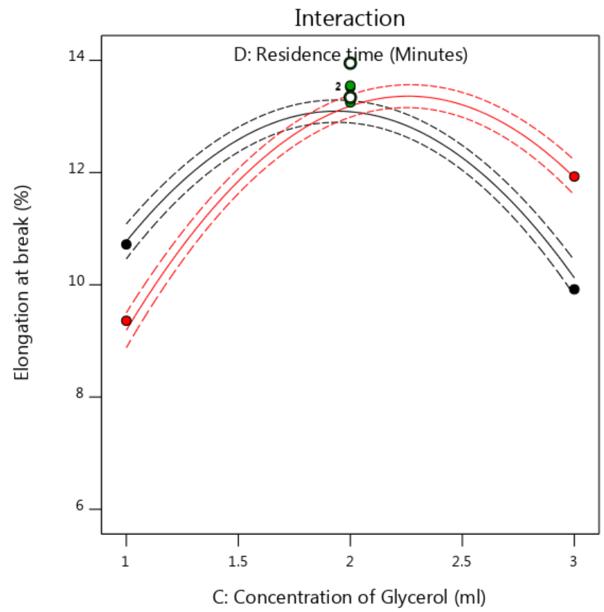


Figure 4-17: Interaction effect of CD (Concentration of Glycerol and Residence time) on EB

4.3.3 Interaction effects of the factors on water absorption

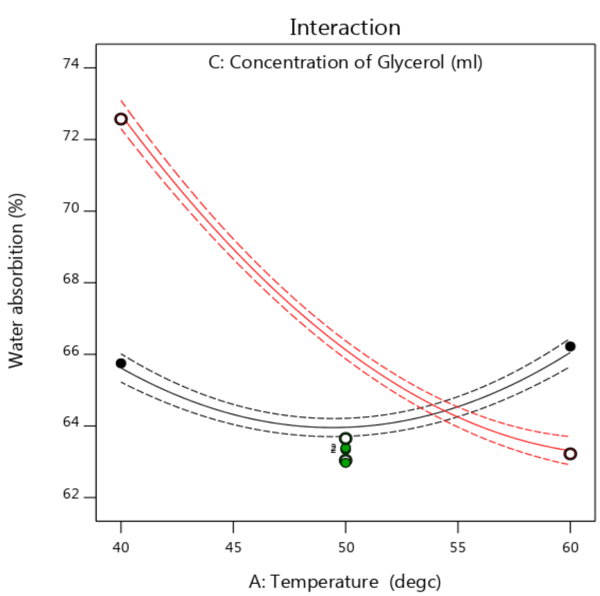


Figure 4-20: Interaction effect of AC (Temperature and concentration of Glycerol) on water absorption

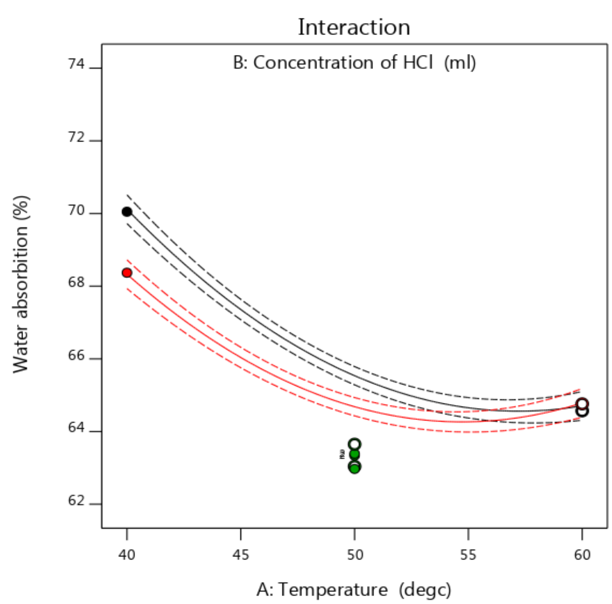


Figure 4-19: Interaction effect of AB (Temperature and concentration of HCL acid) on water absorption

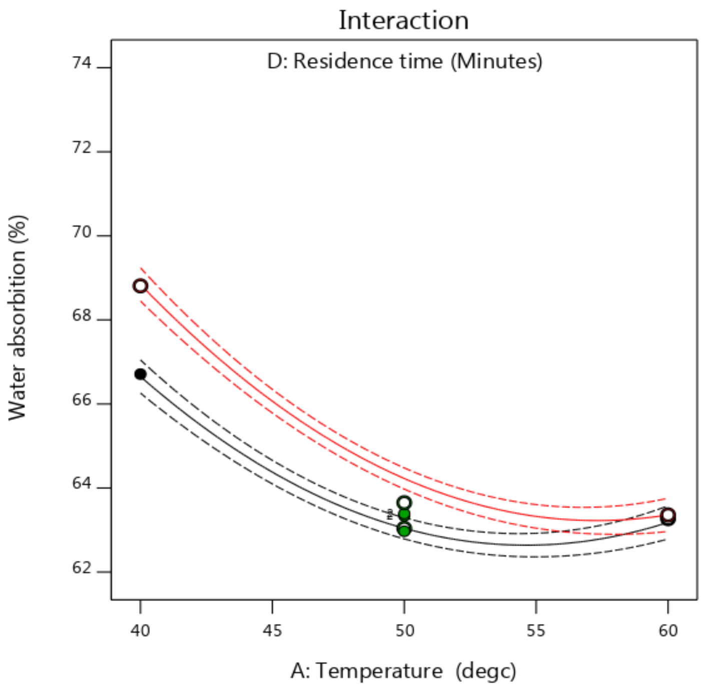


Figure 4-21: Interaction effect of AD (Temperature and Residence time) on water absorption

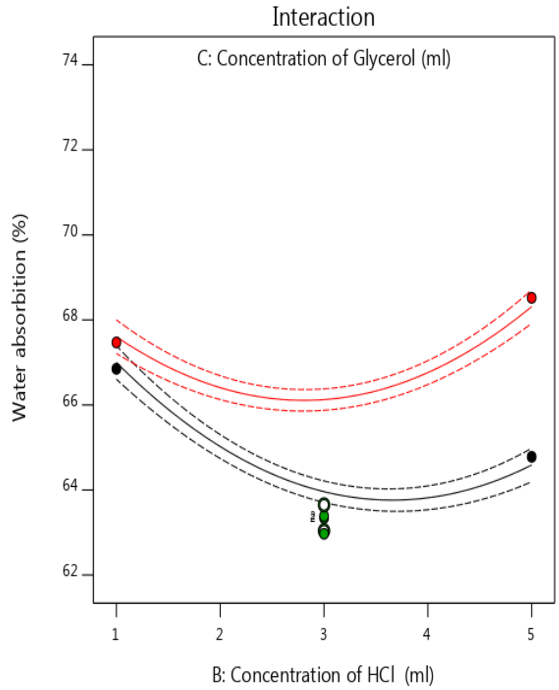


Figure 4-22: Interaction effect of BC (concentration of HCL and concentration of glycerol) on water absorption

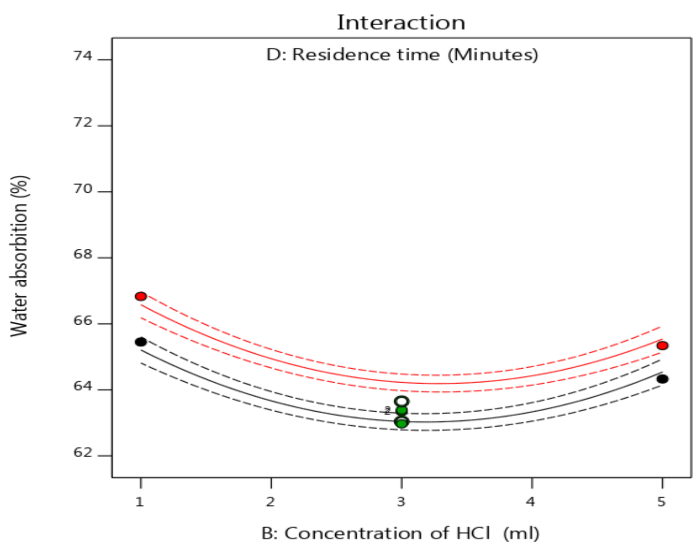


Figure 4-24: Interaction effect of BD (Concentration of HCL and Residence time) on water absorption

