ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

PROCESS ENGINEERING STREAM

Synthesis of Micro-cellulose Reinforced Polyvinyl Alcohol Micro-Biocomposite Materials

By

Tadele Beyene

Advisor: Hundessa Dessalegn (PhD)

A Thesis Submitted to School of Graduate Studies of Addis Ababa University

in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering (Process stream)

Addis Ababa, Ethiopia

June, 2018

Certification

This is to certify that the thesis prepared by Tadele Beyene entitled: **Synthesis of Micro-cellulose Reinforced Polyvinyl Alcohol Micro-Biocomposite Materials** and submitted in partial fulfillment of the requirements for the degree of Master of Sciences in Chemical Engineering complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Approved by the Examining Committee:

______________________	________	________
Internal Examiner	Signature	Date
______________________	_________	________
External Examiner	Signature	Date
Dr.Hundessa Dessalegn	_________	________
Advisor	Signature	Date
__________________________	___________	________
School or Center Chair Person	Signature	Date

Dedication

This theses research is dedicated to my father, who thought me that the best kind of knowledge to have is learnt for his own sake. It is also dedicated to my mother, who thought me that even the largest task can be accomplished if it is done one step at a time.

Declaration

I, Tadele Beyene(candidate) declare that this thesis is my original work which has not been presented for a degree in Addis Ababa University or any other university, and all sources of materials used for the theses have been fully acknowledged.

Tadele Beyene	________	________
Name	Signature	Date
Dr. Hundessa Dessalegn(Advisor)	_________	_________
Name	Signature	Date

Abstract

This study focused on developing and evaluating the performance of cellulose/polyvinyl alcohol microbiocomposites. Cellulose has a potential to become a key resource in the development of biodegradable films composites and therefore, incorporating microcellulose into different materials have become an attractive research topics for production of micro-biocomposite materials. The objective of this study was to fabricate cellulose reinforced polyvinyl alcohol micro-biocomposite materials and evaluate the effectiveness of the reinforcement. The extraction of microcellulose was done by alkaline treatment with 8%-20%wt NaOH aqueous solution with the ratio of 1:10 solid: liquid loading (w/v) in temperatures range of (40 ^{o}C-60 ^{o}C) for (1hr-5hr) and 36.65% optimum yield was obtained. The particle size analysis by dynamic light scattering (DLS) showed the mean particle size found was 871.35μm confirming the product was microcellulose. The Fourier transform infrared spectroscopy (FTIR) indicated the effectiveness of pretreatment in removing lignin and hemicellulose. Solvent casting method was used to reinforce microcellulose in PVOH polymer. Water absorption test results shown that the reinforcement reduced the water absorption of the PVOH from 84% for neat PVOH to 62 % for 8% MCC composite and from 84 % to 75 % for 4% SCB and 84% to 69 % for 4% MCC. Increment in tensile strength from 31 MPa for neat PVOH to 54 MPa for PVOH/ 8%MCC and reduction in elongation at break from 355MPa for neat PVOH to 132 MPa for PVOH/ 8%MCC were observed from the mechanical property test results. The SEM micrograph and optical transparency of the films showed uniform distribution and formation of network structure through hydrogen bonding.

Keywords: bagasse, natural filler, extraction, celluloses, biocomposite, interaction, morphology

Acknowledgements

First and foremost, I would like to explain my deep gratitude to my advisor Dr.Hundessa Dessalegn for his constant and endless support, unreserved advice, encouragement, guiding and assisting in every aspects of difficulties throughout the research process from the very beginning to the last minutes of its completion.

Secondly, I would like to explain my deep gratitude to Mr.Teshale, Mr.Tolossa, Mr.Sultan, Mr.Hintsa and other laboratory technical assistants for their encouragement, priceless assistance and invaluable advice for the accomplishment of the thesis.

Thirdly, I wish to extend my sincerest gratitude to thank Addis Ababa University for facilitation of financial support (School of Chemical and Bio Engineering), science faculty department of chemistry and Leather Industry Development Institute for their help in product characterization and testing.

Finally, I have not forgotten to gratefully acknowledge my God for he has given me strength to accomplish this research.

Table of Contents

Contents **page**

List of Tables

page

List of Figures

page

List of acronyms

ASTM	American Society for Testing and Materials
BCF	Biocomposite film
BCM	Biocomposite material
DLS	Dynamic light scattering
DMA	Dynamic mechanical analysis
FTIR	Fourier transform infrared spectroscopy
MFC	Micro-fibrillated cellulose
PMC	Polymer Matrix Composites
PSA	Particle size analyzer
PVOH	Poly vinyl alcohol
SEM	Scanning electron microscopy
SCB	Sugarcane Bagasse
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
XRD	X-ray diffraction

1. Introduction

1.1 Background

In the present time, development of materials is tending towards green composite due to challenges of global environmental burning issues such as decreasing polar ice cap and hence sea levels rising because of average global temperatures rising, rapidly depleting petroleum resources, etc. The use of green composites for engineering applications has gained high attention from industries in recent years as their potential to reduce waste from non-degradable synthetic materials and their carbon footprint. These issues intensified pressures on engineers, researchers, and industrialists towards manufacturing and new product design using green material partially or fully. The biodegradable waste disposal problem and benchmarks for cleaner as well as safer environment provide an abundant component of scientific research towards eco -composite materials, which easily degrades or bio-assimilated. The abundant presence of natural fiber and any other available agro-waste has been also responsible for latest development in research towards green composite material.

Over the last few years, a number of researchers have been involved in investigating the exploitation of natural fibers as load bearing constituents in composite materials. The use of such materials in composites has increased due to their relative cheapness, ability to recycle and for the fact that they can compete well in terms of strength to weight of material, in addition to providing rigidity(Balaji, Karthikeyan, & Sundar Raj, 2015a).

Ethiopia has abundant availability of natural fibers such as pineapple, bamboo, banana, wheat straw, barley husk and sugarcane. Their use can provide value added novel applications of natural fibers based composites and at the end it gives social benefits and major income for communities who cultivate them. If sugar cane bagasse is used for energy generation by burning it, it results in releasing some amount of carbon dioxide to the environment even if it is well known carbon neutral and high amount of scale formation in the boiler which in turn reduces the rate of heat transfer and service life of the boiler. Therefore, burning bagasse for fuel is not advised that it must be used for other purposes.

Another critical issue is case of environmental polluting plastic materials like polyethylene, polypropylene and polyethylene phthalate which are not biodegradable when they are used up and disposed, and hence we must try to fully or at least partially replace them by biodegradable material for consumption. Synthetic polymers are not biodegradable and they can cause a lot of problems on human and animal health throughout their life cycle as we observe everywhere specially in the countries like Ethiopia in which used products are disposed everywhere on the roads and in the field. A very recent occasion we have observed in Addis Ababa around Ayer Tena particular place locally called Koshe, was a cause for loss of about hundred peoples is the result of long period accumulation of non-biodegradable polymer composites.

Natural fiber composites are suitable materials to make flooring tiles, panels, ceilings, blocks, plastics and partition boards to substitute wood, etc. In comparison with synthetic fibers like glass and carbon, these natural fibers are gaining importance due to their many advantages, such as environment-friendly, reduced greenhouse gas emissions, biodegradability, enhanced energy recovery, low energy consumption, low cost, low density, high heat deflection temperature/ low thermal conductivity, high toughness, high stiffness and acceptable specific strength properties(Anggono, 2015).

Therefore, biodegradable cellulose composites are a potential materials for replacing synthetic materials as they can be used to improve the mechanical properties and biodegradation rate if they are replaced or used as reinforcement in synthetic polymers. As a result, cellulose incorporation into different materials have become an attractive research topics for production of biocomposite materials. Among the different types of Agro wastes available in our country, sugarcane bagasse wastes from sugarcane industries is relatively available and abundant natural resources as a result of sugarcane projects expansion strategy planned by Ethiopian government. Therefore this research will be focused the extraction of cellulose from this sugarcane bagasse waste using alkali treatment. Delignification which is the removal of cellulose lignin part of bagasse is done by using sodium chlorite and acetic acid as bleaching agents and followed by alkaline treatment using sodium hydroxide to remove hemicellulose from sugarcane bagasse. After cellulose is obtained cellulose reinforced poly vinyl alcohol (PVOH) green composite will be developed by solvent blending them with hardener in mixer and molding.

1.2 Problem of the Statement

The reduction of petroleum resources and rising petroleum costs, there is concern with finding cost-effective ways to manufacture different materials from renewable natural resources. A sustainable solution to overcome these diminishing petroleum resources and uncontrolled polymer pollution is extracting microcellulose from agricultural wastes or byproducts such as sugarcane bagasse and blending with polymer matrix for production of micro-biocomposite materials for our daily usage. Most of these polymer products are largely discarded into environment upon usage and are not easily biodegradable. As result, they are leading to serious environmental problem that affects our environment and community as a whole. The other means to reduce such problem is to produce biodegradable composites based on sustainable and renewable natural resources such as micro-cellulose. As a result of this, extraction of microcellulose from bagasse and blending it in polyvinyl alcohol matrix was very interesting to fabricate micro-biocomposite with unique and good specific properties.

1.3 Objective of the Study

1.3.1 General Objective

The general objectives of this research is: fabrication of cellulose reinforced polyvinyl alcohol micro-biocomposite materials.

1.3.2 Specific Objectives

Specific objectives of this research are:

- Extracting cellulose from sugar cane bagasse
- Characterization cellulose and biocomposites by appropriate methods
- Investigation of mechanical and biodegradability properties of composites
- Evaluation of the effectiveness of reinforcement by green composite biodegradation, mechanical and water absorption tests
- Comparison of reinforcement composites with the reference composite

1.4 Scope of the Study

This research primarily focused on micro-biocomposite material product fabrication by extraction of cellulose from sugarcane bagasse and blending it with PVOH. The cellulose was extracted by using alkaline and then characterized by using Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD). Furthermore, the dimensions of cellulose will be determined using a dynamic light scattering (DLS). Finally green composite product will be fabricated and characterized by scanning electron microscopy (SEM), FTIR and mechanical property testing machine.

1.5 Significance of the Study

The finding of the research will be important to discover the performance of cellulose fiber as reinforcing materials in polymer green composites due to their large surface area and the small scale dimensions. Their good mechanical performance shows the potential replacement to glass fiber composite in the emerging advanced composite market. It may give the plastics industry a more economical solution in managing the environmental problems caused by conventional synthetic plastics. Cellulose fibers come from an abundant and renewable resources at low cost, which ensures a continuous fiber supply and a significant material cost saving in the plastics industry.

extracting and reinforcing cellulose in polymer matrix is very important to utilize sugarcane bagasse for production of cellulose based biocomposites. This research contributes for improving the mechanical properties and biodegradability of neat polyvinyl alcohol (PVOH) biocomposites when reinforced because of presence of biodegradable cellulose component and at the same time provides a means for converting all other agricultural wastes into valuable products which results in reduction of environmental problem by avoiding on-site or off-site burning that affect the environment by increasing the amount of carbon dioxide released to environment.

Exploring the potential of the bagasse fiber polymer composites and studying the mechanical properties of composites provides knowledge to conduct further research in this area. If we talk about the future of bagasse fiber, it is very bright because they are cheaper, lighter and environmentally superior to glass, carbon or other synthetic fiber composites in general. Hence, with this properties, searching for cost-effective ways of manufacturing polymeric materials composed of bagasse cellulose is critical and interesting compared to petrochemical based polymers in environmentally friendly ways. Furthermore, this research may pave the way for more detailed and advanced researches to be conducted in the future.

2. Literature Review

2.1 Biocomposite Materials

Composite materials are combinations of two or more materials with different, often complementary properties not obtainable from any discrete material. They are cohesive structures made by physically combining two or more compatible(nearly fitting) materials, different in composition and characteristics and sometimes in form. The composites should not be regarded as simple as a combination of two materials. In the broader significance; the combination has its own distinctive properties. In terms of strength to resistance to heat or some other desirable quality, it is better than either of the components alone or radically different from either of them(Verma, Gope, Maheshwari, & Sharma, 2012). composite materials as heterogeneous materials consisting of two or more solid phases, which are in intimate contact with each other on a microscopic scale Van Suchetclan (Anggono, 2015). They can be also considered as homogeneous materials on a microscopic scale in the sense that any portion of it will have the same physical properties(Verma et al., 2012).‖They are compound materials which are different from alloys by the fact that the individual components retain their characteristics but are so incorporated into the composite to take advantage only of their attributes(characteristics) and not of their short comings. In order to obtain improved materials. Polymer Matrix Composites (PMC) are materials consisting of a polymer (resin) matrix combined with a fibrous reinforcing dispersed phase(Balaji et al., 2015a). PMC are very popular due to their low cost and simple fabrication methods.

Researchers have begun to focus attention on natural fiber composites (i.e., bagasse fiber) reinforced with natural or synthetic polymers. Natural fibers exhibit many advantageous properties; they are a low-density material yielding relatively lightweight composites with high specific properties, they have significant cost advantages and ease of processing along with being highly renewable resource, in turn reducing the dependency on foreign and domestic petroleum oil. Natural fiber composites are likely to be environmentally superior to glass fiber composites in most cases because of: lower environmental impacts compared to glass fiber production, higher fiber content for equivalent performance, reducing more polluting base polymer content, natural fiber light-weight improves fuel efficiency and reduce emissions in the use phase of the component, especially in auto applications, end of life incineration of natural fibers results in recovered energy and carbon credits(Balaji et al., 2015a). They are also environmentally friendly materials at the stage of production, processing and waste; annual renewability and lower energy inputs in production per unit, Commonly known processing methods, Excellent specific strength and high modulus, reduced density of products, Lower cost, Corrosion resistance, High creep resistance, High toughness and Biodegradable.

In recent years, a new class of fully biodegradable green composites have been made by combining natural fibers with biodegradable resins. The major attraction of green composites is that they are fully degradable and sustainable, that is, they are truly green. Green composites may be used effectively in many applications with short lifecycles or products intended for one-time or short-term use before disposal. These natural biodegradable polymers show a range of properties and can compete with non-biodegradable polymers in different industrial field. To fabricate advanced green composites having high strength, cellulose fibers twisted using liquid crystalline solutions prepared by dissolving cellulose in phosphoric acid(Muniyasamy, 2016).

Biocomposites are widely used for different applications in automotive industry, aerospace industry, building industry, furniture industry, bio medical industry, food processing and packaging industry, house hold goods etc. general speaking, natural fibers are preferable to synthetic fibers for the following reasons.

2.1.1 Advantages of Using Natural Fibers for Composites

They are attractive ecological alternatives to glass, carbon and other man made (synthetic) fibers because of: availability/sustainability, renewability, low density/light weight, has significant cost advantages Low price (cost), higher specific properties, bio-decomposability (synthetic fibers do not decompose/degrade biologically) for example synthetic plastics, simple fabrication/process, reduce dependency on foreign and domestic petroleum oil, improves fuel efficiency, reduces emission, end of life incineration of natural fiber results in recovered energy and carbon credits, low energy inputs in production per unit, has commonly known processing methods, corrosion resistance, high creep resistance, environmentally superior to glass/carbon fibers (environmentally friendly), low environmental impact compared to glass and carbon fibers and has higher fiber content for equivalent performance. As a result of these, particularly high cost of synthetic fibers attracted composite community to biocomposite.

2.1.2 Factors Affecting Properties of Composite Materials

Composites consist of one or more discontinuous phases embedded in a continuous phase. The discontinuous phase is usually harder and stronger than the continuous phase and is called the reinforcement‘ or reinforcing material‘, whereas the continuous phase is termed as the ‘matrix‘. Properties of composites are strongly dependent on the properties of their constituent materials, their distribution and the interaction among them. The composite properties may be the volume fraction sum of the properties of the constituents or the constituents may interact in a synergistic way resulting in improved or better properties. The geometry of the reinforcement (shape, size and size distribution) influences the properties of the composite to a great extent. The concentration distribution and orientation of the reinforcement also affect the properties(Menezes, Maciel Filho, & Rocha, 2016). The reinforcement caused by short fibers (cellulose fibers), in the thermoplastic matrix is governed by the following parameters: i) fiber dispersion, ii) fiber-matrix adhesion, iii) fiber aspect ratio, iv) fiber orientation, and v) fiber volume fraction. Processing temp and pressing pressure processing temperature has a significant effect on the mechanical properties for case of melt blending.

I. Fiber Dispersion

Good dispersion in the polymer matrix implies that the fibers are separated from each other (i.e. there are no clumps and agglomerates), and each fiber is surrounded by the matrix. Insufficient fiber dispersion, on the other hand, results in a heterogeneous mixture of resin-rich areas and fiber-rich areas. This is undesirable because the resin-rich areas are weak and the fiber-rich areas (i.e., clumps) are vulnerable to micro-cracking. Micro-cracks contribute to inferior mechanical properties of composites. It is therefore important to ensure homogeneous fiber dispersion in order to achieve maximum strength and performance of the composite materials. There are two major factors that affect the extent of fiber dispersion, fiber-fiber interaction such as strong hydrogen bonding between the fibers, and fiber length. As mentioned before, one of the major drawbacks of using cellulose fibers as reinforcement is because of their poor dispersion characteristics in many thermoplastic melts, such as polypropylene and polystyrene, due to their hydrophilic nature. Fiber surface modification, dispersing agents such as stearic acid, fiber pre-treatments such as acetylation and increasing mixing time are used to overcome these problems. A careful selection of initial fiber lengths, processing aids, processing techniques as well as processing conditions are necessary in order to produce high performance composites.