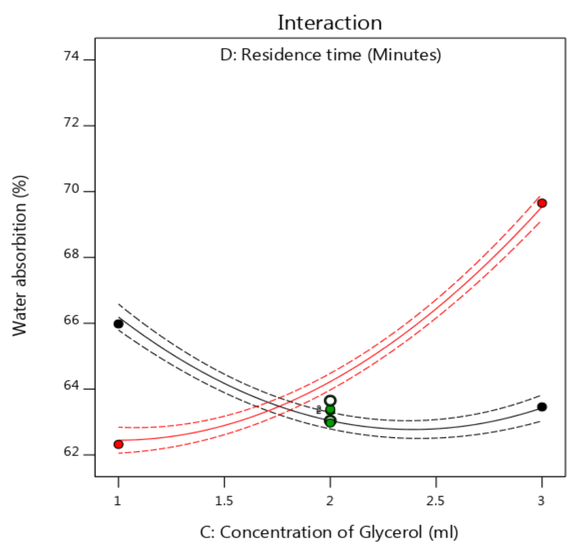


Figure 4-23: Interaction effect of CD (Concentration of Glycerol and Residence time) on water absorption

4.3.4 Interaction effects of the factors on Biodegradability

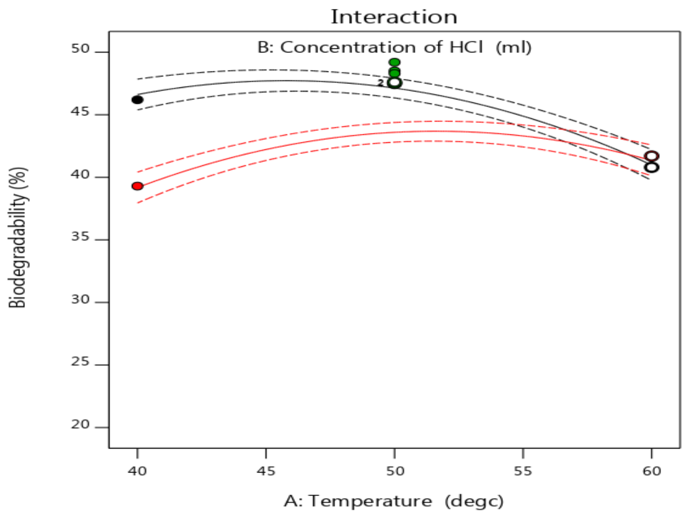


Figure 4-25: Interaction effect of AB (Temperature and concentration of HCL) on Biodegradability

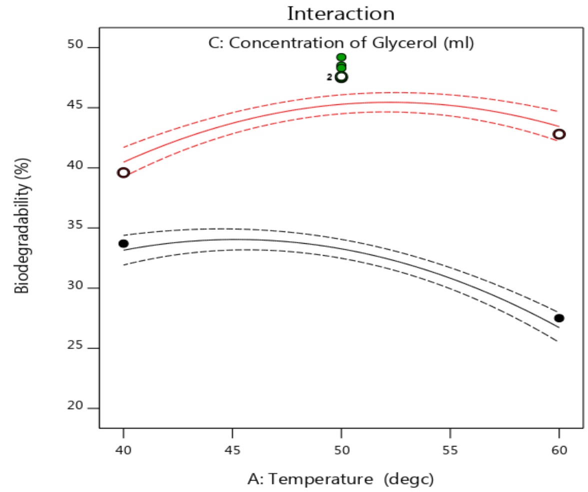


Figure 4-26: Interaction effect of AC (Temperature and concentration of Glycerol) on Biodegradability

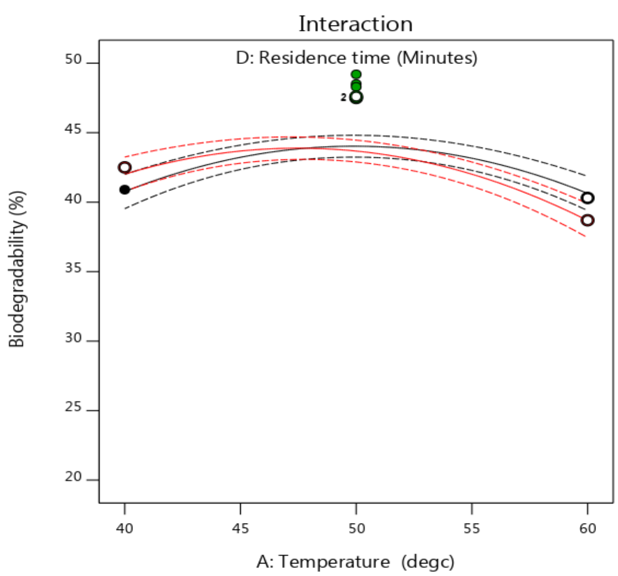


Figure 4-27: Interaction effect of AD (Temperature and Residence time) on Biodegradability

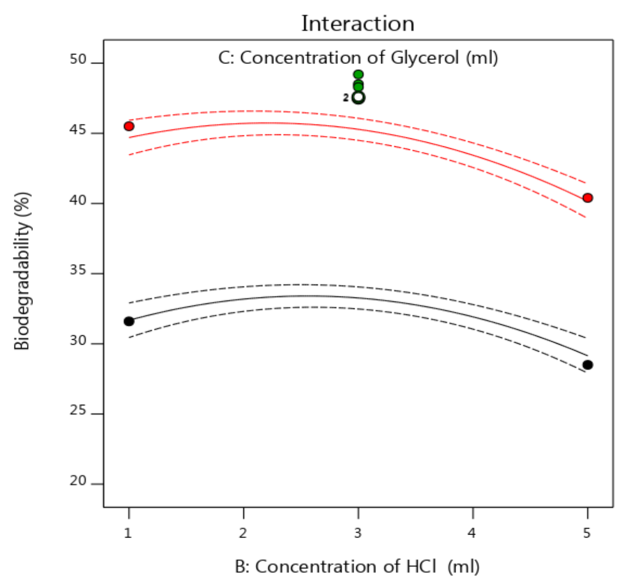


Figure 4-28: Interaction effect of BC (Concentration of HCL and Concentration of glycerol) on Biodegradability

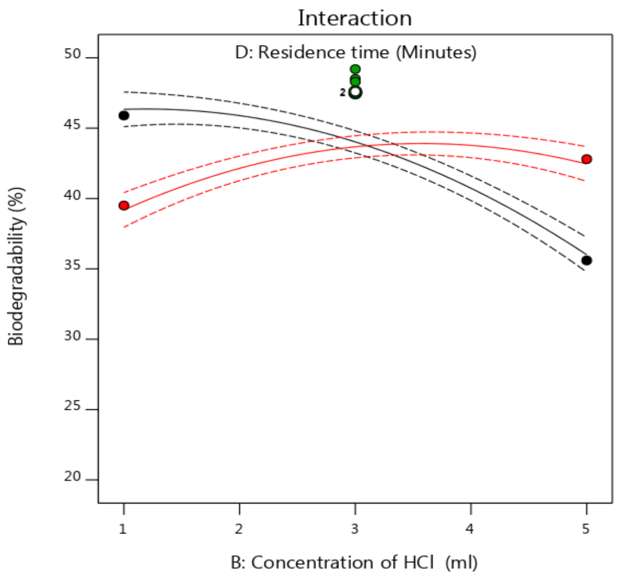


Figure 4-30: Interaction effect of BD (Concentration of HCL and Residence time) on Biodegradability

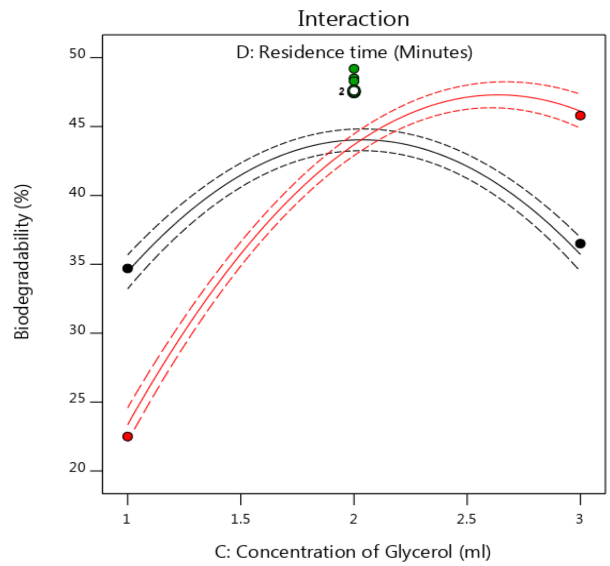


Figure 4-29: Interaction effect of CD (Concentration of Glycerol and Residence time) on Biodegradability

4.4 Effect of $CaCO_3$ on Water absorption of bioplastics (%)

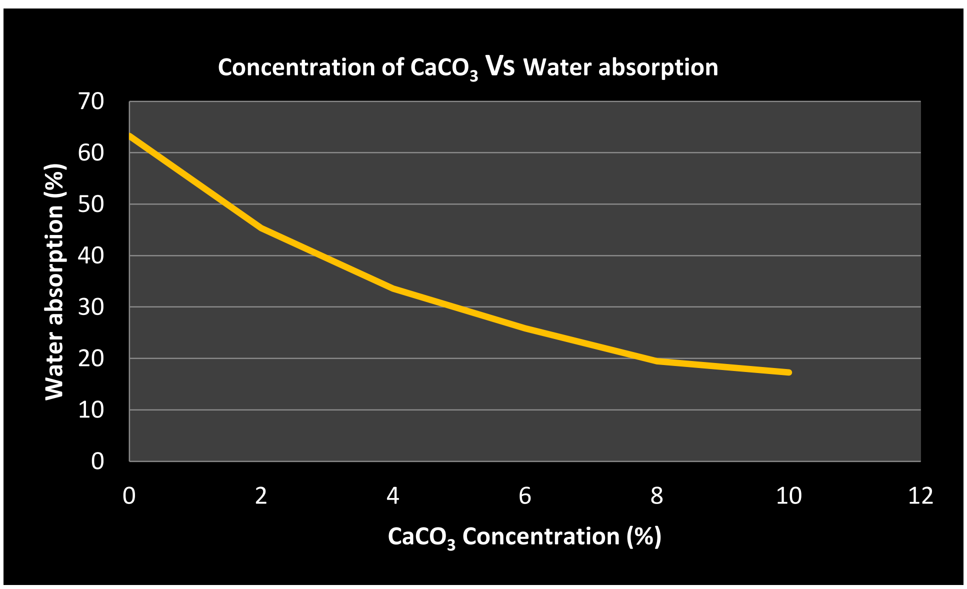


Figure 4-31: Concentration of $CaCO_3$ Vs Water Absorption graph

As it can be observed from figure 4-31 water/moisture absorption of the bioplastic was highly affected by the added $CaCO_3$. With other factors held constant It decreased from 63.25% to 17.27% as the concentration of $CaCO_3$ increases this is because of the hydrophobic nature of the filler which reduces absorption of water vapor in the hydrophilic bioplastics. 10% $CaCO_3$/bioplastics had the lowest (17.27%) moisture absorption. Better distribution throughout the bioplastic/$CaCO_3$ composites and the bonding between matrix and filler also affects the absorption of water vapor.

In general, according to (Penjumras, 2015) there are two mechanisms for diffusion of water in a composite like this. The gap between the matrix and filler can become a pathway of diffusion water or the cracks and weaknesses at the interface of the fiber and the polymer matrix can produce capillary action. Water absorbed into the polymer can be free water or bound water. Free water can move through the micro voids and pores, while bound water molecules disperse in the matrix as they are attached to the polar groups of the polymer.

For lower water absorption it is possible to add the concentration of $CaCO_3$; however, it is more economically feasible if natural fillers such as pineapple leaf fiber, kenaf fiber, water hyacinth fiber, hemp fiber, oil palm empty fruit bunch fiber, palm leaf fiber and sago fiber (Rasat, 2013) were used. And other optional and easily available natural fillers like egg shell can also be used as an alternative source of $CaCO_3$.

4.5 FTIR characterization of the bio-film

Using the optimal parameters, the biofilm was prepared and its functional groups are identified using FTIR. The purpose of the identification of the functional groups is to know the interaction of the ingredients during the production of the biofilms

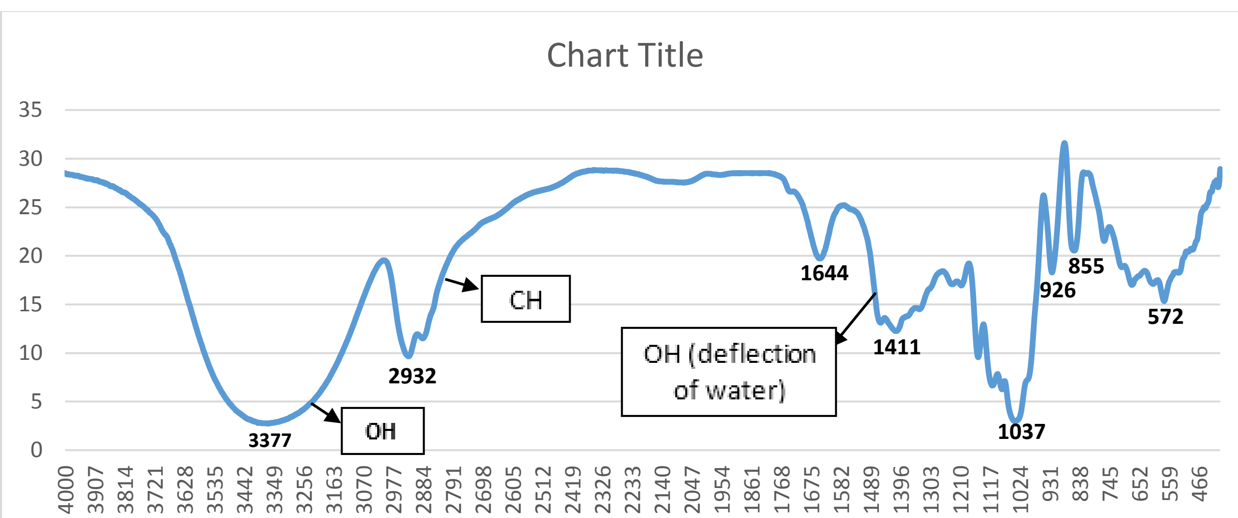


Figure 4-32: FTIR analysis of banana based bioplastics

FTIR spectrum of the synthesized bioplastic is demonstrated in Figure 4-32. In the spectra, it shows band shifting and possible involvement of hydroxyl groups (OH) around the broad intense absorption peaks of 3377 cm^{-1} which represents hydrogen bonded-OH stretch for functional hydroxyl group (O-H) due to the complex vibrational stretching that naturally occurs in the carbohydrate structure. The OH stretching vibrations occur within a broad range of frequencies indicating the presence of free hydroxyl groups and bonded OH bands of carboxylic acids. The peak at 2932cm^{-1} is due to CH stretching asymmetric vibrations of CH groups and the peak at 1411cm^{-1} is due to CH2 and CH3 for functional groups of Alkanes. The peak at 1644cm^{-1} was assigned to the OH group deflection of water which was specifically due to hydroxyl groups bending mode in water molecules. According to (Kizil et al. 2002), the band at 1644 cm^{-1} is a result of water adsorbed in the amorphous region of starch content of the banana peel. This band has the potential to be affected due to crystallinity variations of different starch sources. The peaks obtained at the region below 800 cm-1 attributed to the pyranose ring skeletal vibrations in the glucose unit of starches (Kizil et al. 2002), that might have the peak at 1037 cm^{-1} is due to C-O-H or C-O-R bands. Generally, in bioplastic produced from banana peel, the intense bands seen at 3377, 2932, 1644, 1411, 1037, 926, 855 and 572 cm^{-1} correspond to the O–H/C–O stretching, /C=O/N–H/O–H stretching, /C–O/C=C/C–Hstretching/bending vibrations respectively, and indicate the presence of phenol and alcohols, carboxylic group, amines, amides, ketones, ester, ether, amino acid and aromatic group in OP (Pranav, 2017.) The advantage of knowing the fictional groups of the components in the banana peel based bioplastic was to understand the causes of certain effects of the process variables on the quality of the bioplastic. For example the polymer melting point and Glass Transition Temperature are dependent on the presence of double bonds, aromatic groups, bulky or large side groups in the polymer chain in addition to the effect of the process variable, because those components restrict the flexibility of the chain. In addition to that the presence of stiffening group such as amide, carbonyl in the polymer chain reduces flexibility as they increase the cross-linkage of starch molecules. Therefore knowing the components of the banana peel based bioplastic uses to fully understand why a selected process parameter is behaving in a certain way and its effects on the quality.