Good dispersion implies less fiber clump and agglomeration. Each fiber is surrounded by matrix. Insufficient dispersion causes heterogeneous mixture which is not desired. Two different areas will be formed; matrix (resin) rich area and fiber rich/clump of fibers areas. Because of this, micro-cracking will be formed causing inferior mechanical properties of biocomposite material.

II. Fiber-Matrix Adhesion

Fiber to matrix adhesion plays a very important role in the reinforcement of composites with short fibers. During loading, loads are not applied directly to the fibers but to the matrix(Balaji et al., 2015a). To have composites with excellent mechanical properties, the load must be transferred effectively from the matrix to the fibers. This requires good interaction as well as adhesion between the fibers and the matrix, i.e. strong and efficient fiber-matrix interface. This can be controlled by either surface treatment applied to the fiber or by the use of additives such as coupling agents. Cellulose fibers have not been extensively used to reinforce thermoplastics. This is because of several major drawbacks discussed in the previous section. Poor compatibility with and dispersability in hydrophobic thermoplastics leads to poor wetting and interfacial bonding between the fibers and the matrix resulting in composites with poor mechanical properties. The use of coupling agents, polymer coating materials, fiber pre-treatments, and chemical grafts have been reported to improve wetting as well as interfacial bonding between cellulose fibers and thermoplastic matrices. Generally, poor compatibility implies poor dispersion, poor wetting, poor bonding between fiber and matrix.

III. Fiber Aspect Ratio

Fiber aspect ratio, i.e. the length to diameter ratio(Lc/D) of a fiber, is a critical parameter in a composite. For each short-fiber composite system, there is a critical fiber aspect ratio that may be defined as the minimum fiber aspect ratio in which the maximum allowable fiber stress can be achieved for a given load. This parameter is determined not only by fiber and matrix properties, but also by the quality of the fiber/matrix interface. Load is transferred from the matrix to the fiber by shear along the fiber/matrix interface. For maximum reinforcement, the fiber aspect ratio of any composite system should be above its critical value. This will ensure maximum stress transfer to the fibers before the composite fails. If the fiber aspect ratio is lower than its critical value, insufficient stress will be transferred and reinforcement by the fibers will be inefficient, which means the fibers are not loaded to their maximum stress value. By contrast, if the fiber aspect ratio is too high, the fibers may get entangled during mixing causing problems with fiber dispersion.

IV. Geometry of Reinforcement

Geometry of reinforcement (shape, size, fiber orientation) single direction orientation is desired (results in max reinforcement). Orientation of each single fiber with respect to loading axis is desired. Fiber orientation is another important parameter that influences the mechanical behavior of short-fiber composites. This is because the fibers in such composites are rarely oriented in a single direction, which is necessary for the fibers to offer maximum reinforcement effects. As a result, the degree of reinforcement in a short-fiber composite is found to be strongly dependent on the orientation of each individual fiber with respect to the loading axis.

V. Fiber Volume Fraction

Like other composite systems, the properties of short-fiber composites are also crucially determined by fiber concentration. At low fiber volume fraction, a drastic decrease in tensile strength is usually observed.

2.1.3 Elements of Composite Materials

A composite material is one which is made of at least two elements working together to give material properties that are different to the properties of those elements on their own. Most composites consist of a bulk material (‘matrix‘ which is resin/polymer/) and a reinforcement(fibers) of some kind, added primarily to increase the strength and stiffness of the neat resin system (matrix). Matrices are bonded with fibers for better properties by preventing fibers from each other in order to prevent abrasion/scratch and formation of new surface defect. The matrix acts as a bridge to hold the fibers in place.

2.2 Importance of Matrix in a Composite

Many materials when they are in a fibrous form exhibit very good strength property but to achieve these properties the fibers should be bonded by a suitable matrix. The matrix isolates the fibers from one another in order to prevent abrasion/scratch and formation of new surface defects and acts as a bridge to hold the fibers in place. A good matrix should possess ability to deform easily under applied load transferring the load onto the fibers and evenly distributes stress concentration or load(Verma et al., 2012). In general, epoxy resin / polymer matrix materials selected should have: excellent adhesive strength to different materials, high resistance to chemical and atmospheric/moisture attack, high dimensional stability, fatigue resistance/ free from internal stresses, heat resistance, excellent mechanical and electrical properties, Odorless, tasteless and completely nontoxic, Negligible shrinkage. There are three types of matrices: metal matrix, ceramic matrix and polymer matrix:

Table 2.1. Polymer Matrices of Natural Fiber

Thermosetting plastics	Epoxy, Polyester, Phenolic, Polyurethane & Polyimide.
Thermoplastics	Polypropylene, Polyethylene, Polyamide, Polystyrene and olyvinylchloride
Rubber and natural polymers	India-rubber, Modified starch and Cellulose esters, Polyhydroxy-butiricacid, Polylactide

However, the main disadvantages of natural fibers and matrix is the relative high moisture sorption. Therefore, chemical treatments are considered in modifying the fiber surface properties. Some of the major advantages and limitations of resin matrix are shown in Table2.2 below.

Table 2.2. Advantages and Limitations of Resin Matrix

Advantages	**Limitations**
low densities	low transverse strength
good corrosion resistance	low operational temperature limits
low thermal conductivities	relative high moisture sorption,(main disadvantages of natural fibers and matrix)
low electrical conductivities	
translucence	
aesthetic color effects	

The main disadvantage is high moisture sorption which can be reduced by chemical treatment (surface modification) of fibers/cellulose. Most matrices are unstable under high temperature (greater than 200 ^{o}c)

Reinforcement: the purpose of the reinforcement in a composite material is to increase the mechanical properties of the neat resin system. All of the different fibers used in composites have different properties and so affect the properties of the composite in different ways. For most of the applications, the fibers need to be arranged into some form of sheet, known as a fabric, to make handling possible.

2.3 Classification of Composite materials

Composite materials can be classified in different ways. The two broad classes of composites are (1) Particulate composites and (2) Fibrous composites.

A. Particulate Composites

As the name itself indicates, the reinforcement is of particle in nature. It may be spherical, cubic, tetragonal, a platelet, or of other regular or irregular shape. In general, particles are not very effective in improving fracture resistance but they enhance the stiffness of the composite to a limited extent(Verma et al., 2012). Particle fillers are widely used to improve the properties of matrix materials such as thermal and electrical conductivities, improve performance at elevated temperatures, reduce friction, increase wear and abrasion resistance, improve machinability, increase surface hardness and reduce shrinkage.

B. Fibrous Composites

A fiber is characterized by its length being much greater compared to its cross-sectional dimensions. The dimensions of the reinforcement determine its capability of contributing its properties to the composite. Fibers are very effective in improving the fracture resistance of the matrix since a reinforcement having a long dimension discourages the growth of incipient cracks normal to the reinforcement that might otherwise lead to failure, particularly with brittle matrices. Highly modified surface implies highly fibrillated surface and the process is called mercerization or alkaline treatment.

A lot of researches were done on bagasse-reinforced biocomposite materials development and characterization. Vazquez A. et al (1999) reported processing and properties of bagasse fiber-polypropylene composites. Four different chemical treatments of the vegetal fibers were performed in order to improve interface adhesion with the thermoplastic matrix: namely isocyanate, acrylic acid, mercerization and washing with alkaline solution were applied. The effects of the treatment reactions on the chemical structure of the fibers were analyzed by infrared spectroscopy. Optical photomicrographs indicate that a highly fibrillated surface is achieved when fibers are mercerized. The tensile strength and the elongation at break of the polypropylene matrix composite decrease with the incorporation of bagasse fibers without treatment. However, isocyanate and mercerization treatments enhance the tensile properties of the composite. Moreover, treated fibers have the best creep measurements. That is mercerized fiber have the highest creep activation energy. Fourier transform infrared (FTIR), thermo gravimetric analysis or dynamic mechanical thermal analysis, differential scanning calorimetry (DSC) will be used to characterize the chemical and thermal properties of the treated fibers.

Shibata S. et al (2006) prepared biodegradable composites reinforced with bagasse fiber before and after alkali treatments and mechanical properties were investigated. Mechanical properties of the composites made from alkali treated fibers were superior to the untreated fibers. Composites of 1% NaOH solution treated fibers showed maximum improvement. Approximately 13% improvement in tensile strength, 14% in flexural strength and 30% in impact strength had been found, respectively. After alkali treatment, increase in strength and aspect ratio of the fiber contributed to the enhancement in the mechanical properties of the composites. SEM observations on the fracture surface of composites showed that the surface modification of the fiber occurred and improved fiber–matrix adhesion. Zheng Yu-Tao et al (2007) studied the surface treatments of bagasse fiber with benzoic acid as a surface/interface modifier and the mechanical properties of BF-polyvinyl chloride composite. A typical process for the preparation of the composite was mixture of polyvinyl chloride, BF, benzoic acid and other processing additives were dry-blended in a two-roll mill followed by compression molding. The experimental results indicated that the ratio of polyvinyl chloride /bagasse fiber, the content of benzoic acid and processing temperature had a significant effect on the mechanical properties of the composite. Tayeb et al (2008) studied abrasive wear behavior of polymer reinforced with natural fiber. Specifically, untreated sugarcane fiber was used in two forms to reinforce polyester. Chopped SCFs with different lengths (1, 5, 10 mm) randomly dispersed and continuously unidirectional fibers with two different orientations were prepared using hand-lay-up and closed mould techniques. Despite the good adhesion between fiber and matrix, results of mechanical tests showed poor tensile strength of SCRP composite. This was attributed to the weak site inside the fiber itself which could not bear the stress transfer from matrix via the fiber. Generally, mechanical properties of composites made from alkali treated fibers is superior to untreated fibers.

This research focuses on investigation of developing bagasse fiber reinforced composite material of bagasse fiber mixed in poly vinyl alcohol matrix. Alkali treatment using 17.5% NaOH will be used to modify bagasse fibers surface. Their surface adhesive bonding to poly vinyl alcohol resin or their reinforcement capacity to obtain the maximum strength will be investigated.

2.4 Application Areas of Biocomposite Materials

Biocomposites are widely used for different applications such as biomedical industries, food processing and packaging industries, house hold goods industries, furniture industries, automotive industries, aerospace industries, building industries.

2.5 Sugarcane Bagasse

2.5.1 Chemical Composition of Sugarcane Bagasse

The sugarcane bagasse (SCB) is a fibrous residue extensively generated in high extent (about 30%) in the agro-industry that remains in a sugarcane mill after total crushing the sugarcane stalk and extracting of its juice(Anggono, 2015). It is surplus after the crushing and extraction of juice from the sugarcane since sugarcane is cultivated in mass. It contains 48.7% short fibers (cellulose, hemicellulose, lignin, pectin and waxes/extractives), water or moisture content 49%, and small amounts (2.3%) of soluble solids. The fiber contents are 50%cellulose, 25%hemicellulose, 25% lignin[85]. Some researchers jot down the bagasse contents in range (intervals): 40-50% cellulose, 25-35% hemicellulose, 18-24% (lignin, minor amounts of minerals, waxes and other compounds)[87]. Whereas some others refer that it contains 45-55% cellulose, 20-25 % hemicellulose, 18-24% lignin, 1-4% ash and less than 1% waxes (extractives)[100].

Contribution percentage of each of these components varies according to the variety, maturity, method of harvesting sugar cane and the efficiency of the crushing plant. The bagasse, thus, produced after juice extraction poses a disposal problem and it is one of the largest agriculture residues in the world. Many research have been conducted to use bagasse as a renewable feedstock and domestic fuel for power generation and for the production of bio-based material. It is mainly used as a burning raw material (85%) in boilers by the sugarcane factories(Anggono, 2015). The use of bagasse as fuel will produce significant amount of carbon during its use, which is not desirable. Even the efficiency of the burning process is low due to low caloric power of bagasse(Anggono, 2015). Even though, there is an excess of bagasse the consumption of bagasse is very low for other purposes. Usually this excess is deposited on empty fields altering the landscape. Also, the sugar cane mill management encounters problems regarding regulations of clean air from the Environmental Protection Agency, due to the quality of the smoke released in the atmosphere. Presently 85% of bagasse production is burnt. Even so, there is an excess of bagasse usually this excess is deposited on empty fields altering the landscape(see the following picture taken from wonji sugar factory). Approximately 9% of bagasse is used in alcohol (ethanol) production(Verma et al., 2012). But again, due to the low level of sucrose left in bagasse, the efficiency of the ethanol production is quite low.

Figure 2.1: sugar cane bagasse disposed in the field form Wonji sugar factory

Sugarcane bagasse wastes are chosen as an ideal raw material in manufacturing new products because of their low fabricating costs and high quality green end material. When appropriate modifications and manufacturing procedures are applied, bagasse displays improved mechanical properties. Primarily, bagasse contains cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances. Large amount of hydroxyl group in cellulose gives natural fiber hydrophilic properties when used to reinforce hydrophobic matrix; the result is a very poor interface and poor resistance to moisture absorption(Verma et al., 2012). Hemicellulosic polymers are branched, fully amorphous and have a significantly lower molecular weight than cellulose. Because of its open structure containing many hydroxyl and acetyl groups, hemicellulose is partly soluble in water and hygroscopic (changes in its humidity or simply take up water and retain it specially from atmosphere) (Verma et al., 2012). Hemicellulose is primarily (presumably) strongly bonded to cellulose fibrils by hydrogen bonds. Lignins are amorphous, highly complex, mainly aromatic, polymers of phenyl propane units(Verma et al., 2012) but have the least water sorption of the natural fiber components(Verma et al., 2012). Because of the low interfacial properties between fiber and polymer matrix often reduce their potential as reinforcing agents due to the hydrophilic nature of natural fibers, chemical modifications are considered to optimize the interface of fibers. Bagasse has bulk density from250kg/m^3 to 320kg/m^3 (Verma et al., 2012).

Figure 2.2 sugarcane bagasse

Table 2.3. Average Bagasse Compositions

Items	Percentage (%)
Fiber	48.7
Moisture	49.0
Soluble solids	2.3

Table 2.4. Chemical composition of bagasse fibers

composition of bagasse fibers	Values
Cellulose (%)	45-55
Hemi cellulose (%)	20-25
Lignin (%)	18-24
Pectin (%)	0.6-0.8
Ash (%)	1-4
Extractives (%)	1.5-9

2.6 Cellulose

The major constituents of higher plant cell walls are group of polymers with backbones made up of ß-1,4-linked monosaccharides. The dominant one among them is cellulose, which is the ß-1,4-homopolymer of anhydro-D-glucose units and it is the most common organic compound with formula $(C_6H_{10}O_5)_n$ representing about $1.5*10^{12}$ tons of total annual biomass production(Kalia, S.; Kaith, B.S., Kaur, 2011). Cellulose is a polysaccharide containing a linear chain of several hundred ß-(1,4) linked D-glucose units. It is the primary structural component responsible for much of the mechanical strength of the cell wall. Its structural properties derive from its ability to retain a semi crystalline state of aggregation even in an aqueous environment; this is unusual for a polysaccharide. Each type of cellulose has its own cell geometry, and the geometrical conditions determine the mechanical properties. Solid cellulose forms with regions of high order crystalline regions and regions of low order amorphous regions. It is stabilized by hydrogen bond and is environmentally friendly, biocompatible and renewable material. Cellulose is used for: coating, laminating, sorption media, additives in building materials, pharmaceutical, food, cosmetics, etc.

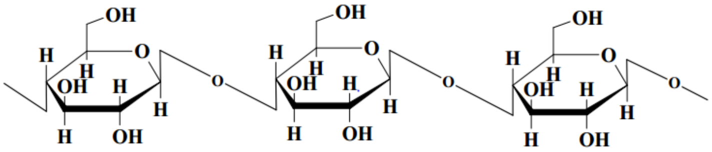


Figure 2.3 structure of cellulose.