4.6 Optimal of process variables

As it is shown in table 4-7 a numerical response optimization technique was adopted to determine the optimum workable conditions for banana based biofilms synthesis. The main criterion for constrained optimization were minimum possible water absorption, and maximum possible tensile strength, elongation at break and biodegradability keeping the factor values in range drying Temperature (40-60 ^{0}c), HCl acid concentration (1-5 ml/25 g banana peel), glycerol concentration (1 to 3/25 g banana peel), hydrolysis residence time (5-15 minutes)

Table 4-7: Constraints for the optimization

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:Temperature	is in range	40	60	1	1	3
B:Concentration of HCl	is in range	1	5	1	1	3
C:Concentration of Glycerol	is in range	1	3	1	1	3
D:Residence time	is in range	5	25	1	1	3
Tensile strength 1	maximize	6.085	9.516	1	1	3
Elongation at break	maximize	7.05	13.95	1	1	3
Water Absorption	minimize	62.32	72.57	1	1	3
Biodegradability	maximize	22.5	49.2	1	1	3

The numerical optimization is reported the parameters, and the process variables are optimized, 23 solutions were found. As it is presented on Table 4-8 the numerical optimization resulted in 23 solutions but for further analysis of the film the average of the twenty three solutions was taken. The average values of the 4 factors were drying temperature (**52.424** ^{o}C), Glycerol concentration **(8.384%v/w**), hydrochloric acid concentration (**11.748%v/w**), and hydrolysis residence time (**14.501minutes**) which provides tensile strength (**9.348**),Elongation at break of (**13.524)** water absorption (**62.883**) and biodegradability (**48.389**) as an optimum response.

Table 4-8: Numerical optimization solutions

Number	Temperature (^{0}c)	Concentration of HCl	Concentration of Glycerol	Residence time	Tensile strength	Elongation at a break	Water Absorption	Biodegradability	Desirability	
1	52.424	2.937	2.096	14.501	9.348	13.524	62.883	48.389	0.951	Selected
2	52.372	2.937	2.096	14.047	9.345	13.521	62.878	48.382	0.951	
3	52.379	2.937	2.126	14.191	9.347	13.523	62.870	48.413	0.951	
4	52.436	2.935	2.123	14.154	9.348	13.523	62.879	48.413	0.951	
5	52.366	2.935	2.106	14.140	9.348	13.524	62.881	48.440	0.950	
6	52.279	2.939	2.144	14.296	9.348	13.524	62.873	48.389	0.951	
7	52.462	2.939	2.055	14.250	9.345	13.524	62.886	48.389	0.951	
8	52.264	2.939	2.063	14.568	9.348	13.524	62.886	48.389	0.951	
9	52.475	2.938	2.069	14.580	9.346	13.529	62.881	48.389	0.951	
10	52.437	2.939	2.078	14.550	9.344	13.524	62.880	48.365	0.952	
11	52.385	2.939	2.058	14.977	9.348	13.524	62.870	48.428	0.952	
12	52.196	2.932	2.091	14.986	9.349	13.524	62.849	48.432	0.951	
13	52.314	2.937	2.092	14.742	9.349	13.522	62.871	48.389	0.951	
14	52.318	2.937	2.090	14.513	9.349	13.524	62.874	48.473	0.951	
15	52.546	2.935	2.090	14.351	9.349	13.528	62.886	48.389	0.951	
16	52.566	2.935	2.084	14.235	9.348	13.524	62.889	48.389	0.951	
17	52.502	2.935	2.096	14.507	9.348	13.524	62.886	48.315	0.952	
18	52.517	2.937	2.096	14.146	9.348	13.525	62.871	48.389	0.952	
19	52.333	2.937	2.096	14.597	9.348	13.522	62.872	48.264	0.951	
20	52.198	2.933	2.096	14.447	9.347	13.522	62.884	48.389	0.951	
21	52.454	2.931	2.156	14.448	9.348	13.523	62.888	48.389	0.950	
22	52.879	2.934	2.176	14.967	9.347	13.523	62.871	48.508	0.950	
23	53.114	2.931	2.096	14.709	9.348	13.526	62.876	48.389	0.950	

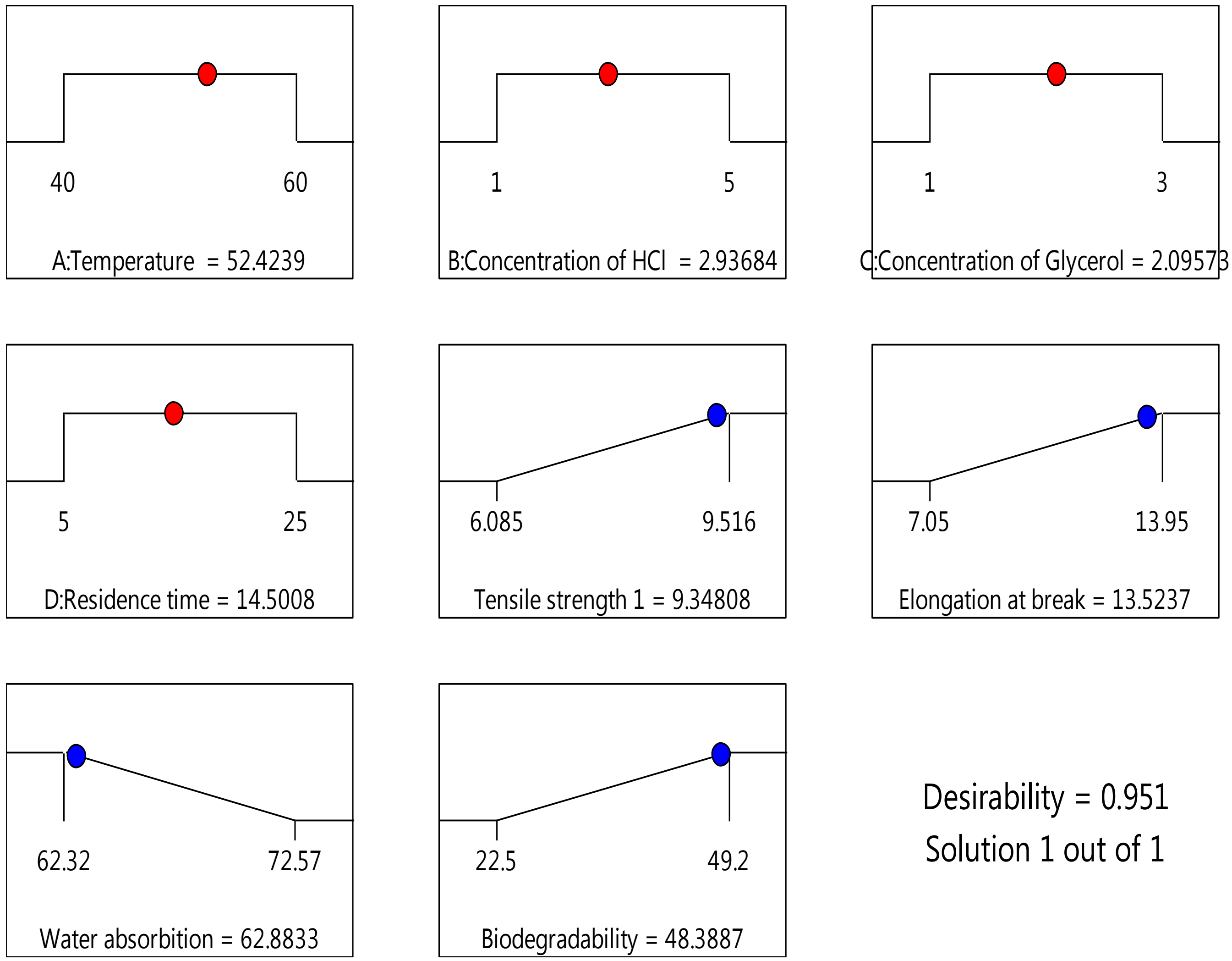


Figure 4-33: Numerical Optimization Ramps

Figure 4-34 shows the optimal factor settlings are indicated with red points and optimal response prediction values are displayed in blue. A desirability of 1.00 means the goals were easy to reach and better results may be available. The optimum values with relatively closer desirability (95.1%) and the one which meets best with desired criteria was selected out of the 23 solutions. the main goal of optimization is to find a good set of process conditions (parameters) that meets all the goals and give off enhanced results. Accordingly a bioplastic with tensile strength of 9.348 MPA, 13.524% Elongation at break, 62.883% water absorption and 48.389% biodegradability could be obtained a Temperature of 52.424 ^{o}C, Glycerol concentration (8.384%v/w), hydrochloric acid concentration (11.748%v/w), and hydrolysis residence time (14.501minutes).

Chapter Five

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this study, a bioplastic from banana peel was synthesized by varying the operating conditions (drying temperature, concentration of HCL and glycerol and residence time for hydrolysis) in order to obtain good quality bioplastic with optimum biodegradability, physical and mechanical property. From the achieved result it is safe to say the objectives stated earlier in the project almost met the results except the water absorption which was letter improved by adding calcium carbonate as filler.

A three-variable, three-level box Behnken design was used to study the simultaneous effect of process variables. A statistically significant model ($p<0.0001$ for all factors) was developed to describe the relationship between the tensile strength, water absorption, biodegradability and the chosen independent variables.

The bioplastic production conditions were optimized using response surface methodology and the statistical model showed a good fit with the experimental data (R^2 = 0.9962, R^2=0.9940, R^2 = 0.9955, R2=0.9938) for tensile strength, elongation at break, water absorption and biodegradability respectively with a low standard deviation. From the results, it was observed that, the process conditions have significant effects on the physical and mechanical property of the produced bioplastic. ANOVA showed that the effects of all variables were significant and quadratic models were developed for predicting the responses.

Optimal values of process conditions which gave maximum tensile strength, elongation at break and biodegradability and minimum water absorption were selected using numerical optimization of design expert. Based on the experimental result obtained, the interaction effect has significant effect on the responses. The optimum result was obtained after conducting the experiment at selected optimum condition which are drying temperature (52.424), Glycerol concentration (8.384%v/w), hydrochloric acid concentration(11.748%v/w), and hydrolysis residence time (14.501 minutes) with a high value of combined desirability (0.951). These values were selected from 23 alternative optimal solutions set by design expert, based on considerations and compromise of mechanical and physical quality of the bioplastic.

FTIR analyzed the functional groups of the synthesized bioplastic and biodegradability of the synthesized bioplastic has been measured for 30 days for each sample at different process variables.

After assessing the results of the prior experiments, an additional experiment was held to improve the water/moisture absorption using a $CaCO_3$ as filler and an effective improvement was observed in which the water/moisture absorption decreased by 27.30% From the filler free bioplastic keeping all the other parameters at the optimum value.

Generally from this study it was observed that fair quality bioplastic can be prepared from a material which is discarded as a waste material (banana peel) and banana peel obtain a fiber nature (presence of amide groups) as it was observed from the FTIR result and has relatively a lower water/moisture absorption than the other starch based bioplastics such as corn and cassava starch based bioplastics but it still needs an additional filler for better quality and wide range of applications, it can possibly be used in food and beverage packaging with the help of further studies in addition to the dry material packaging such as dry fruit packaging and plastic shopping bags. Therefore different natural and chemical fillers such as $CaCO_3$, $BaSO_4$, kaolin and quartz can be used to improve the bioplastics property with further studies and experiments on means of improving the quality this raw material is an ideal sustainable synthesis of bioplastics in the future.

5.2. Recommendation

Further Research can be carried out for better understanding of the Process and thereby improving the quality of the Product. Other commonly available starch sources can be explored. Food wastes like mango seeds and corn kernels also have high starch content. Hence these can also be utilized as a raw material for synthesis of polymeric films.

Varying the concentration of the reagents might alter the properties of the polymeric films obtained. Synthesis of polymeric films can also be carried out after extraction of starch from banana peels instead of processing it as a whole to see if it improves the polymeric properties. The banana peels consists of many different components apart from starch. Currently only the reaction with starch has been considered. The interaction of all the other components with the reagents may also have an effect which must also be quantified.

In this research work it was attempted to show that $CaCO_3$ filler has the ability to improve the water/moisture absorption briefly but further it can be studied using alternative natural fibers and their corresponding effects on the property of bioplastics other than water absorption. Different waste based sources of $CaCO_3$ can also be used as alternative methods to improve the quality of the synthesized such as egg shell. In addition to that from visual observation the stiffness of the modified bioplastic increased a little bit and appeared losing some of its elasticity than before. Therefore further studies could be carried out on evaluating an optimum concentration of filler content for packaging bioplastics and the effects of using filler on other properties of the bioplastics such as elongation at break.

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APPENDICES

Appendix A: Experimental results of measurements

Appendix A1: Experimental results to measure film's water absorption

	Wi(g)	Wf(g)	Water Absorption (%) WA=Wf-WI*100% / Wi
1	0.089	0.1513	70.05
2	0.076	0.125	64.57
3	0.088	0.147	68.37
4	0.073	0.120	64.76
5	0.091	0.151	65.98
6	0.086	0.195	63.46
7	0.0810	0.1315	62.32
8	0.079	0.134	69.65
9	0.093	0.153	66.71
10	0.091	0.148	63.27
11	0.081	0.136	68.81
12	0.072	0.117	63.36
13	0.087	0.145	66.85
14	0.096	0.157	63.78
15	0.094	0.158	68.47
16	0.076	0.128	68.52
17	0.075	0.124	65.75
18	0.063	0.102	63.22
19	0.077	0.132	72.57
20	0.084	0.137	63.89
21	0.081	0.134	65.45
22	0.079	0.129	64.33
23	0.083	0.138	66.83
24	0.080	0.132	65.34
25	0.075	0.122	63.34
26	0.068	0.111	64.04
27	0.059	0.096	62.97
28	0.098	0.160	63.39
29	0.088	0.144	63.65

Appendix A2: Experimental results to measure film's water absorption of modified BP

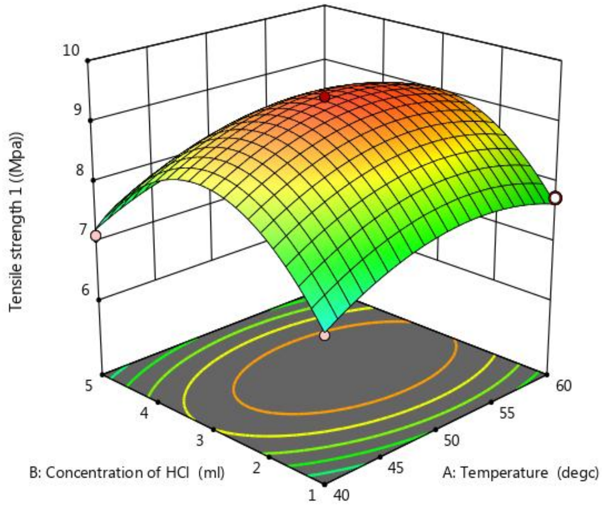
Concentration of $CaCO_3$	Wi(g)	Wf(g)	Water Absorption (%) WA=Wf-WI*100% / Wi
0%	0.08248	0.1346	63.25
2%	0.08413	0.1223	45.32
4%	0.08577	0.1146	33.58
6%	0.08762	0.1102	25.83
8%	0.08917	0.1065	19.47
10%	0.09082	0.1065	17.27