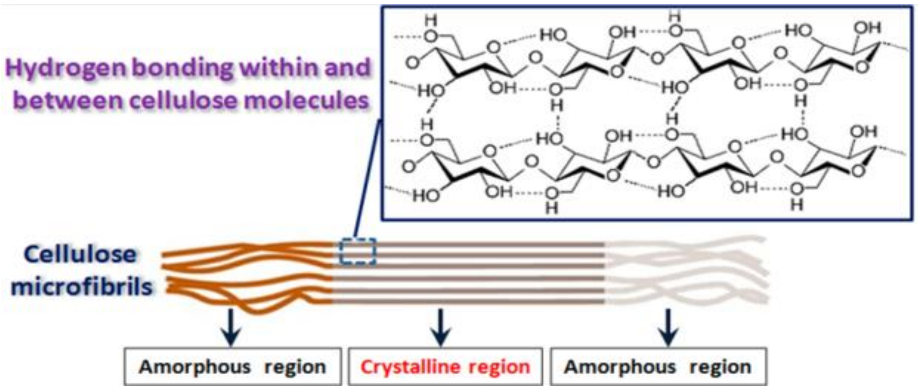


Figure 2.4 scheme of interaction between molecular chains within the crystalline region of cellulose micro-fibrils

2.6.1 Cellulose pretreatment

Modification results in improved performance of the composites produced. This can be done through several approaches, including plasma activation and graft polymerization with vinyl monomer. Chemical process is a means extraction by decomposition called degumming, in which the gummy materials and the pectin are removed(Marcicano & Jr, 2013). Chemical modification of cellulose fibers is usually applied to correct for deficiencies of the fibers. Sugarcane bagasse is submerged in heated tanks containing water solutions of sulphuric acid, chlorinated lime, sodium or potassium hydroxide and soda ash to dissolve the pectin component. Unwanted non-cellulosic components adhering to the fibers can be removed by dispersion and emulsion-forming process. Acetylation of some of the hydroxyl groups present in the fibers can be used for modifying fibers and then modified fibers can be characterized by FTIR, DLS, TGA and SEM.

The incorporation of cellulose fibers into synthetic polymers is often associated with a lack of fiber dispersion due to the wide differences in polarity and also the strong intermolecular hydrogen bonding between the fibers. This lack of fiber dispersion can result in clumping and agglomeration of cellulose fibers which will act as stress concentration points to initiate cracks during loading. This effect contributes to inferior mechanical properties. This problem can be overcome by pretreatment of the fibers which helps to separate fibers from each other, eliminating the hydrogen bonding that holds them together. This approach also induces bond formation between the fibers and the matrix resulting in improved composite properties.

Dispersion aids, such as stearic acid, mineral oil and maleated ethylene which facilitates fiber dispersion by decreasing both the size and number of fiber aggregates as a result of significantly reduced fiber to fiber interaction and improved fiber wetting by the polymer matrix. Addition of stearic acid during the compounding greatly improves the fiber dispersion in the polymer matrix compared to untreated fibers as seen in SEM micrographs of fracture surfaces of the corresponding composites. This effect can also reflected in improved mechanical properties of the composites. Cellulose fibers are not compatible, i.e., do not wet, with many thermoplastic matrices and this is also due to differences in polarity. Cellulose fibers are hydrophilic while most of the thermoplastics (polyolefins) are hydrophobic. This leads to the presence of voids or porosity, and to weak fiber-matrix interfaces and poor overall mechanical properties. There are several possible strategies for improving compatibility between cellulose and thermoplastic matrices, and the most extensively used methods are the use of coupling or compatibilization agents, and surface treatments of the fibers. Coupling agents such as isocyanates and silanes modify the fiber-matrix interface by forming a bridge of chemical bonds between the two components. This results in improved fiber-matrix adhesion, which is reflected in the mechanical properties of the composite produced. NaOH solution is used for surface treatment of cellulose fibers(Kalia et al., 2011)**.**

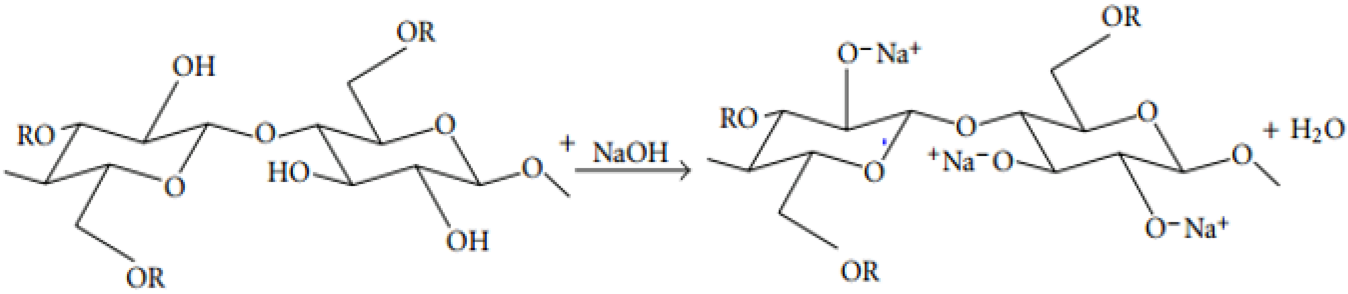


Figure 2.5 alkaline treatment of cellulose (cellulose and mercerized cellulose)

Surface Modification of Cellulose Fibers is a very interesting issue. In order to develop composites with better mechanical properties and environmental performance, it becomes necessary to increase the hydrophobicity of the cellulose fibers and to improve the interface between matrix and fibers. Lack of good interfacial adhesion, low melting point, and poor resistance towards moisture make the use of plant cellulose fiber reinforced composites less attractive. Pretreatments of the cellulose fiber can clean the fiber surface, chemically modify the surface, stop the moisture absorption process, and increase the surface roughness. Among the various pretreatment techniques, silylation, mercerization, peroxide, benzoylation, graft copolymerization, and bacterial cellulose treatment are the best methods for surface modification of natural fibers.

2.6.1.1 Mercerization Surface Modification

Mercerization is the common method to produce high quality fibers. The figure 2.5 above shows the probable mechanism of mercerization of cellulose fibers. Mercerization leads to fibrillation which causes the breaking down of the composite fiber bundle into smaller fibers. Mercerization reduces fiber diameter, thereby increases the aspect ratio which leads to the development of a rough surface topography that results in better fiber-matrix interface adhesion and an increase in mechanical properties(Muniyasamy, 2015). Moreover, mercerization increases the number of possible reactive sites and allows better fiber wetting. Mercerization has an effect on the chemical composition of the bagasse fibers, degree of polymerization, and molecular orientation of the cellulose crystallites due to cementing substances like lignin and hemicellulose which were removed during the mercerization process. As a result, mercerization had a long-lasting effect on the mechanical properties of bagasse fibers, mainly on fiber strength and stiffness(Wirawan, Sapuan, Yunus, & Abdan, 2012). A 10–30% sodium hydroxide solution produces the best effects on natural fiber properties. Bagasse fibers were soaked into 2.5, 5, 10, 13, 15, 18, 20, 25, or 30% NaOH solutions, and it was found that 5%, 18%, or 10% of sodium hydroxide solution was the appropriate concentration for mercerization. Bagasse fibers were treated with 5% alkali solution for 0, 2, 4, 6, and 8 h at 30◦ (Gupta & Bhatnagar, 2015). The fibers were then dried at room temperature for 48 h followed by oven drying at 100 ^{o}C for 6 h. It has been reported by Garcia-Jaldon et al (Muniyasamy, 2015) that 2% alkali solution at 200 ^{o}C and 1.5MPa pressure for 90s was suitable for degumming and defibrillation to individual fibers. Several workers have carried out work on alkali treatment and reported that mercerization leads to an increase in the amount of amorphous cellulose at the cost of crystalline cellulose and the removal of hydrogen bonding in the network structure(Muniyasamy, 2015). The jute fibers were washed with detergent (2 vol % in aqueous solution, 15% active matter) and then immersed in beakers with a solution of 5 wt. % NaOH for 24 h at room temperature. After that, the fibers were washed thoroughly with distilled water to remove the excess of NaOH and dried at 70 ºC for 24 h under vacuum(Nallappan, 2011). The banana fibers were cleaned and refluxed in 0.25% solution of NaOH for 1 h and then washed in very dilute acid to remove the non-reacted alkali. Washing was continued until the fibers were alkali free. The washed fibers were then dried in an oven at 70 ◦C for 3h.

Generally speaking, Pretreatment/surface modification and using coupling or dispersion agents can reduce hydrophilic properties of cellulose or on the other hand, they can increase wetting/dispersion/hydrophobicity of cellulose fibers, interfacial bonding between cellulose and matrix. Bagasse Pretreatment also decrease moisture sorption of biocomposite material.

2.6.2 Cellulose Characterization

a. Fourier Transform Infra-Red spectroscopy(FTIR)

FTIR is used to see formation of new bonds during hydrolysis process by analyzing functional groups and shows removal of lignin and hemicellulose (tests formation and changes in functional groups). Wave length (λ) is used in Fourier transformation infrared spectrometer analysis.

b. Morphology

It is the study of structure of cellulose and is measured by Dynamic light scattering(DLS) or particle size analyzer(PSA) to test for the average particle size whereas Scanning transmission electron microscopy(SEM) or transmission electron microscopy (TEM) is used to determine the shape(spherical, cylindrical, rectangular, cross-sectional, prism). Particle size analyzer is used to determine average diameter, average length in nano-meter and micro-meter and average weight.

c. Crystallinity X-ray diffraction (XRD)

Measures degree of crystallinity by calculating percentage of cellulose crystallinity index (cci). It is also used for studying optical transmission properties characterization where Diffractometer is used (measures degree of diffraction).

$$\%\mathrm{CI} = \left(\frac{\mathrm{I002} - \mathrm{Iam}}{\mathrm{I002}}\right) * 100 \quad (2.1)$$

Where 0.02 is step size (peak height of crystalline cellulose), $I_{0.02}$ is intensity value of crystalline cellulose, I_{am} is amorphous region

2.6.3 Applications of Cellulose

Cellulose has a long history of use in the pharmaceutical industry. The material has excellent compaction properties when blended with other pharmaceutical excipients so that drug-loaded tablets form dense matrices suitable for the oral administration of drugs. Polysaccharides, natural polymers, fabricated into hydrophilic matrices remain popular biomaterials for controlled-release dosage forms and uses of a hydrophilic polymer matrix is one of the most popular approaches in formulating an extended release dosage forms. This is due to the fact that these formulations are relatively flexible, and a well-designed system usually gives reproducible release profiles. Drug release is the process by which a drug leaves a drug product and is subjected to absorption, distribution, metabolism, and excretion, eventually becoming available for pharmacologic action. Crystalline micro-cellulose offers several potential advantages as a drug delivery excipient. Crystalline micro-cellulose and other types of cellulose in advanced pelleting systems whereby the rate of tablet disintegration and drug release may be controlled by micro-particle inclusion, excipient layering or tablet coating.

The very large surface area and negative charge of crystalline micro-cellulose suggest that large amounts of drugs might be bound to the surface of this material with the potential for high payloads and optimal control of dosing. Other microcrystalline materials, such as microcrystalline clays, have been shown to bind and subsequently release drugs in a controlled manner via ion exchange mechanisms and are being investigated for use in pharmaceutical formulations. The established biocompatibility of cellulose supports the use of micro-cellulose for a similar purpose. The abundant surface hydroxyl groups on crystalline micro-cellulose provide a site for the surface modification of the material with a range of chemical groups by a variety of methods. Surface modification may be used to modulate the loading and release of drugs that would not normally bind to micro-cellulose, such as non-ionized and hydrophobic.

2.7 Cellulose Composites Fabrication

The potential of micro-composites in various sectors of research and application is promising and attracting increasing investments. In the micro-composite industry, a reinforcing particle is usually considered as a micro-particle when at least one of its linear dimensions is very small. Owing to the hierarchical structure and semi-crystalline nature of cellulose, micro-particles can be extracted from this naturally occurring polymer. Native cellulose fibers are built up by smaller and mechanically stronger long thin filaments, the micro-fibrils consisting of alternating crystalline and non-crystalline domains. Multiple mechanical shearing actions can be used to release more or less individually these micro-fibrils. This material is usually called micro-fibrillated cellulose (MFC). Longitudinal cutting of these micro-fibrils can be performed by submitting the biomass to a strong acid hydrolysis treatment, allowing dissolution of amorphous domains. The ensuing nanoparticles occur as rod-like microcrystals or whiskers with dimensions depending on the source of cellulose and preparation procedure. Impressive mechanical properties and reinforcing capability, abundance, low weight, and biodegradability of cellulose microcrystals make them ideal candidates for the processing of polymer micro-composites(Kalia et al., 2011)**.** With a Young's modulus around 150GPa and a surface area of several hundred $m^2 \cdot g^{-1}$, they have the potential to significantly reinforce polymers at low filler loadings. A broad range of applications of micro-cellulose exists even if a high number of unknown remains at date. Tens of scientific publications and experts show its potential even if most of the studies focus on their mechanical properties as reinforcing phase and their liquid crystal self-ordering properties. However, as for any nanoparticle, the main challenge is related to their homogeneous dispersion within a polymeric matrix. Natural fiber composites are prepared using various composites manufacturing methods such as compression molding, injection molding, resin transfer molding, and vacuum bagging.

The production of the composites is optimized in relation to temperature, pressure, and molding time. It is often necessary to preheat the natural fibers to reduce the moisture before processing the composites. High temperatures degrade the cellulose; thus, negatively affecting the mechanical properties of the composites. Inefficient fiber dispersion in the matrix causes fiber agglomeration which decreases the tensile strength(Lu, Wu, Negulescu, & Chen, 2006). Most of the previous research on natural fiber composites has focused on reinforcements such as flax, hemp, sisal and jute, and thermoplastic and thermoset matrices. Some of these composites have been produced using matrices made of derivatives from cellulose, starch, and lactic acid to develop fully biodegradable composites or biocomposites (Corradini et al., 2009).

The main criteria for the selection of the appropriate process technology for natural-fiber composite manufacture include the desired product geometry, the performance needed, and the cost and the ease of manufacture. The fabrication methods for natural fiber composites are similar to those used for glass fibers. The most commonly used manufacturing processes are introduced in the following. Although many variants on these techniques exist, this overview gives a good indication of the production possibilities. There are other methods to fabricate biocomposites of which some are listed below.

i. Hand Laminating

The fibers are placed in a mould and the resin is later applied by rollers. One option is to cure using a vacuum bag, as then excess air is removed and the atmospheric pressure exerts pressure to compact the part. The simplicity, low cost of tooling, and flexibility of design are the main advantages of the procedure. On the other end, the long production time, intensive labor, and low automation potential, consist some of the disadvantages.

ii. Resin Transfer Molding

The resin transfer molding technique requires the fibers to be placed inside a mould consisting of two solid parts (close mould technique). A tube connects the mould with a supply of liquid resin, which is injected at low pressure through the mould, impregnating the fibers. The resulting part is cured at room temperature or above until the end of the curing reaction, when the mould is opened and the product removed. Parameters such as injection pressure, fiber content, and mould temperature have a great influence on the development of the temperature profiles and the thermal boundary layers, especially for thin cavities. This technique has the advantage of rapid manufacturing of large, complex, and high performance parts. Several types of resins (epoxy, polyester, phenolic, and acrylic) can be used for RTM as long as their viscosity is low enough to ensure a proper wetting of the fiber. An alternative variant of this process is the vacuum injection or vacuum-assisted resin transfer molding, where a single solid mould and a foil (polymeric film) are used. The vacuum-assisted resin transfer molding process is a very clean and low cost manufacturing method: resin is processed into a dry reinforcement on a vacuum-bagged tool, using only the partial vacuum to drive the resin. As one of the tool faces is flexible, the moulded laminate thickness depends partially on the compressibility of the fiber-resin composite before curing and the vacuum negative pressure.

iii. Compression Molding

Compression molding is another major technique for the construction of fiber-reinforced polymers, which involves a semi-finished composite sheet widely known as sheet molding compound (SMC) that is later moulded into the final parts by compression. For the SMC the process consists of a rolling film of resin on which fibers are added. A second film of resin is then added, so as to later be compressed in a composite sheet that may be stored for few days. To get the final product the reinforced sheet is then placed into a press to take its desired shape. Advantages of compression molding are the very high volume production ability, the excellent part reproducibility and the short cycle times. Processing times of <2min are reached during the compression molding of three-dimensional components with a high forming degree. It has also been shown that the adhesion of natural fibers and matrix resin is important in order to obtain good mechanical properties of natural fiber composites, and the mechanical properties were improved by the molding condition, the molding pressure and temperature. A big concern with compression molding that needs always to be considered is the maximum pressure before the damage of the fibers and the structure.

a. Injection Molding

Injection molding process is suitable to form complex shapes and fine details with excellent surface finish and good dimensional accuracy for high production rate and low labor cost. In the injection molding resin granules and short fibers are mixed into a heated barrel and transported to the mould cavity by a spindle. Injection molding is another process among the most important for the manufacturing of plastics/composites and can produce from very small products such as bottle tops to very large car body parts.

b. Pultrusion

Pultrusion is a continuous process to manufacture composite profiles at any length. The impregnated fibers are pulled through a die, which is shaped according to the desired cross-section of the product. The resulting profile is shaped until the resin is dry. Advantages of this process are the ability to build thin wall structures, the large variety of cross-sectional shapes and the possibility for high degree of automation. In the laboratory**,** cellulose composites can be fabricated by reinforcing of cellulose crystal in low density polyvinyl alcohol using solvent casting method and batch melt blending methods:

2.7.1 Fabrication of Cellulose Composites Using Solvent Casting

Cellulose micro-particles are obtained as stable aqueous suspensions and most investigations focused on hydro-soluble (or at least hydro-dispersible) or latex-form polymers. The main advantage is that the dispersion state of the micro-particles is kept when using an aqueous medium for the processing. After dissolution of the hydro-soluble or hydro-dispersible polymer, the aqueous solution can be mixed with the aqueous suspension of cellulosic micro-particles. The resulting mixture is generally cast and evaporated to obtain a solid micro-particles film. It can also be freeze-dried and hot-pressed. Hot distilled water is used as standard solvent and cellulose is first dispersed in this standard casting solution of hot water and ultra-sonication takes place. Glycerol is used as dispersing agent for chemically modified cellulose. The polymer solution is prepared by dissolving it in hot water which is finally to be mixed with cellulose suspension for cellulose suspension reinforcement of the polymer. After manually mixing (stirring) for required period at constant speed the solution will be poured/ casted onto a glass petri dish and freeze dried or dried at reduced pressure inside a vacuum oven to remove the solvent. The sample will be demolded to obtain sheet of cellulose – polyvinyl alcohol (PVOH) film. But if at large scale it can be extruded and injection molded. This method is selected for this research because of simplicity and manually done at lab scale without searching for automated machines.