Appendix A3: Experimental result data for measuring films biodegradability

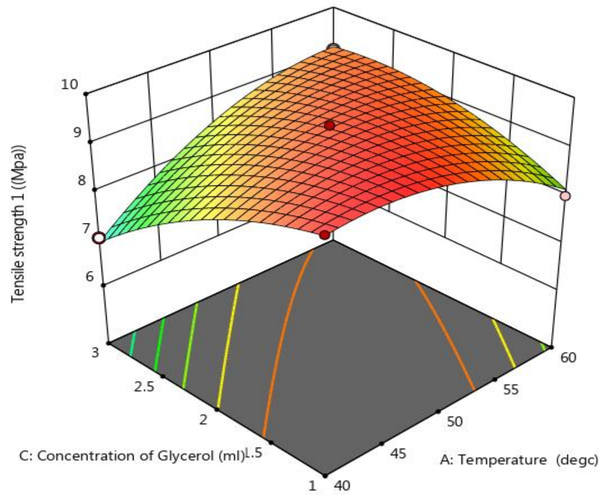
	Initial mass(g)	Final mass(g)	Microbial resistance (biodegradability) (%)= Mi-Mf*100 / Mi
1	0.053	0.028	46.2
2	0.049	0.029	40.8
3	0.058	0.035	39.3
4	0.042	0.026	41.7
5	0.057	0.036	36.7
6	0.044	0.028	36.5
7	0.055	0.042	22.5
8	0.047	0.025	45.8
9	0.041	0.024	40.9
10	0.058	0.034	40.3
11	0.052	0.021	42.5
12	0.048	0.029	38.7
13	0.046	0.031	31.6
14	0.053	0.037	28.5
15	0.041	0.022	45.5
16	0.050	0.028	42.4
17	0.053	0.034	35.7
18	0.058	0.041	28.5
19	0.045	0.027	39.6
20	0.048	0.027	43.8
21	0.057	0.030	45.9
22	0.049	0.031	35.6
23	0.044	0.026	39.5
24	0.048	0.027	42.8
25	0.056	0.028	49.2
26	0.051	0.026	47.5
27	0.043	0.023	46.5
28	0.052	0.026	48.3
29	0.056	0.028	49.6

Appendix B: 3D representation of effect of interactions on responses

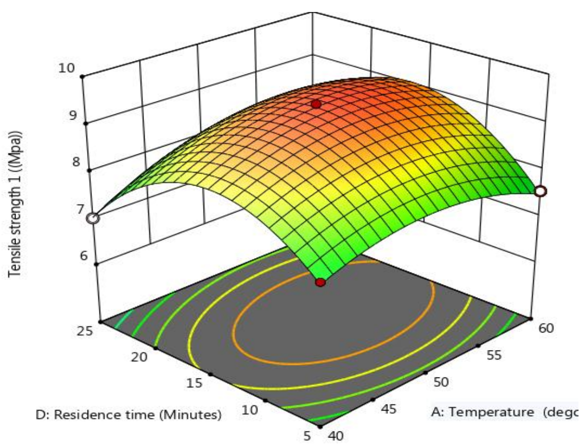
Appendix B1: 3D representation of interaction effect on tensile strength



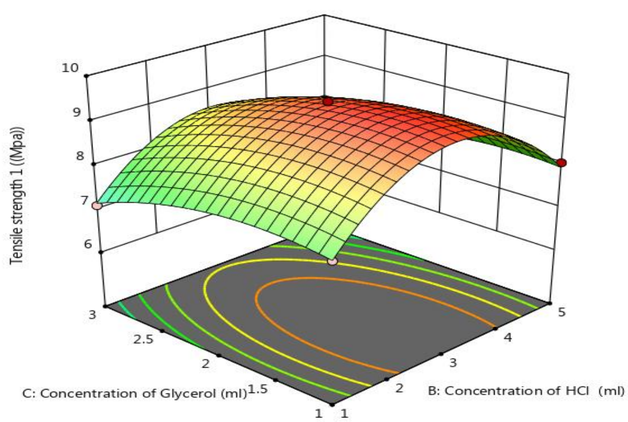
AB (Temperature and concentration of HCL)



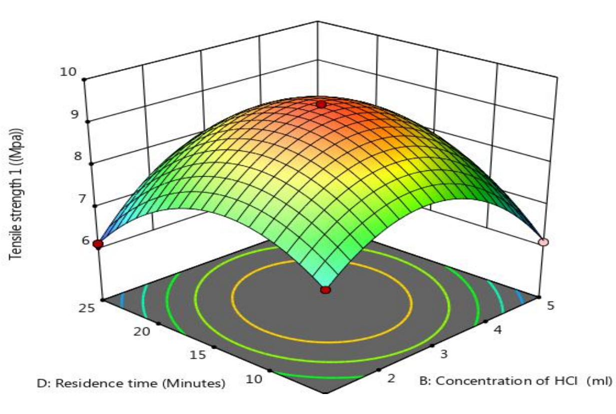
AC (Temperature and concentration of Glycerol)



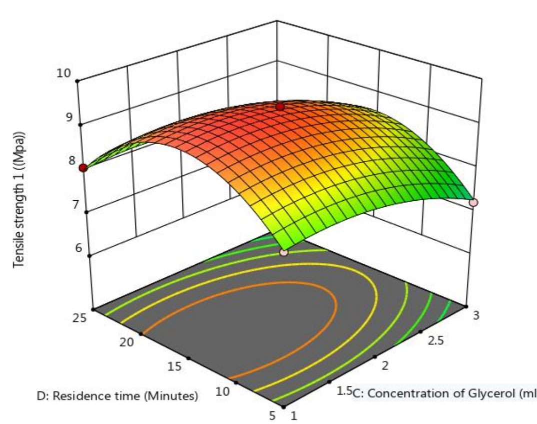
AD (Temperature and Residence time)



BC (concentration of HCl and concentration of Glycerol)

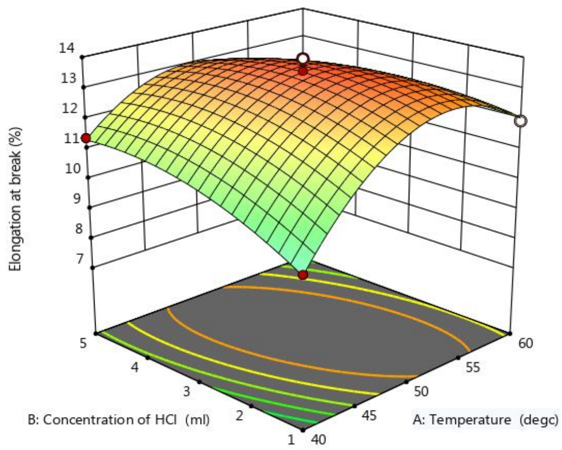


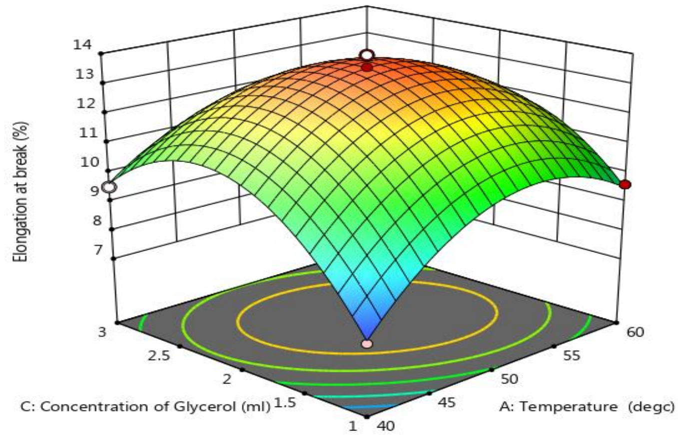
BD (Concentration of HCl and Residence Time)