2.7.2 Fabrication of Cellulose Composites Using Batch Melt Blending

Batch mixer is used to produce cellulose composites with and without solvents addition simply by melt blending. Combine the Plasticizer (wax/glycerol) and poly vinyl alcohol and then mix them in the batch mixer. Further adding cellulose and blending will take place. Adding compatibilizer and melted composite will be poured into molder and compressed (hot pressing) between two plates or hydraulic press and finally the compressed composite will be cooled to make the film. This method is not used for this research because of lack of extruding and mechanical molding machine.

Interfacial Interactions: All natural fibers are (in different extent) hydrophilic in nature. This is attributed mainly to the lignocellulose into their structure, which contain strongly polarized hydroxyl groups(Lu et al., 2006). These fibers, therefore, are inherently incompatible with many well-known and popular in composite manufacturing resins. Only some thermosets such as the phenol-formaldehyde and related polymers are less hydrophilic and thus less problematic.

This discrepancy leads often to the formation of ineffective interface between the fibers and the matrix. The major limitations of using these fibers as reinforcements in such matrices include poor interfacial adhesion between polar hydrophilic fibers and nonpolar-hydrophobic matrix, and difficulties in mixing due to poor wetting of the fibers with the matrix. The role of the matrix in a fiber-reinforced composite is to transfer the load to the stiff fibers through shear stresses at the interface. This process requires a good bond between the polymeric matrix and the fibers(S.NAGAKALYAN1 .ANOOPISAN . B.VIJAYKIRAN, 2015). Poor adhesion at the interface means that the full capabilities of the composite cannot be exploited and leaves it vulnerable to environmental attacks that may weaken it, thus reducing its life span. Insufficient adhesion between the polymer and the fibers results in poor mechanical properties of the natural fiber-reinforced polymer composites.

Pretreatments of the fibers can clean the fiber surface, chemically modify the surface, stop the moisture absorption process, and increase the surface roughness. These properties may be improved by both physical and chemical treatments. Treatment such as maleic anhydride, organosilanes, isocyanates, sodium hydroxide, permanganate, and peroxide are widely used.

i. Physical Treatment

Physical treatments change the structural and surface properties of the fibers and thereby influence the mechanical bonding to polymers. Corona treatment is one of the most popular techniques for surface oxidation activation through electric discharge that changes the surface energy of the cellulose fibers. Cold plasma treatment is another electric discharge technique and can have the same surface effects and increase the fiber matrix adhesion(Kalia et al., 2011**).** A traditional physical method is mercerization. In this process, the fibers are treated with an aqueous solution of a strong base (alkali treatment) so as to produce great swelling that results in changes of their structure, dimensions, morphology, and mechanical properties (Kalia et al., 2011**).**

ii. **Chemical Treatment**

Among the most effective methods of chemical treatment is graft copolymerization(Kalia et al., 2011)**.** The cellulose is treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Under the radiation, the cellulose molecule cracks and radicals are formed. Using them a suitable (compatible with the matrix) solution it is possible to create a copolymer with properties and characteristics of both the fibers and the matrix. Graft copolymers of natural fibers with vinyl monomers provide better adhesion between matrix and fiber. Gauthier et al. reported that adhesion may be improved by using coupling agents like maleic anhydride to incorporate hydroxyl groups on the matrix through hydro-philization and consequently enhancing the wetting effect of the resin on the fibers. The hydroxyl groups then interact with –OH molecules on the lignocellulosic fibers via hydrogen bonding, thus producing stronger bond. George et al. reviewed the physical and chemical treatments that may improve the fiber-matrix adhesion and manufactured biocomposites by applying an alkaline solution to the fibers. Natural fibers are mainly composed of cellulose, whose elementary unit, anhydro d-glucose, contains three hydroxyl (OH) groups. These hydroxyl groups form intra- and intermolecular bonds, causing all vegetable fibers to be hydrophilic. The alkaline solution regenerated the lost cellulose and dissolved unwanted microscopic pits or cracks on the fibers resulting in better fiber-matrix adhesion.

Coupling agents are based on the concept that when two materials are incompatible, a third material with intermediate properties can bring the compatibility to the mixture (Kalia et al., 2011). They have two functions: to react with OH groups of the cellulose and to react with the functional groups of the matrix with the goal of facilitating stress transfer between the fibers and the matrix. Numerous studies have been conducted on the use of coupling agents including organosilanes, triazine, and maleicanhydride. Mineral oils, maleated ethylene, stearic acid are some of the well-known dispersion aids of which stearic acid is best coupling agent for matrix and best solvent for cellulose._Surfactants have hydrophilic and hydrophobic ends with linking groups. A good dispersion/adhesion is gained by, dispersion agent, pretreatment, coupling agent, surface modification, polymer coating material

2.8 Composite Characterization and Evaluation of the Reinforcement

Plant fibers are basically composite materials designed by nature and consist of a collection of long and thin cells made up of hollow cellulose fibrils held together by a lignin and hemicellulose matrix (Kalia et al., 2011). The strength and stiffness of the fibers are provided by hydrogen bonds and other linkages. The overall properties of the fibers depend on the individual properties of each of its components. Hemicellulose is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber. On the other hand, lignin (or pectin) is thermally stable but is responsible for UV degradation of the fiber. On a composite, the properties of the fibers are combined with those of the matrix, which is responsible to transfer the external loads to the stiff fibers through shear stresses at the interface as well as keep the fibers together in a specific structural form. Thus, the properties of the composite are a combination of the properties of the ingredients and their prediction and estimation becomes a difficult job.

2.8.1 Biocomposite Films Characterization

Micro-biocomposite was characterized by analytical techniques like: 1)Fourier Transform Infra-red (FTIR) spectroscopy to examine state of crystallinity and functional group of the surface, 2)Scanning electron microscopy (SEM) to analyze its morphology 3) X-ray Diffraction (XRD) was employed to determine crystallinity. Tensile test specimens are prepared from cured samples. Tensile test was performed using tensile test machine. Testing the sample was for better understanding of the surface adhesive bonding at the interface of the cellulose-polyvinyl alcohol (PVOH) fibers as well as to learn the effectiveness of the alkali treatment in modifying fiber surface properties. SEM was used to observe the surface morphology and microstructure of untreated and alkali treated bagasse fibers. Fracture surface of the tensile test specimens are also studied using SEM to investigate the interfacial properties between bagasse fibers and polyvinyl alcohol (PVOH) matrix. The post-harvested agricultural biomass (sugarcane bagasse) were grounded into a coarse powder. mechanical grinding is able to physically destroyed cellulose crystals and brake cellulose chains, resulting in small crystals with short chain length.

A. Mechanical Tests

1. Tensile Strength

The foremost requirement for a designer of a polymeric product is the data on the mechanical properties. The mechanical properties are tension, compression, flexural, shear, deformation or stress, hardness, scratch, friction and abrasion. The study of stress in relation to strain in tension depicts the tensile properties of the material. Tensile test data are widely used for defining the quality of different lots of polymeric materials. They are also useful for the purpose of engineering design and understanding the characteristics of the materials(Harja & Arbut, 2008). The mechanical test will be conducted for determining the change in mechanical properties (tensile strength, Young's modulus, and stress-strain) in relation to ageing time, biodegradation time and reinforcement. The test will be determined using universal test machine and mechanical properties will be determined and used as indicators of degradation properties.

Natural fibers are about 50% lighter than glass fibers, and in general cheaper. It is widely acknowledged that natural fiber composites combine good mechanical properties with a low specific mass and offer an alternative material to glass fiber-reinforced plastics in many technical applications. The ultimate strength of any composite depends on several factors, most important of which are the properties of the components and the volume fraction. Wambua et al. studied the importance and effect of the volume fraction on the tensile strength of natural fiber composites. They reported that an increase in the fiber weight fraction produces an increase in the tensile strength. Nishino(Kargarzadeh, Ioelovich, Ahmad, Thomas, & Dufresne, 2017) studied the mechanical properties of kenaf/ poly-L-lactide (PLLA) composites. He concluded that the modulus of the composites increases with the increase of the volume fraction, but only up to a certain level. When this threshold is achieved, further increase of the fiber fraction leads to a dramatic reduction of the composite properties.

Water content has also a dramatic effect on the properties of natural-fiber composites. Espert et al. showed this effect on cellulose/polypropylene composites by submerging samples into distilled water under different temperatures. The samples were removed from the water at certain times and the water absorption was measured. The results of tensile tests showed a significant effect of the water content to the young's modulus of the samples, and an even bigger effect on the tensile strength. The studies also concluded that the effect of the water to the properties is highly influenced by the fiber content, the matrix and mainly the temperature. Thwe and Liao investigated the same effect on bamboo-fiber composites and resulted that both the tensile strength and modulus have decreased after aging in water at 25 and 75 ◦C for prolonged period. The extent of strength and stiffness loss depends upon aging time and temperature. They also concluded that tensile strength and stiffness are enhanced by inclusion of a coupling agent, maleic anhydride polypropylene, in matrix material as a result of improved interfacial bonding. Tensile test results indicated that Young's Modulus and tensile strength tended to decrease while the elongation at break had a slight increase.

$$\text{Tensile strength of the film} = \frac{\text{Maximum breaking load applied}}{\text{cross sectional area of the film}} \tag{2.2}$$

$$\text{Percentage elongation of the film} = \frac{(\text{final length at break} - \text{initial length})}{\text{initial length}} \tag{2.3}$$

$$\text{Youngs modulus} = \frac{\text{stress}}{\text{satrain}} \tag{2.4}$$

2. Impact Performance

There are only few studies known about the impact behavior of natural-fiber reinforced composites. Fiber content and fiber length have also a contribution to the impact performance of the composite. Tobias (Balaji, Karthikeyan, & Sundar Raj, 2015b) examined this influence with banana-fiber composites and concluded that smaller fiber lengths have higher impact strength which also increases for higher fiber content. Contradictorily, the fiber length was also studied by Garkhail et al. on flax/Polypropylene composites. The results showed that (as in glass fiber composites) the impact strength increases with increasing fiber length until a plateau level is reached. After that level, the impact performance drops depending on the pretreatment of the fibers and the adhesion of the fer/matrix interface.

Mueller (Arsène, M-A Savastano Jr, H. Allameh, S. M. Ghavami & Soboyejo, 2003) investigated the effect of several material parameters on the impact strength of compression-molding components of hemp-,bagasse- flax- and kenaf-polypropylene composites. The studies showed a strong influence of the thermal process conditions during the molding. He concluded that for every material studied there is an optimum temperature that results to a peak of the impact strength. Higher and lower processing temperature resulted in lower mechanical values that could be explained by a thermal decomposition of the fibers. Strong impact of the fiber fineness was also proved, with the impact performance getting higher from composites with fiber of higher fineness. The effect of temperature and water on the impact properties of natural-fiber thermoplastics were reviewed by De Bruijn(Wulandari, Rochliadi, & Arcana, 2016) and showed not significant effect on the impact properties of the composites. However, the results showed that the impact strength was 20 to 25% to that of glass-reinforced thermoplastics.

A significant contribution of coupling agents on the impact strength has also been reported. When the composites have no coupling agent, a part of the energy is lost in the interface, by for example debonding and friction effects. Maleic-anhydride-treated jute composites showed higher impact strength than untreated samples made out of the same process.

3. Fatigue Crack

The cyclic loading of natural fiber composites is still poorly investigated. Gassan(Sahari & Sapuan, 2011) investigated the fatigue behavior of flax and jute epoxy resin composites. Fiber type, textile architecture, interphase properties, and fiber properties and content were found to affect the fatigue behavior strongly. It was also found that natural fiber-reinforced plastics with higher fiber strength and modulus, stronger fiber-matrix adhesion, or higher fiber fractions possess higher critical loads for damage initiation and higher failure loads. In addition, damage propagation rates were reduced. Furthermore, unidirectional composites were less sensitive to fatigue-induced damage than woven reinforced ones. Savastano et al. presented the results of experimental studies of resistance-curve behavior and fatigue crack growth in cementitious matrices reinforced with natural fibers such as sisal, banana, and bleached eucalyptus pulp. Fatigue crack growth was observed to occur in three stages: an initial decelerated growth, a steady-state growth, and a final catastrophic crack growth. In the case of the composites reinforced with sisal and banana fibers, most of fatigue life was spent in the second stage of steady-state crack growth. The results showed that fatigue crack growth in the composites occurred via matrix cracking, crack deflection around fibers, and crack-bridging by un-cracked fibers and ligaments, whilst fiber pullout was also observed.

The fatigue performance of sisal/epoxy composites was also studied by Towo and Ansell(Menezes et al., 2016) which looked into the effect of surface modification on the fatigue performance of the composite. The results show that NaOH surface treatment has a significant effect on the tensile modulus and strength of the material, but the fatigue life is not highly influenced, especially in low stress levels. Their conclusion states that the behavior of sisal fiber composites is similar to that of conventional synthetic fiber composites and static and fatigue strengths are suitably high for many commercial applications. Towo et al. also studied the fatigue properties of flax/polyester with alkali-treated and untreated fibers. In this case they observed a high influence of the treatment on the fatigue life of the components and they also underlined that the polyester matrix samples had lower life than the epoxy samples.

B. FTIR Spectroscopy

The FTIR measurement will be conducted to examine and evaluate state of degradation or modification of reinforced polymer by functional group identification. This will helps to evaluate the effectiveness of the reinforcement as a function of morphology change or function group change.

C. Average Degree of Polymerization

During degradation process, polymers shows change in molecular weight due to chain scission or cleavage of bonds. This parameter can be used to evaluate effectiveness of the reinforcement whether the reinforcement will makes the composite more exposed to degradation or not. Hence, the change in average molecular weight will be measured using capillary viscosity method by dissolving in suitable solvent such as xylene or dichlorobenzene.

D. Water Absorption Test

Mechanical properties and moisture absorption behavior are related to each other. Films which absorb less water will show better mechanical properties(Kumar, Negi, Bhardwaj, & Choudhary, 2013). Sensitivity of plastic materials to water absorption depends on their chemical nature. The process involved in the water absorption by plastic materials depends on two parameters: the diffusion coefficient and the equilibrium uptake. The former governs the kinetics of water absorption and is highly temperature-dependent. Equilibrium uptake is not affected by temperature. The standard methods for water absorption are mostly short-term tests; hence the results obtained are limited only to surface diffusion phenomena and not equilibrium throughout the thickness of the test specimen. Water absorption capacity depends on composition and material type. To evaluate effectiveness of reinforcement, water absorption test will be done to determine the water absorption capacity of the reinforced polypropylene. The water absorption test will be conducted by immersing beaker containing distilled water (water immersion test) following standard methods. Percentage increase in weight during immersion in distilled water at room temperature is:

$$\text{Water absorption capacity} = \left(\frac{\text{Wi}-\text{Wd}}{\text{Wd}}\right) * 100 \qquad (2.5)$$

Where w_i and w_d are weight after and before immersion respectively.

E. Scanning Electron Microscopy (SEM)

To evaluate effectiveness of reinforced polyethylene in relation to surface morphology and surface erosion Scanning Electron Microscopy will be employed. This will helps to analysis degradation morphology of the dispersed polymer matrix, homogeneity distribution of cellulose crystal in the matrix such as particle dispersion (shape, size, agglomeration, orientation).

F. Accelerated Aging and Biodegradation Test

Biodegradation test is characterizing the aged samples, all the samples will be then exposed to biodegradation burying them deep in the soil. Both composite films and pure polypropylene (reference material) will be buried in soil for degradation study at room temperature and in 25cm depth, washed and dried in oven. The buried samples dug out after some time intervals(Acharya, Mishra, & Mehar, 2011). The mechanical properties of the samples such as Tensile and flexural strength dynamic mechanical analysis (DMA) will be then measured. In case of accelerated Aging Test, reference samples and composite films will be subjected to accelerated aging in climatic chamber (oven) and withdraw successively from the chamber after exposing them for period of time. There will be characteristic changes and they will be measured in order to evaluate the effectiveness and efficiency of the cellulose dispersed in polypropylene matrix. Mechanical (strength, elasticity, fragility, stress, etc.), chemical(acidity, carbonyl content, degree of polymerization, etc.) and physical change (viscosity, yellowing, fading, etc.) will happen which will be measured characterized using analytical techniques

2.8.2 Evaluation of Effectiveness of Reinforcement

The measured data and thee results will be analyzed using comparative and cluster analysis methods. The comparisons will be done between reinforced polyethylene as well as with the reference sample. The comparative analysis and clustering the results will be performed for each groups and before and after before and after aging and biodegradation test.

2.9 Applications of Polymer Composites

The charm of the use of synthetic fibres in polymer composites is fading, because these are expensive, non-biodegradable, and pollute the environment. There is an increasing movement of scientists and engineers who are dedicated to minimizing the environmental impact of polymer composite production. Environmental footprints must be diminished at every stage of the life cycle of the polymer composite. Using natural fibers with polymers based on renewable resources will allow many environmental issues to be solved. By embedding bio-fibers with renewable resource based biopolymers such as cellulosic plastics; polylactides; starch plastics; polyhydroxy alkanoates (bacterial polyesters); soy-based plastics, the so-called green biocomposites could soon be the future. Nowadays, biocomposites have been the subject of extensive research, specifically in construction and building industry due to their many advantages such as lower weight, and lower manufacturing costs. Currently, not only builders, but also many home owners are interested in using biocomposites for different products such as decking, fencing, and so on. Biocomposites may be classified, with respect to their applications in building industry into two main groups: structural and nonstructural biocomposites(Kalia et al., 2011).

Structural Application: A structural Biocomposites can be defined as one that is needed to carry a load in use. For instance, building industry, load-bearing walls, stairs, roof systems, and subflooring are examples of structural biocomposites. Structural biocomposites can range broadly in performance, from high performance to low performance materials. Bio-based composite materials have been tested for suitability in roof structure. Structural beams have been designed, manufactured, and tested, yielding good results. Soy oil-based resin and cellulose fibers, in the form of paper sheets made from recycled cardboard boxes may be used for the manufacture of the composite structures.

Stay-in-place bridge forms are utilized to span the distance between bridge girders. The Stay-in-place forms made from biocomposites have many benefits in comparison to steel forms. Biocomposite-based SIP forms are porous or breathable. Therefore, this lets water to evaporate through the form and to avoid any rebar corrosion. The form is also biodegradable; a bio-based form has the potential to break down in the future, allowing underside inspection of the bridge deck. In addition, the form is lighter compared to a steel form, allowing faster and cheaper installations.

Nonstructural Application: A nonstructural biocomposites can be defined as one that need not carry a load during service. Materials such as thermoplastics, wood particles, and textiles are used to make this kind of Biocomposites. Nonstructural biocomposites are used for products such as ceiling tiles, furniture, windows, and doors. Wood fiber plastic composites are made in standard lumber profile cross-section dimensions in exterior construction. These bio-products are utilized as dock surface boards, deck, picnic tables, landscape timbers, and industrial flooring. Many manufacturers recommend that biocomposites need gaps on both edges and ends for their thermal expansion. Furthermore, wood-based bio-products are gapped for expansion due to the moisture absorption.

Biocomposites are utilized for the construction of composite panels. There are three types of panels: fiberboard, particleboard, and mineral-bonded panels. Bagasse fibers are used for particleboards, fiberboards, and composition panel production. Cereal straw is the second most usual agro-based fiber in panel production. The high percentages of silica in cereal straw make them naturally fire resistant. Also, the low density of straw panels has made them strong. Results show that houses built by these panels are resistant to earthquake. Straw is also used in particleboards. Rice husks are also fibrous and need little energy input to make the husks ready for use. Rice husks or their ash are used in fiber cement blocks and other cement products. The presence of rice husks in building products helps to increase acoustic and thermal properties.

At micro level, micro-composites the potential applicability of micro-cellulose is widely extended. Applications of micro-cellulose are mainly considered to be in paper and packaging products, although construction, automotive, furniture, electronics, pharmacy, and cosmetics are also being considered. For companies producing electroacoustic devices, micro-cellulose is used as a membrane for high quality sound. Additionally, it is applied in membrane for combustible cells (hydrogen); additives for high quality electronic paper (e-paper); ultra-filtrating membranes (water purification); membranes used to retrieve mineral and oils(Kalia et al., 2011), and nowadays, micro-cellulose has been greatly discussed and researched a huge variety of applications. The high strength and stiffness as well as the small dimensions of micro-cellulose may well impart useful properties to composite materials reinforced with these fibers, which could subsequently be used in wide range of applications.

i. Electronic Industry

Among various applications studied so far, which has already reached the level of practical use is related to sound/audio diaphragms, micro-cellulose has been found to bear two essential properties: high sonic velocity and low dynamic loss. In fact, the sonic velocity of pure film was almost equivalent to those of aluminium and titanium. Jonas and Farah stated that SONY had already been using it in headphones diaphragm. The micro-cellulose diaphragms are developed by dehydration and compressed to a thickness of 20 microns in a diaphragm die. The advantage of the ultrathin micro-cellulose diaphragm is that it can produce the same sound velocity as an aluminum or titanium diaphragm, along with the warm, delicate sound that a paper diaphragm provides. Trebles are sparkling clear, and bass notes are remarkably deep and rich in these types of headphones. Digital Displays. Cellulose has always been the prime medium for displaying information in our society; nowadays, efforts have been made to find dynamic display technology, for example in electronic paper. Micro-cellulose is dimensionally stable and has a paper-like appearance which puts it into the leading role for the electronic paper’s basic structure. Additionally, since cellulose microcrystalline is a low-cost, readily abundant material from a renewable and sustainable resource, its use provides a substantial environmental advantage compared with other materials.

ii. Medical

Recently, microcrystalline has been called as the eyes of biomaterial highly applicable to biomedical industry which includes skins replacements for burnings and wounds; drugs releasing system; blood vessel growth; nerves, gum and dura mater reconstruction; scaffolds for tissue engineering; stent covering and bone reconstruction. Figure 2.9 shows some applications of microcrystalline within biomedical field. Micro-cellulose mats are very effective in promoting autolytic debridement, reducing pain, and accelerating granulation, all of which are important for proper wound healing. These micro-bio-cellulose membranes can be created in any shape and size, which is beneficial for the treatment of large and difficult to cover areas of the body.

Barud(Aboody, 2013)has developed a biological membrane with bacterial cellulose and standardized extract of propolis. Propolis has many biological properties including antimicrobial and anti-inflammatory activities. All the above mentioned characteristics present, which make the membrane a good treatment for burns and chronic wounds. Odontology is challenged to find ideal materials to replace the bones in several procedures, as bones malformation, maxillary, and facial deformities. The biggest challenge is the loss of alveolar bone. Micro-cellulose having suitable porosity which gives the mat an infection barrier, loss of fluids, painkiller effect, allows medicines to be easily applied and it also absorbs the purulent fluids during all inflammatory stages, expelling it later on in a controlled and painless manner.

Polyvinyl alcohol (PVOH) is a hydrophilic biocompatible polymer with various characteristics desired for biomedical applications. It can be transformed into a solid hydrogel with good mechanical properties by physical crosslinking, using freeze-thaw cycles. Hydrophilic micro-cellulose fibers of an average diameter of 50 nm are used in combination with PVOH to form biocompatible micro-composites. According to Millon and Wan, the resulting micro-composites possess a broad range of mechanical properties and can be made with mechanical properties similar to that of cardiovascular tissues, such as aorta and heart valve leaflets. On their studies, the stress-strain properties for porcine aorta are matched by at least one type of PVOH/micro-cellulose micro-composite in both the circumferential and the axial tissue directions. A PVOH/micro-cellulose micro-composite with similar properties as heart valve tissue is also developed. Relaxation properties of all samples, which are important for cardiovascular applications, were also studied and found to relax at a faster rate and to a lower residual stress than the tissues they might replace. So, finally the new PVOH/micro-cellulose composite is a promising material for cardiovascular soft tissue replacement applications. Thus, the prepared micro-cellulose/PVOH composite frames are suitable for cell adhesion/attachment, suggesting that these scaffolds (skeletons) can be used for wound dressing or tissue-engineering applications.

3. Methodology

3.1 Proximate Analysis of raw bagasse

1. Approximate density test

Apparatus: analytical balance, size reduced bagasse, beaker, piece of paper

Method: The bulk density was determined by calculating the ratio of the mass to the volume occupied. A container of known volume was weighed and filled with each sample and reweighed. Because of void space between fibers, it was very difficult to find the exact value of bulk density. The difference between the initial weight of the container and the final weight was the weight of the sample. The bulk density was calculated from the relationship:

$$\text{Bulk density} = \frac{\text{Wbc}-\text{Wc}}{\text{Vbc}} \tag{3.1}$$

Where: Wbc = Mass of the sample and the container, Wc = Mass of the container and Vbc = Volume occupied by the bagasse.

2. Determination of Ash Content

Materials and Chemicals: crucible, furnace, analytical balance, size reduced bagasse, piece of paper

Method: Ash content was determined using the ASTM D 2017 (1998). 3g of bagasse placed in a pre-weighted crucible was incinerated in a muffle furnace at 760 ^{0}C until complete ash was achieved (8minutes). The crucible was then transferred into a desiccators for cooling. Three replicates were made. The cooled samples were then weighed. The ash content was calculated using equation (3.2).

$$\text{Ash content}(\%) = \left(\frac{(\text{W2}-\text{W0})}{\text{W1}-\text{W0}}\right) * 100 \tag{3.2}$$

Where: W_0 = Weight of the crucible, W_1 = Weight of the crucible + sample before incineration and W_2 = Weight of the crucible + sample after incineration. Weight difference between dried fiber sample and sample after calcination/combustion without oxygen/ at 800 ^oC for 4hr.

3. Determination of Moisture Content

The moisture content of sugarcane bagasse was determined by the oven drying method. This was carried out at temperature of 103 ± 2 ^oC in accordance with the ASTM D 1037 (1991). It could also be determined directly using moisture analyzer. The moisture content was calculated using equation (3.3).

$$\text{Moisture of bagasse } = \left(\frac{\text{Wi}-\text{Wf}}{\text{Wi}}\right) * 100 \qquad (3.3)$$

Where: Wi = initial mass of bagasse, Wf = final mass of bagasse

4. **Determination of Volatile Matter**

Materials and chemicals: Furnas, desiccator, analytical balance, piece of paper, bagasse

Method: The volatile matter was determined according to ISO 562/1974. 2g of the samples of the bagasse was incinerated in crucible at temperature of 800 ^{0}C for 5 minutes and allowed to cool down in desiccator. Based on dry basis the volatile matter content can be calculated by using equation (3.4) and the result will be discussed in chapter four

$$\%\text{Volatile Matter Content} = \left(\frac{\text{initial weight}-\text{final weight}}{\text{initial weight}}\right) * 100 \qquad (3.4)$$

3.2 Procedures for Extraction of Bagasse Cellulose

Raw bagasse was taken from Wonji sugar factory and it was washed by distilled water and sun dried until it gets constant weight. The sun dried bagasse was reduced in size using size reducing unit operation. Size reduction is very important so that unexposed parts of the bagasse are easily exposed to the solvents and ready for extraction. Washing with distilled water is used for removing water solubles and dirty particles on the interface to facilitate direct contact between fibers and chemicals so that the max chemical reaction occurs. Washing with distilled water was until water color change is stopped by adding and removing distilled water again and again and then bagasse samples were dried at 60 ^{o}C for 12 h. Generally, the following procedures were used to extract the cellulose.

1. **Dewaxing and Extractives Removal**

Materials and chemicals: Soxlet extractor, oven, beakers, trays, eye glass, gloves, plastic bags, aluminium foil, benzene, methanol analytical balance, absolute ethanol, piece of paper, dried bagasse

Method: 200g of the dried bagasse was dewaxed with Benzene: methanol with a ratio of 2:1 v/v 70 ^{o}C for 6h and extracted with 96% absolute ethanol at 60 ^{o}C for 14h in Soxlet extractor. The time counting starts when temperature reaches 60^{o}C. After removal of the extractives, the residue was oven dried until constant weight is gained at 105 ^{o}C. The mass of extractives were then Calculated (% w/w) by weight difference between extractive-free lignocellulose biomass and extractive-loaded bagasse. That is two hundred minus mass of extractive-free lignocellulose biomass.

2. Delignification and Bleaching

Materials and chemicals: water bath, oven, analytical balance, beakers, trays, eye glass, gloves, plastic bags ,aluminium foil, piece of paper, extractive free dried bagasse

Method: The sample bagasse which was free of extractives was oven dried until it gets constant weight and 40g was taken for delignification and bleaching using glacial acetic acid acidified 0.75% w/v $NaClO_2$ aqueous solution to a pH of 4 at different temperatures(50°C - 90°C) for different time duration from (1hr-3hr) until the holocellulose sample exhibited a pale yellow color(see appendix E). 25ml $NaClO_2$ was used per gram of Extractive free fiber (v/w). On the other hand, the ratio of sugarcane bagasse to acidified solution of $NaClO_2$ is 1:25(w/v). By vacuum filtration of suspension, the bleaching process was repeat four times until the fiber color becomes white or yellow color disappears and then continuously washed until PH was nearly equal to seven (pH $\approx$ 7). Any material passing through the filter paper was recovered by vacuum filtration on another pre-weighed filter paper. In each case, the beaker was cooled and the soluble lignin was decanted from the insoluble holocellulose whereas the holocellulose sample was vacuum-filtered until it changes to white while the soluble lignin was removed in the filtrate. After removal of lignin and bleaching, the bleached fiber was oven dried at 55°C for 24hr until constant weight was maintained and then the mass of holocellulose was weighed which is equal to the sum of the mass of hemicellulose and α cellulose. Lignin content was Determined by subtracting the holocellulose mass (g)(dry basis) from Extractive free fiber mass(g). Mechanical Stirrer was 150 rpm.

3. Hemicellulose Removal

Materials and chemicals: water bath, vacuum filter, oven, trays, analytical standard balance, eye glass, gloves, plastic bags, aluminium foil, piece of paper, extractive freed and de-lignified bagasse(hollo-cellulose)

Method: The dried hollo-cellulose was treated with varying concentration of aqueous solution of sodium hydroxide (8%w/v-20%w/v) with the ratio of 1:10 solid: liquid loading(w/v) in water bath at different temperatures(40 °C-60 °C) under continuous vigorous stirring by varying reaction time from(1hr-5hr). The suspension was gradually cooled to room temperature and then filtered through vacuum filtration and washed repeatedly by distilled water until it becomes neutral. This step was repeated until the α-cellulose was free of acid as indicated by blue litmus paper. PH can be adjusted by glacial acetic acid. The residue was transferred to a pre-weighed aluminium dish having aluminium foil and dried to a constant weight at 105 °C in an oven for 6h. The mass of hemicellulose was determined by subtracting the dried mass of cellulose from the feed holocellulosse mass (dry basis). Pulp total yield at room temperature is calculated by dividing pulp mass after pulping(g) dry basis by bagasse mass(g) dry basis times 100%(equation 3.5) and the result would be discussed in under results and discussion.

$$\text{Pulp total yield} = \left(\frac{\text{m}}{\text{M}}\right) * 100\% \tag{3.5}$$

Where: m is pulp mass after pulping(g) dry basis, M is bagasse mass before pulping(g) dry basis and finally the purified cellulose was air dried and stored in air tight poly bag for characterization.

3.3 Cellulose characterization

i. Fourier Transform Infra-Red Spectroscopy(FTIR)

Materials: Fourier Transform Infra-Red Spectroscopy(FTIR)

Method: This test was done at Addis Ababa University science faculty department of chemistry. FTIR is used to see formation of new bonds during hydrolysis process by analyzing functional groups and shows removal of lignin and hemicellulose (tests formation and changes in functional groups). Wave length (λ) is used in Fourier transformation infrared spectrometer analysis. The picture and the results will be discussed in next chapter. The results, pictures.

ii. Morphology

Materials: Scanning electron microscopy and Dynamic light scattering

Method: These tests were done at Leather Industry Development Institute. It is the study of structure of cellulose and Dynamic light scattering(DLS) was used as particle size analyzer(PSA) to test for the average particle size(average diameter(μm), average length (μm) and average weight(g)), the shape(spherical, cylindrical, rectangular, cross-sectional, prism).

iii. Crystallinity test

X-ray Diffraction (XRD)

Measures degree of crystallinity by calculating percentage of cellulose crystallinity index (CCI). It is also used for studying optical transmission properties characterization where Diffractometer is used (measures degree of diffraction). Equation (2.1) was used for calculation of crystallinity index.