CD (Concentration of Glycerol and Residence Time)

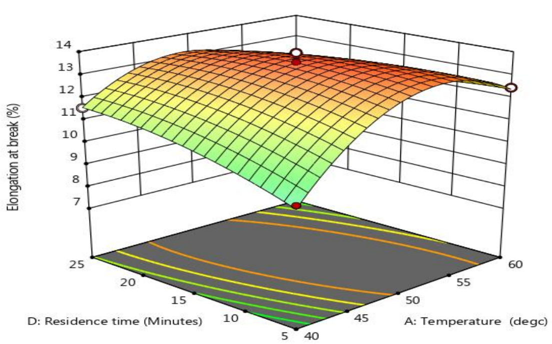
Appendix B2: 3D representation of interaction effect on Elongation at break

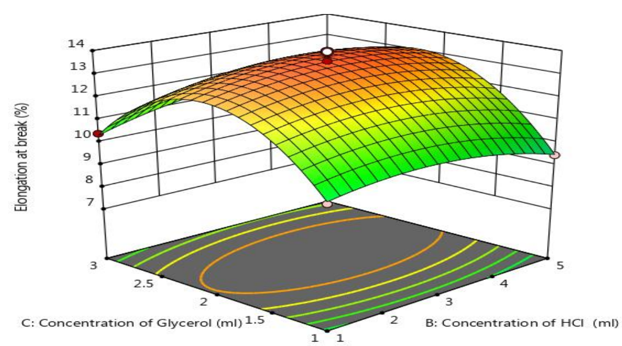




AD (Temperature and Residence time)

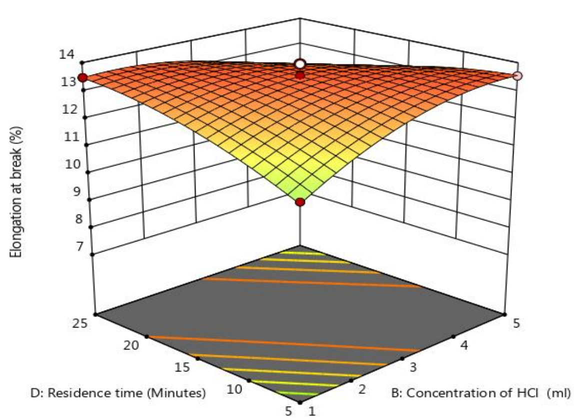
BC (concentration of HCl and concentration of Glycerol)

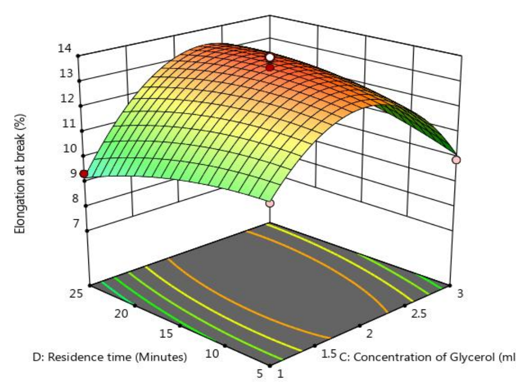




AB (Temperature and concentration of HCL)

AC (Temperature and concentration of Glycerol)

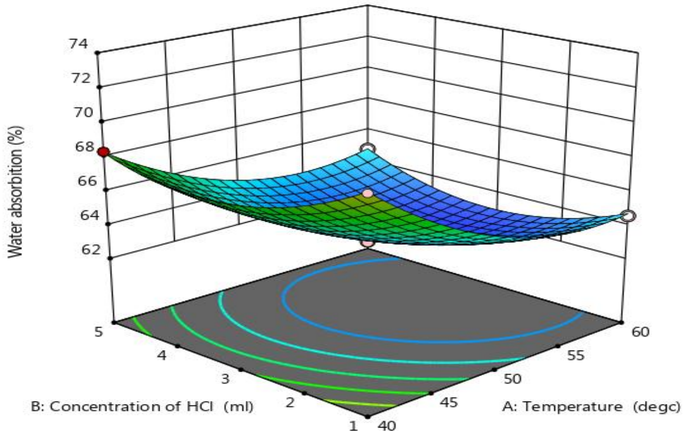




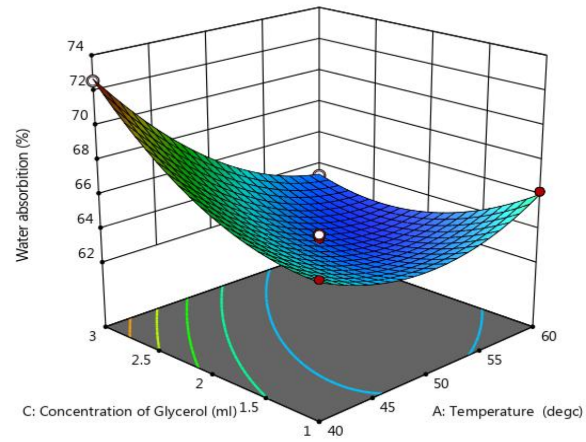
BD (Concentration of HCl and Residence Time)

CD (Concentration of Glycerol and Residence Time)

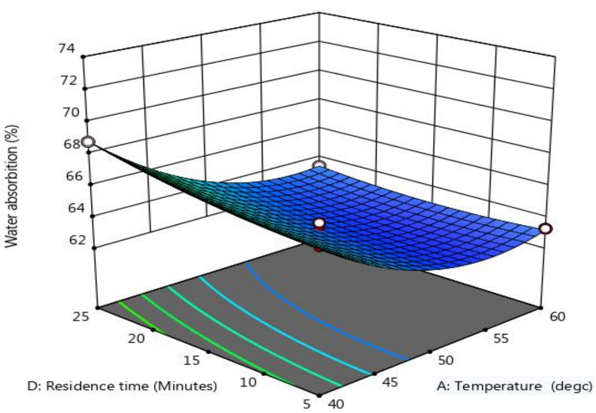
Appendix B3: 3D representation of interaction effect on Water absorption



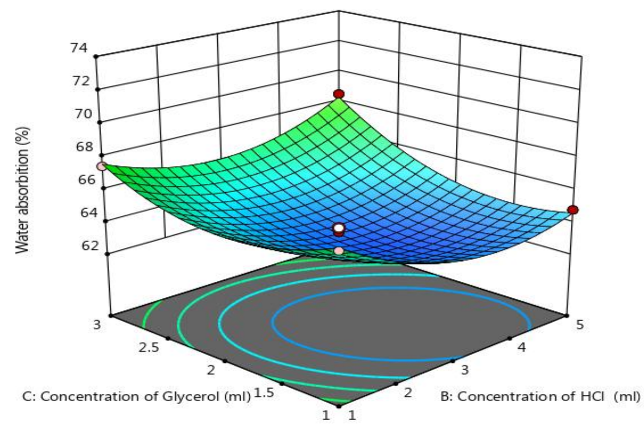
AB (Temperature and concentration of HCL)



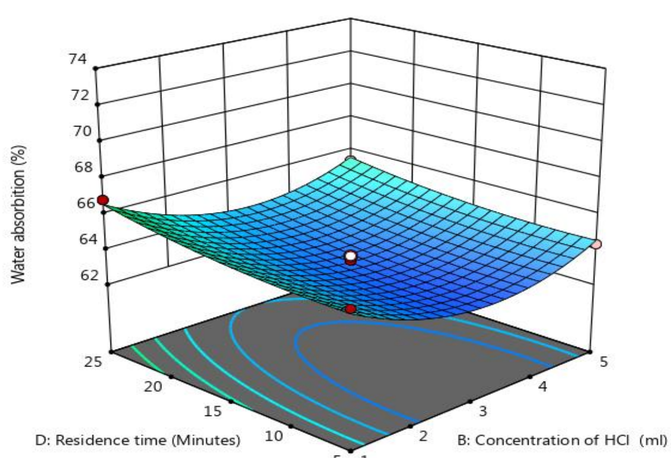
AC (Temperature and concentration of Glycerol)