3.4 Biocomposite Material Fabrication

Materials and Chemical reagents: water bath, analytical standard balance, eye glass, gloves, plastic bags, stirrer, beakers, glass type petri dish, oven, trays, aluminium foil, distilled water, polyvinyl alcohol, micro-cellulose, Maleic anhydride and glycerol. All chemicals and reagents used in this study were of analytical grade and commercially available

Method: Experimental design looks like the following using design expert software Box Behnken method which is best to reduce number of experiments and best for optimization of the process conditions when compared with other experimental design methods. Solvent casting method was chosen for this experiment. Polyvinyl alcohol and micro-cellulose reinforced composite films were prepared using a solvent casting method. Water bath was adjusted to the required temperature and mixing time needed for each sample. Neat polyvinyl alcohol solution(control sample) was prepared by dissolving 5g of Polyvinyl alcohol powder in 50ml of hot distilled water which is at a weight ratio of 1:9 (polyvinyl alcohol : water) or 10%wt of polyvinyl alcohol solution at different temperatures under vigorous mechanical stirring in a covered beaker until the polymer had completely dissolved.

The solution was kept under stirring to reach room temperature. After the solution was cooled to room temperature, it was sonicated overnight so as to remove bubbles from the solution (degassing) and then 30 mL of it was casted on glass petri dish just after small amount of glycerol/ gelatinizer/plasticizer(30% (w/w)) was added on the surface of petri dish so as to prevent sticking of the solution to the surface of petri dish and dried at $50^{o}C$ to form a reference film(biocomposite material from pure matrix). It was kept for 2-3 days until constant weight of the samples were achieved.

In similar way, polyvinyl alcohol was dissolved in hot distilled water and polymer solution was prepared at required (favorable) temp of $80^{o}C$ for casting with the fibers. After the solution was cooled to room temperature, it was sonicated overnight so as to remove bubbles of the solution. Cellulose fibers were dispersed in this casting solution of polymer at different concentration of fiber(0%, 4% and 8%), reaction time(30min, 60min and 90min) and blending temperatures($70^{O}C$, 80 ^{O}C and 90 ^{O}C) to form suspensions of PVOH/cellulose fiber as per the experimental design designed by design expert. The suspension was manually vigorously mixed at constant speed for required period (time) or until totally homogeneous solution is formed. Continuous stirring was important for the polymer to penetrate into the cellulose network. During stirring, the micro-composite suspensions were left uncovered to allow excess water to evaporate. After the suspension was cooled to room temperature, it was sonicated overnight so as to remove bubbles of the suspension(degassing) and to make uniform dispersion of the fibers(optimize dispersion) at room temperature. The mixtures were stored in the refrigerator; any given batch was stored for no longer than 1 week prior to its use. Glycerol served as dispersing agent, as plastisizer and sticking preventer simply by filling only the cover surface of petri dish. Small amount of glycerol was added to prevent sticking to the glass petri dish. The petri dish was filled by blended solution with controlled levelling(visualy) for expected thickness of composite to be developed. The samples were dried at $50^{o}C$ for 2-3 days until constant weight of the samples were achieved to avoid the plasticizing effect of moisture during characterization. The resultant films were peeled(demolded) from the casting surface and place in desiccator for three days before mechanical characterization. Putting in desiccator helps the films not to absorb moisture from nearby environment. The tensile strength, elongation at break, water absorption capacity response results would be discussed and summarized in the next chapter.

3.5 Characterization of Biocomposite Films and Evaluation of Reinforcement

This is done for pure matrix composite and cellulose reinforced biocomposite and then compared in terms of moisture absorption, tensile strength, morphology and thermal property. Scanning electron microscopy and thermal gravimetric analyzer were used to test morphology and thermal property of a composite.

3.5.1 Biodegradation Tests

Biodegradation test is deep burying in the soil and was carried out at ambient temperature Specimens of each composite were placed in a series of perforated boxes of strong polyvinyl chloride (water packaging) containing moisturized soil. The specimens (40 × 10 mm) were buried 150 mm beneath the surface of soil which was regularly moistened with distilled water. The samples were removed at predetermined time points, washed with water several times in order to ensure the stop of the degradation then dug out of the soil after 18 days and dried at room temperature to a constant weight, and then were stored in darkness until testing. The specimens were weighed on the analytical balance in order to determine the average weight loss using equation(3.6).

$$\text{Weight loss} = \left(\frac{\text{Wo}-\text{Wt}}{\text{Wo}}\right) * 100 \tag{3.6}$$

Where Wo is the initial mass and Wt is the remaining mass at any given time, t. All results are the average of three replicates. The result and discussion would be in chapter four. The buried samples will be dug out after some time intervals.

3.5.2 Characterization of Biocomposite Films

1. **Water Absorption Test**

One of the factors affecting Plastic properties is water absorption capacity which depend on composition and type of material. Addition of additives (reinforcement) with micro-cellulose results in affinity to water. To evaluate effectiveness of reinforcement, water absorption test will be needed to determine the water absorption capacity of the reinforced Polyvinyl Alcohol (PVOH). The water absorption test will be conducted by immersing beaker containing distilled water (Water Immersion Test) following standard methods. During this, the percentage increase in weight during immersion in distilled water at room temp will be calculated as follows.

$$\text{Water Absorption Capacity} = \left(\frac{\text{Wi}-\text{Wd}}{\text{Wd}}\right) * 100\% \tag{3.7}$$

Where Wi = wet weight after immersion Wd = dry weight before Immersion

This is used for comparing biocomposite materials of pure polyvinyl alcohol with differently concentrated (cellulose reinforced) biocomposite materials. Since cellulose is highly hydrophilic, it will immediately start to absorb water from the air/environment when composites are cured at high temperature.

2. FTIR Spectroscopy

The FTIR measurement was be conducted at Addis Ababa University faculty of science department of chemistry to examine and evaluate state of degradation or modification of reinforced polymer by functional group identification. This will helps to evaluate the effectiveness of the reinforcement as function of morphology change or function group change.

3. Mechanical Test

The mechanical test was conducted at Leather Industry Development Institute and helps to determine the change in mechanical properties (tensile strength, Young's modulus, stress- strain, elongation) in relation to ageing time, biodegradation time and reinforcement. The tests were done as per ASTM standards using universal test machine and mechanical properties were determined. Equations (2.2) and (2.3) were used for calculation of tensile strength and elongation at break.

4. Scanning Electron Microscopy (SEM)

This test was done at LIDI and it result was very essential to evaluate effectiveness of re-inforcement by testing surface morphology and the net worked structure of the composites or the interaction between the matrix and the micro-cellulose. The morphology of the composite and uniformity of dispersion of micro-cellulose(shape, size, agglomeration, orientation) in the matrix were tested by Surface Erosion Scanning Electron Microscopy. Whereas Scanning electron microscopy(SEM) was used to see structural networking of the biocomposites.

3.5.3 Evaluation of Effectiveness of Reinforcement

The measured data and the results will be analyzed using comparative and cluster analysis methods. The comparisons will be done between reinforced Polyvinyl Alcohol (PVOH) as well as with the reference sample. The comparative analysis and clustering the results will be performed for each groups and before and after before and after aging and biodegradation test.

4. Results and Discussions

4.1 Proximate Analysis of Raw Sugarcane Bagasse

4.1.1 Bulk Density Approximation

The average bulk density of bagasse was calculated using equation (3.1) after the samples were dried and maintained at constant weight for different fifteen samples(fifteen duplicates). Average bulk density of sugar cane samples was 274.93kg/m^3 and it is in the range 320kg/m^3 to 250kg/m^3 given in the literature. The bulk density reduces as the moisture content reduced by increasing the drying time and therefore, to get constant bulk density the weight of samples must be constant. Low density improves handling and transportation of the material.

Table 4.1 Mean bulk density of bagasse

samples	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
Bulk density (Kg/m^3)	275	275	274.8	276	275	275	275.3	275.2	274.9	274.7	275	275.1	275.01	274	273.9
mean value	274.93														

4.1.2 Moisture Content

The moisture contents of crushed bagasse samples as received from the mill were analyzed using moisture content analyzer at 105^{o}C and were found to range from 36% to 65% for ten duplicates of samples tested on the same date. Literature value states moisture content in the range of 45% – 55%. The mean moisture content of these randomly selected bagasse samples of 1 gram each was 50.9% which is the desired value stated in the literature.

Table 4.2: Mean moisture content(%) of sugarcane bagasse samples

Samples	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	Mean value(%)
Moisture content(%)	54	40	58	50	44	65	63	38	36	61	50.9

4.1.3 Ash Content Determination

This test was done after the bagasse samples were achieved constant weight. Ash content was determined using the ASTM D 2017 0.4g of bagasse placed in pre-weighted crucible was incinerated in a muffle furnace at 760^{o}C until complete ash was achieved. The crucible was then transferred into desiccator for cooling. Equation 3.2 was used to calculate ash content and Table 4.3 shows the result obtained from lab work. The average ash content for six samples was determined to be 7.39(%).

Table 4.3 Bagasse ash content

Samples	S_1	S_2	S_3	S_4	S_5	S_6	Mean value
Massafter burnt(g)	0.030	0.028	0.029	0.029	0.029	0.03	
Ash content (%)	7.52	7.01	7.48	7.45	7.4	7.5	7.39

4.1.4 Determination of Volatile Matter

The volatile matter was determined according to ISO 562/1974. 2.4 g of bagasse samples were incinerated in crucible at temperature of 800 ^{0}C for 5 minutes and allowed to cool down in desiccator. Based on dry basis the volatile matter content was calculated using equation 3.4 and the result shown that the mean value of the samples was 74.66% Table 4.4 was percentage volatile matter for equal amount of samples (2.4g) and six duplicates.

Table 4.4 Bagasse volatile matter content.

Samples	S_1	S_2	S_3	S_4	S_5	S_6	Mean value
Mass after fired(g)	1.67	1.87	1.78	1.77	1.74	1.63	
Volatile matter (%)	82	77.8	74	73.75	72.4	68	74.66

4.2 Extraction of Cellulose from Bagasse

The results gained and the plots taken from design expert the relationship between variables and the output responses are all given by table (4.5). The micro-cellulose suspension obtained from sugarcane bagasse after extractives removal, delignification bleaching and alkaline treatment was lighter than the delignification and bleaching steps. This was due to the removal of the extractives, lignin and hemicellulose contents. The amount of lignin, hemicellulose and α-cellulose(%) in suspension were calculated by drying in the oven for 24 hours at 105 °C and using mass difference equation. The variation in yield for each experiment is attributed to the increase in sample handling during processing especially in relation to recovery of insoluble material. Average yield values for lignin, hemicellulose and α-cellulose in percentage(w/w) with respect to the initial amount of dried values used were found to be 22.25%, 22.63% and 36.65 %.

Delignification for various duration following the optimum extraction conditions(24hr and 77^{O}C) resulted in lignin yield in the range of (18.7%-23.8%) where as that of the literature range was (15–35%). From design expert analysis result, the lowest and maximum yields were when time and temperature are (1hr, 50 ^{O}C) and (3hr, 90

^{O}C) respectively. The yields recorded were in the published range of 15-35%. The lignin removal rate after an hour was very slow and finally stops when time duration approaches 3hr and temperature was 90 ^{O}C which indicates that the delignification was not being completed during the first hour of delignification period as most literatures recommended. Generally, the high lignin values recorded seems to suggest that there was inefficient separation of the insoluble holocellulose from the soluble lignin following delignification. This step was affected by vacuum filtration and was considered the most difficult step in the Jayme-Wise procedure. A considerable effort had to be made to recover “fines” from the filtrate. It is possible that some “fines” that could not be recovered using the method employed were lost to the soluble lignin fraction thereby contributing to an enhancement of the lignin levels.

Alkaline hydrolysis of the holocellulose for various time duration, base concentration and temperature removed hemicellulose content and gave α-cellulose yield which is the highest content. The lower α-cellulose levels obtained for several experiments compared to the published values of (40–55%)% for bagasse can be attributed to the low holocellulose recovery due to enhancement of the lignin recovery. literature values are more or less a little greater than the obtained values of alpha cellulosse this is expected to be due to loss of sample occurred during processing of duplicates. For cellulose extraction, as it was observed from design expert graphs, the yield increases with long reaction time and higher base concentration and temperature effect is not that much significant. The base breaks cellulose chains and separates the crystalline and amorphous parts. This process breaks down the disordered and the amorphous parts of cellulose which is hemicellulose and removed it by dissolving. Finally alpha cellulose was produced. As expected, the cellulose content in sugar cane bagasse was the highest. There are lot of factors involved for the results including the method used to measure chemical compositions and the origin of the cell wall structure or sugarcane variety.

Figure 4.1: Extracted cellulose sample after dried

4.2.1 Extraction Results and Plots

1. **Extractives Removal**

Table 4.5 Percentage of extractives

Std	Run	Time(hr)	Temperature(°C)	Extractives(%w/w)
1	16	8	70	13.8
2	2	24	70	16.8
3	8	8	70	13.8
4	3	24	70	16.8
5	10	8	40	13.4
6	5	24	40	15.5
7	17	8	100	15.1
8	4	24	100	16.3
9	6	16	40	14.2
10	15	16	40	14.2
11	13	16	100	15.3
12	14	16	100	15.3
13	1	16	70	16.2
14	11	16	70	16.2
15	7	16	70	16.2
16	12	16	70	16.2
17	9	16	70	15

The results from extraction steps clearly indicated that an optimum Soxhlet extraction time of 24h is required for removal of extractives at the optimum temperature of 77°C as shown by design expert results and plots. It is clearly observable that as extraction time increase the amount of extractive obtained also increases. Similarly with increment in temperature, it also increases but finally it tends to decrease because, as temperature exceeds boiling point of the solvent the solvent tends to totally evaporate. The following two figures shows that the used data and the values of the responses are in the expected ranges.

Figure (4.2) indicates that increasing time and temperature increases extractives but only to limited temperature. This implies there is interaction between the variables and the interaction plot for temperature and time is shown by figure (4.3). Figure (4.3) reveals that the interaction between the two variables temperature and time duration. Time is directly proportional to the amount of extractives whereas temperature increment further reduces the yield of desired output. Therefore, even if time has direct relation to extraction, due to temperature interaction after some time increment amount of extractives is forced to decrease.

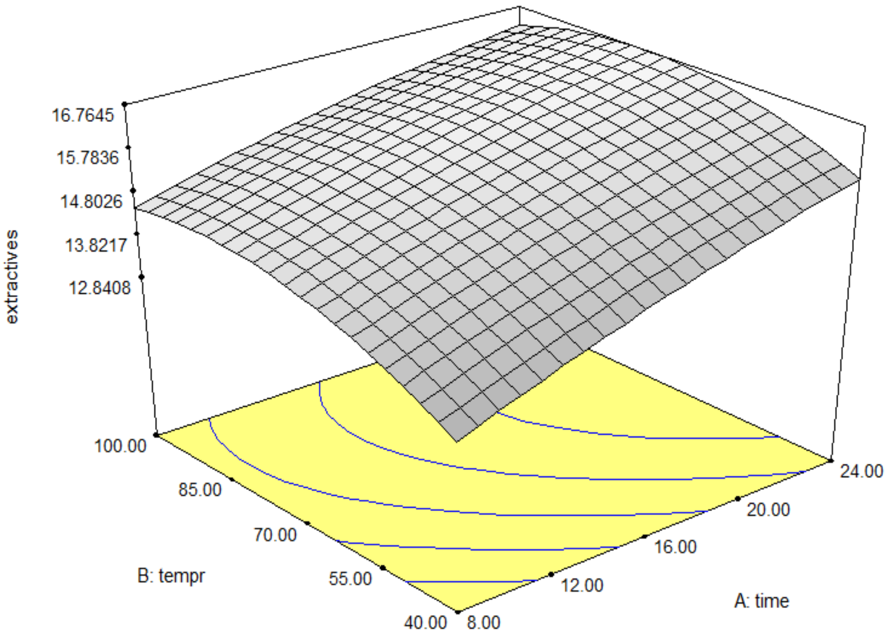


Figure 4.2 3D surface plot of extractives removal step

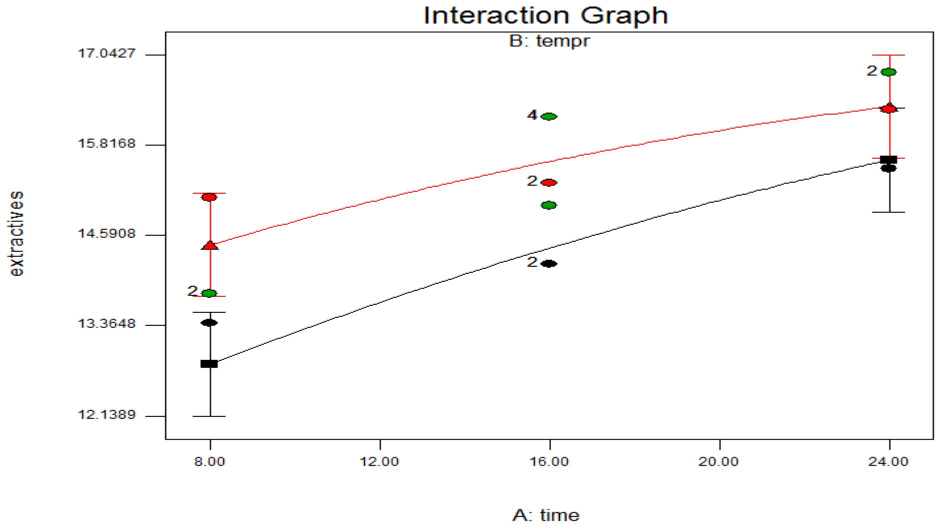


Figure 4.3 interaction plot of time and temperature

Model equation:

$E = 6.18560+0.30765t+0.15023T-3.02220E\text{-}003t^2-8.26023E\text{-}004T^2-9.37500E\text{-}004Tt$

Where E is extractives content, t is time, T is temperature.

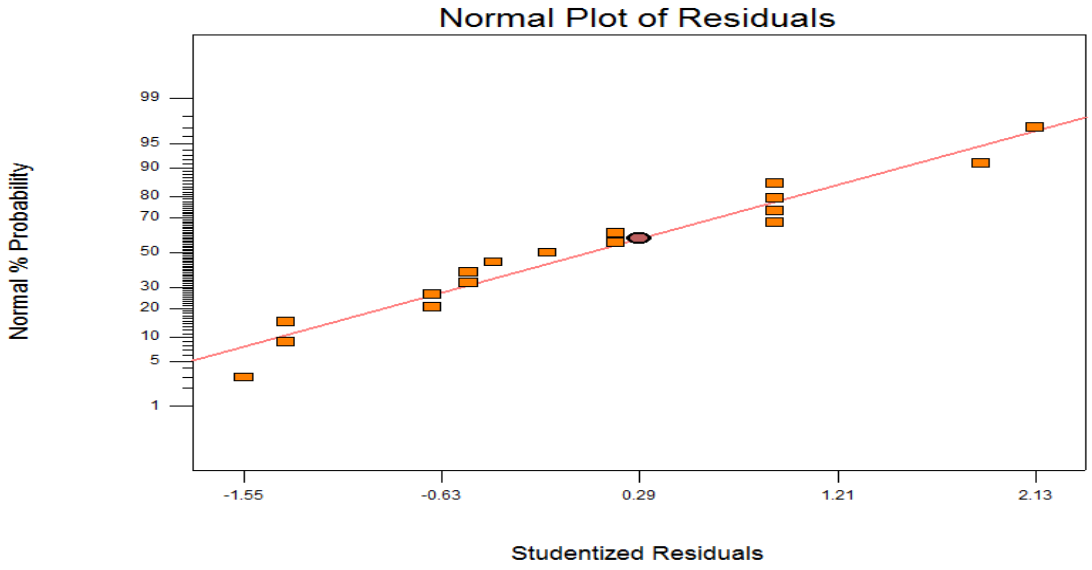


Figure 4.4 diagnosis graph: normal plot versus studentized

2. Delignification Step

Delignification is the process by which lignin content of bagasse was removed so that we can easily access the cellulose part of the biomass. The sample bagasse which was free of extractives was oven dried until it gets constant weight and 40g was taken for delignification and bleaching using glacial acetic acid acidified 0.75% w/v NaClO$_2$ aqueous solution to a pH of 4 at different temperatures(50^{o}C - 90^{o}C) for different time duration from (1hr-3hr) until the holocellulose sample exhibited a pale yellow color. Table (4.6) display the lignin yields at various conditions. Lignin yield is dependent on mixing time and mixing temperature. The effect of varying the variables on the amount of lignin removal was shown by interaction effect and one variable effects as indicated graphically. As it can be seen from the interaction plot delignification rate increases initially and tends to uniform when time and temperature are at the thresh hold values(optimum values). But if the conditions exceed the thresh hold values it tends to decrease, this is because of interaction of one factor on the other. The ratio of sugarcane bagasse to acidified solution of NaClO$_2$ was 1:25(w/v). By vacuum filtration of suspension, the bleaching process was repeat four times until the fiber color becomes white or yellow color disappears and then continuously washed until PH was nearly equal to seven (pH ≈ 7). Any material passing through the filter paper was recovered by vacuum filtration on another pre-weighed filter paper. In each case, the beaker was cooled and the dissolved lignin was decanted from the insoluble holocellulose whereas the holocellulose sample was vacuum-filtered until it changes to white while the soluble lignin was removed in the filtrate. After removal of lignin and bleaching, the bleached fiber was oven dried at 55^{o}C for 24hr until constant weight was maintained and then the mass of holocellulose was weighed which is equal to the sum of the mass of hemicellulose and α cellulose. Lignin content was Determined by subtracting the holocellulose mass (g)(dry basis) from Extractive free fiber mass(g).

Table 4.6 lignin yield

Std	**Run**	**Time(hr)**	**Temprature(°C)**	**Lignin(% w/w)**
1	9	1	50	18.7
2	8	3	50	21.7
3	12	1	90	21.8
4	7	3	90	23.8
5	17	1	70	19.84
6	6	3	70	23.7
7	15	1	70	19.85
8	5	3	70	23.3
9	14	2	50	21.5
10	11	2	90	23.2
11	3	2	50	22.6
12	2	2	90	23.6
13	10	2	70	22.9
14	16	2	70	22.89
15	13	2	70	23
16	1	2	70	22.9
17	4	2	70	22.9

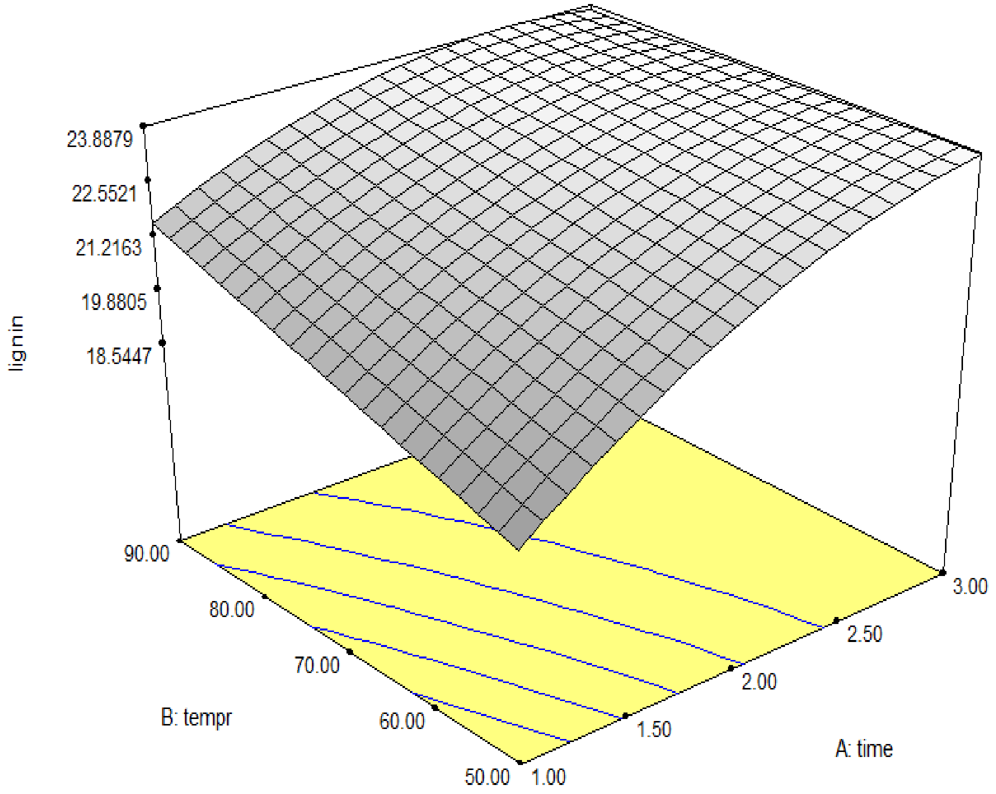


Figure 4.5 3D plot of delignification process.

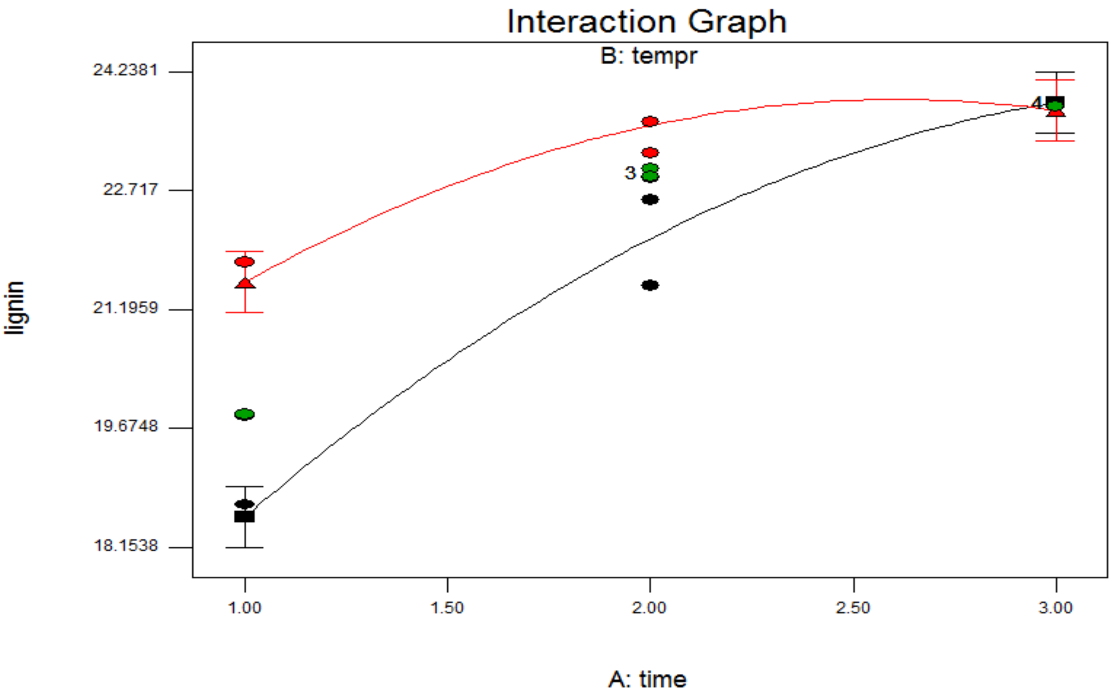


Figure 4.6 Variables interaction plot (temp and time interaction)

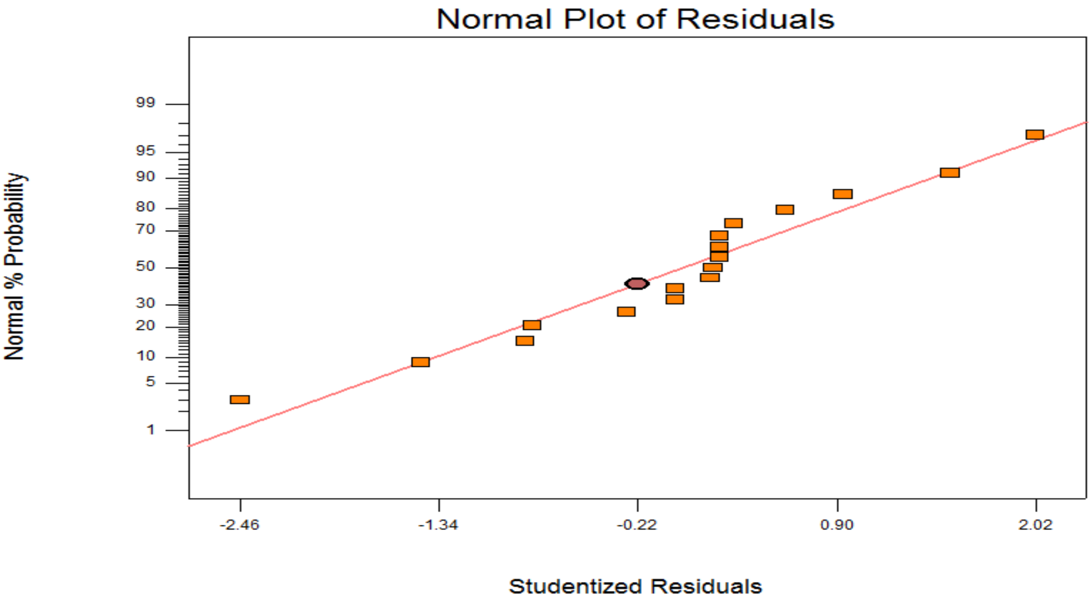


Figure 4.7 diagnosis graph: normal plot versus studentized

Model equation:

$L = 7.41780+8.22138t+0.11573T-0.90816t^{2}-1.41447E-005T^{2}-0.038750tT$
Where L is lignin ceontent, t is time, T is temperature.

1. Hemicellulose Removal Step

Table 4.7 Hemicellulose yield

Std	Run	Time(hr)	Temp (^oC)	Base concentration(g/ml)	Hemicellulose (%w/w)
1	8	1	40	14	20.12
2	4	5	40	14	23.23
3	3	1	60	14	20.77
4	5	5	60	14	24.01
5	17	1	50	8	20.8
6	13	5	50	8	21.5
7	16	1	50	20	23.99
8	15	5	50	20	26.35
9	10	3	40	8	21.26
10	9	3	60	8	21.35
11	11	3	40	20	26.3
12	12	3	60	20	22.5
13	6	3	50	14	22.5
14	7	3	50	14	22.5
15	1	3	50	14	22.5
16	2	3	50	14	22.5
17	14	3	50	14	22.5