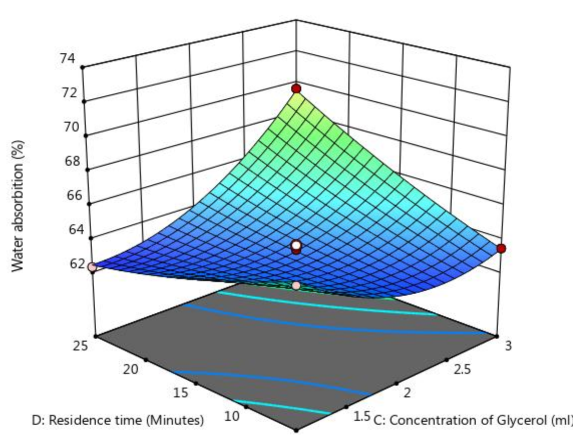
AD (Temperature and Residence time)



BC (concentration of HCl and concentration of Glycerol)

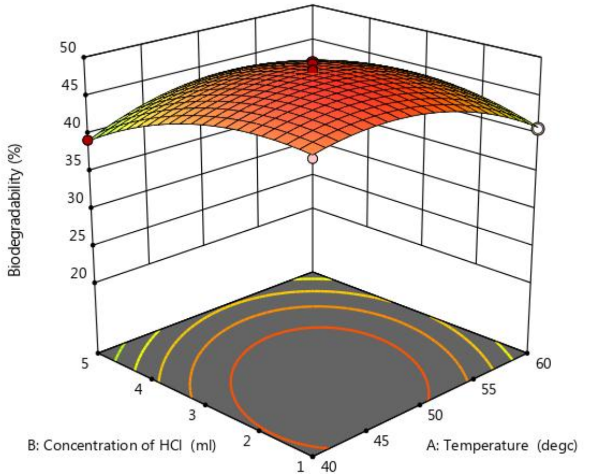


BD (Concentration of HCl and Residence Time)

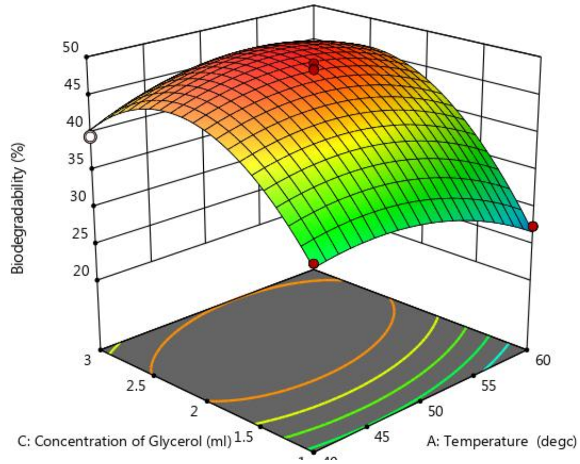


CD (Concentration of Glycerol and Residence Time)

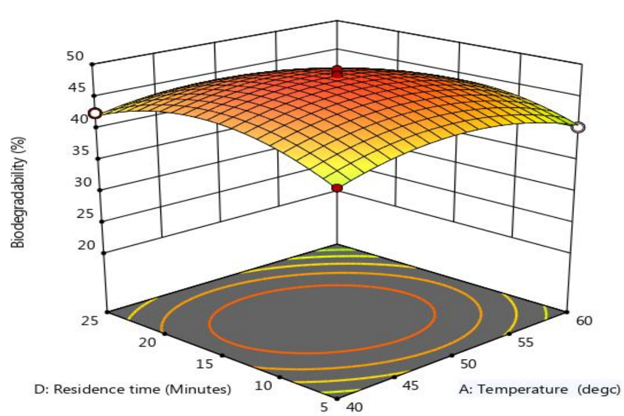
Appendix B4: 3D representation of interaction effect on Biodegradability



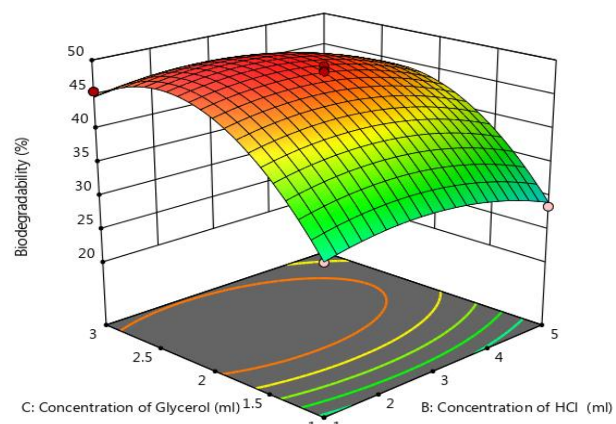
AB (Temperature and concentration of HCL)



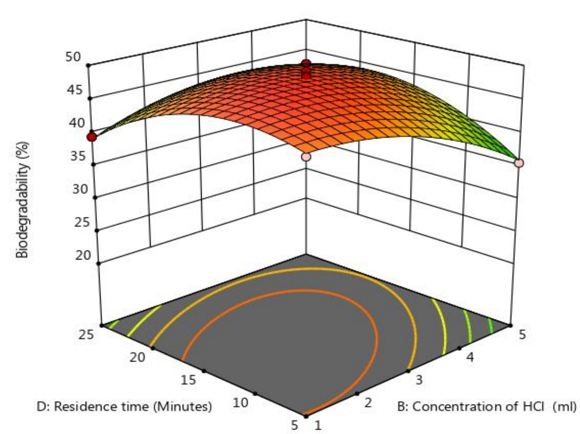
AC (Temperature and concentration of Glycerol)



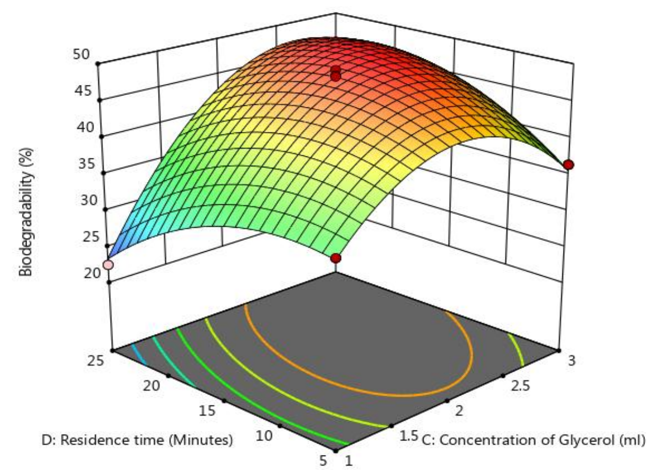
AD (Temperature and Residence time)



BC (concentration of HCl and concentration of Glycerol)



BD (Concentration of HCl and Residence Time)



CD (Concentration of Glycerol and Residence Time)

Appendix C: FTIR correlation table

Functional group names	Characteristic Absorption(cm-1)	Type of vibration causing IR absorption
Phenols and alcohols	3550-3200	Hydrogen bonded- OH stretch
Carboxylic acids	3000-2500	Hydrogen bonded-OH stretch
	1780 - 1710	C=O stretch
Ketones	1750-1680	C=O stretch
Aldehyde	1740-1690	C=O stretch
Ester	1750-1735	C=O stretch
Amide	1690-1630	C=O stretch
	3700-3500	N-H stretch
Ethers, alcohols and sugars	1300-1000	C-O-C and C-OH
Alkenes and aromatic cpds	1000-650	=C-H
Amine	3500-3300	N-H stretch
Nitrile	2260-2220	C-N stretch
Alkane	2950-2850	C-H stretch
	1500-1440	H-C-H stretch
Alkene	3100-3010	C - H stretch
	1680-1620	C=C stretch
Alkyne	3300	C - H stretch
	2260-2100	C≡ C stretch
Aromatic	3030	C - H stretch
	860-680	C-H bending
	1700-1500	C=C bending

Appendix D: Selected samples to show physical change and gradual degradability of the bio film within 30 day

Day 1	15 days	20 days	25 days	30 days
				
				

Appendix E: Photos Taken At Different Stages of Laboratory Works