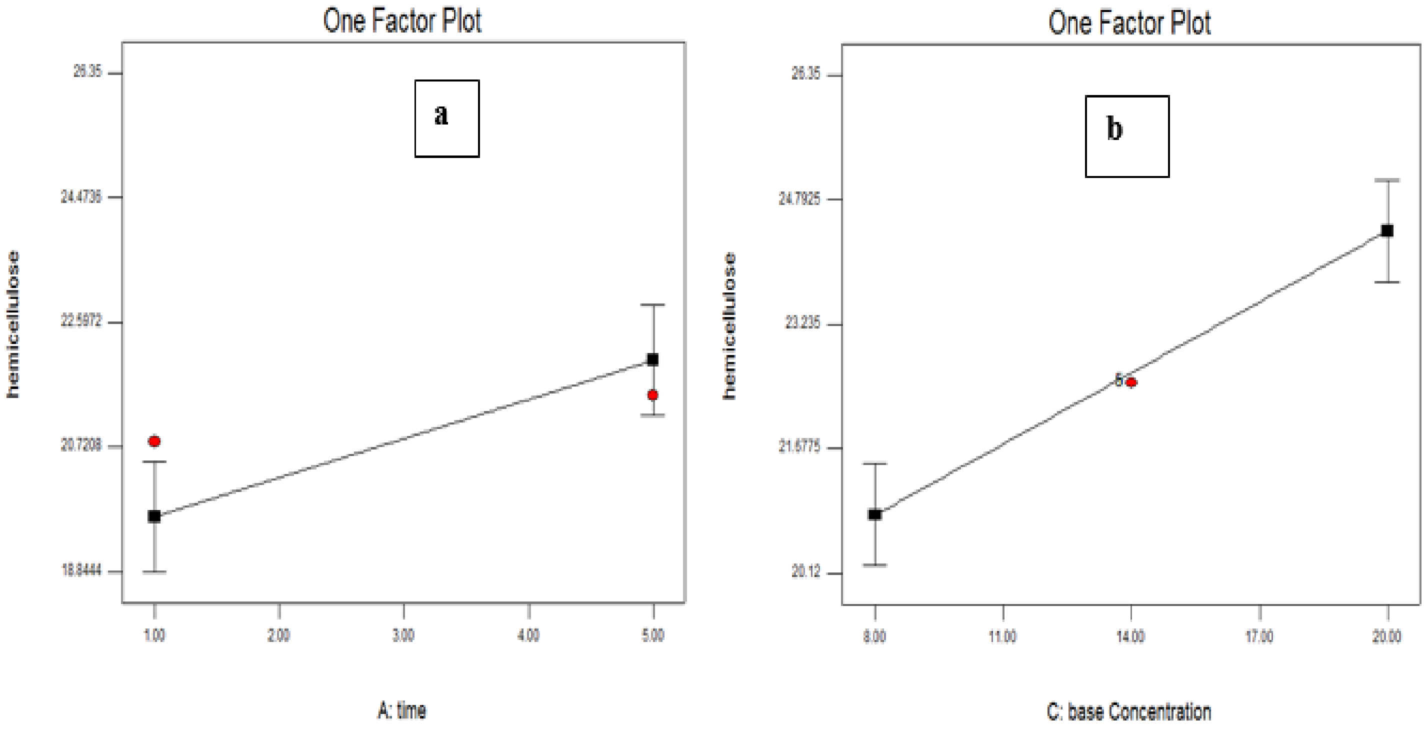


Figure 4.8 plot of one factor effect: a) time and b) base concentration

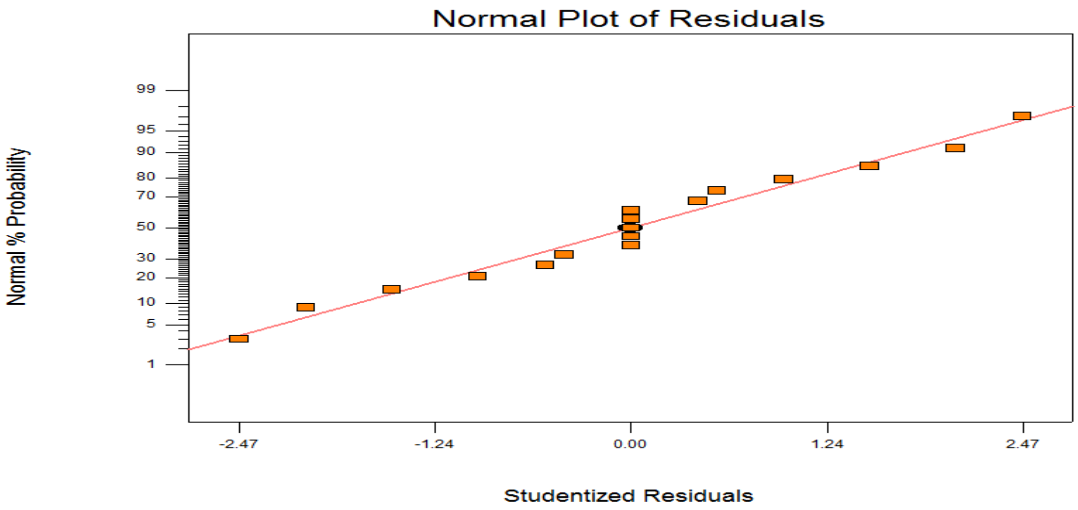


Figure 4.9 diagnosis graph: normal plot versus studentized

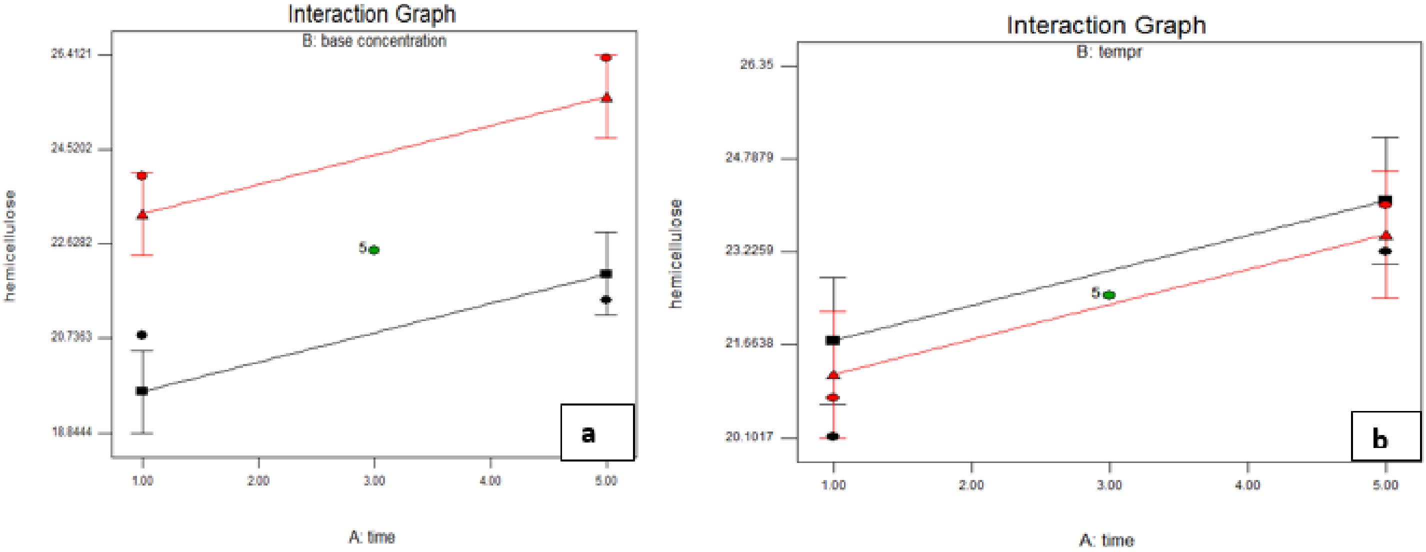


Figure 4.10 interaction plot of time and temperature

The above one factor plots and interaction plots shown that increasing reaction time and base concentration increases hemicellulose amount but may also remove small amount of alpha cellulose and hence affects its recovery if these factors are above their thresh hold value. The optimum points to achieve the optimum result are 2h, 13.64g/ml and 40^{o}C. This shows that by selection criteria of min time, min temp, min base conc and max hemicellulose yield.

Model equation:

$H = 18.13844+0.58812t-0.028500t+0.29646b$ where H is hemicellulose amount, t is time and T is temperature

4.3 Characterization of Cellulose

4.3.1. Particle Size Analysis

Figure 4.14 shows the results of particle size analysis of micro-cellulose by DLS where particle size distribution shown as function of particle diameter. The distribution showed trimodal distribution as shown by three peaks with corresponding particle size of 90 ±17.01 µm, 650 ±173.4 µm and 7000 ± 416.5 µm respectively. The mean particle size obtained was 871.35µm which implies that the obtained result was micro-size micro-cellulose. Intensity level in percent for each peak implies that the contribution of each peaks for overall number of particles counted. The first peak is diameter of the cellulose crystals, the second is length of cellulose crystals and the third is small amount of agglomerated cellulose arisen from attraction of cellulose through hydrogen bonding.

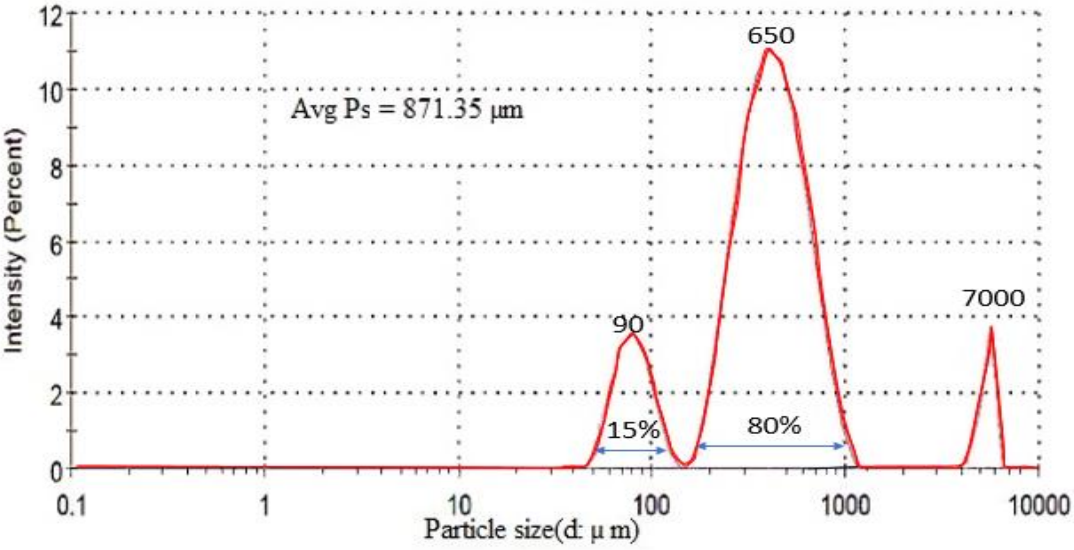


Figure 4.11: Particle size distribution of cellulose obtained from DLS measurement.

The poly-dispersibility index for the analysis was found to be 0.695 which was in the normal range. This result indicates the obtained analysis had well in uniformity and narrower size distribution compared higher which has non-uniform and very broad size distribution.

4.3.2 Structure Characterization

FTIR spectra of sugarcane bagasse and sugarcane bagasse cellulose are shown in Figure 4.12. The sugarcane bagasse showed similar patterns with the dominant peaks observed at approximately 3340 cm^{-1} (O–H stretch), 2892 cm^{-1} (C–H vibrations), 1730 cm^{-1} (C=O stretching), 1627 cm^{-1} and 1513 cm^{-1} (C=C aromatic), 1245 cm^{-1} (O-H vibration of phenolic group), 1110 cm^{-1} (C–O–C stretching), 1051 cm^{-1} (O–H stretching), and 897 cm^{-1} (α-glycosidic linkage). The spectra of sugarcane bagasse fibers, cellulose and cellulose were given as percentage of transmittance versus wave number. The main transmittance region range was 4000 cm^{-1} – 400 cm^{-1}. The peaks are typical for ligno-cellulosic materials and are known for sugar cane bagasse. The peaks at 1241 cm^{-1} and 1722

cm^{-1} in the celluloses, normally linked to aromatic skeletal vibrations of lignin and hemicelluloses, were reduced and others are almost invisible as compared to untreated counterparts. This indicated removal of lignin and hemicelluloses, as well as an exposure of cellulose. The broader and intense peak for the bagasse and cellulose was an implication of the stretching bond of polysaccharide O-H group. The peak due to C-H symmetrical stretching was an implication of presence of small amount of polysaccharide waxes and oil in the raw material and the cellulose that was left undissolved and not removed. This implies that extraction of waxes and oil was required during pretreatment such as soxhlet extraction.

A peak representing the water absorbed to the bagasse fibers was decreased in cellulose spectrum due to removal of hemicellulose. In the bagasse fiber spectrum C=C is the stretching aromatic ring of lignin component whereas C – O is stretching aryl groups of lignin. In similar manner from O-C (from methoxy) and C=C stretching from aromatic ring implies the presence of lignin in the raw sugarcane bagasse. However, all the spectra were disappeared in cellulose confirming that the lignin was removed which is the indication of effectiveness of the applied chemical treatment for the removal of lignin component from the bagasse fibers. The bending vibration of CH and C-O group in polysaccharide aromatic rings of cellulose and hemicellulose were intense in bagasse fibers spectra and its intensity was reduced in cellulose. This reduction implies the hemicellulose removal.

Table 4.8 FTIR characterization of bagasse and cellulose

Wave number (cm-1)	**Bagasse and Cellulose FTIR Spectra(cm^{-1})**		**peak Assignment**
	Bagasse	**Cellulosse**	
3400	3400	3400	O- H stretching of cellulose
2900	2900	2900	O- H stretching of cellulose
1632	1632	1632	Water aborted to bagasse fiber
1608	1608	-	C=C stretching of lignin
1512	1512	-	Aromatic ring of C=C lignin
1446	1446	-	methoxy - O- C of lignin
1432	1432	1432	C-H stretching of cellulose
1384 -1318	1384 -1318(intense)	1384 - 1318(smaller)	C-H and C-O groups in cellulose and hemicellulose
1248	1248	-	C-O stretching of aryl group of lignin
1160	1160	1160	C-O-C stretching of cellulose
896	896	896	C-H stretching of cellulose
832	832	-	Aromatic ring of lignin

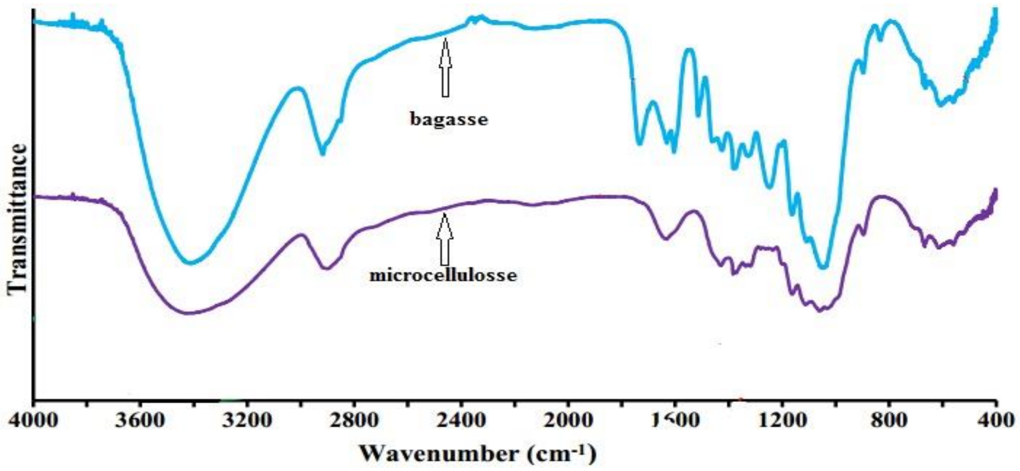


Figure 4.12 FTIR spectra of untreated sugarcane bagasse and sugarcane bagasse micro-cellulose

4.3.3 Crystallinity Characterization

The samples were analyzed over a scanning scope of 2θ from 0° to 40° with a step increment of 0.02°/s at room temperature. Figure 4.12 shown XRD analysis for evaluation of crystallinity of sugarcane bagasse and cellulose extracted from it. The diffraction pattern of SCB indicated typical behavior of cellulose I type, which showed major intensity peaks related to crystalline structure at 2θ values of around 15.5 and 22.5. The Segal method was used to calculate crystallinity index values of the samples. Crystallinity index (CI) was obtained from the ratio of the maximum peak intensity 002 (I_{002}, $2\theta = 22.5$) and halo depression (Iam,$2\theta = 18.5$) between peaks 001 and 002 according to equation(2.1). Where I_{002} is the maximum intensity of the 002 peak and Iam the minimal depression of the amorphous structure. According to the result, bagasse was characterized by the lower relative crystallinity index, because of higher content of amorphous hemicellulose, and lignin. The treatment with sodium hydoxide and bleaching agents removed the lignin and hemicellulose content and increased the degree of crystallinity index by almost 20%. In this study the effect corresponded to the chemical composition. This is underlined by the fact that the highest containing cellulose has the higher crystallinity compared to bagasse counterpart. The removal of lignin and hemicellulose are shown by FTIR results (the structure or bond of cellulose comparison). Nonetheless, the difference in crystallinity index values obviously arose from the difference in compactness of the cell walls, which responded differently to cellulose extractions. Thus, the high amorphous nature of the fiber can be realized through the broadening of the peaks.

The crystallinity index CI for bagasse and cellulose was 53.9 and 61.2 by using Segal method. Crystallinity increased when other bagasse components were removed leaving the micro-cellulose alone(Figure 4.13). This change was due to difference in chemical composition

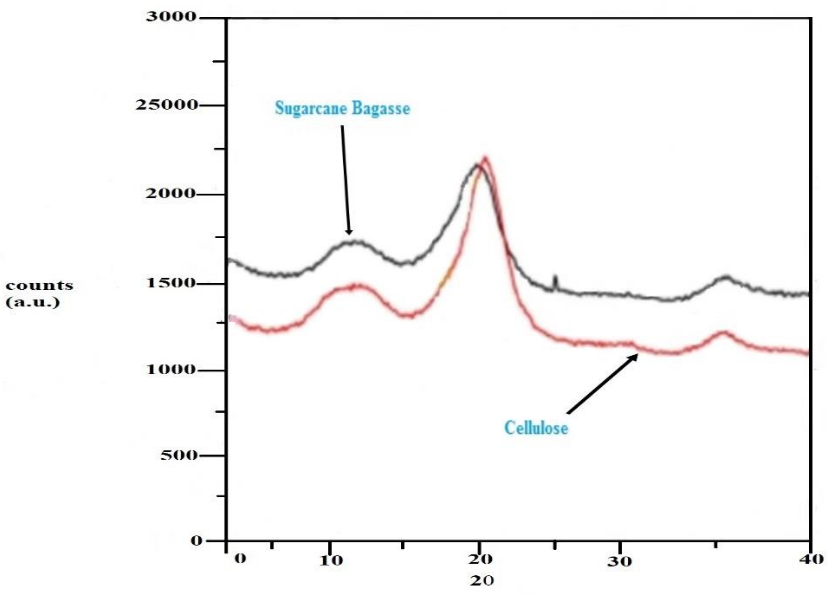


Figure 4.13 XRD data analysis of bagasse and bagasse cellulose.

4.4 Biocomposite Films Characterization

One of the factors affecting Plastic properties is water absorption capacity which depend on composition and type of material. The water absorption test was conducted by water immersion test. The FTIR measurement was conducted at Addis Ababa University faculty of science department of chemistry to examine and evaluate state of degradation or modification of reinforced polymer by functional group identification. It helps to evaluate the effectiveness of the reinforcement as function of morphology change or function group change. Mechanical property tests were conducted at Leather Industry Development Institute. The tests were done as per ASTM standards using universal test machine and mechanical properties were determined. Equations (2.2) and (2.3) were used for calculation of tensile strength and elongation at break. SEM test was done at LIDI. The morphology of the composite and uniformity of dispersion of micro-cellulose in the matrix were tested.

The biocomposite films produced by solvent casting were given in figure 4.14. Flexible and transparent films having approximately 0.1 mm average thickness were obtained. The films were with different concentration of cellulose as shown by %(w/w) of micro-cellulose to PVOH 0%, 4% and 8%. Transparency decreased as the amount of fiber increased because of lack of uniform dispersion exactly the same to that of lower fiber concentration due to agglomeration at higher fiber content. Flexibility also decreased as fiber content increased from 0% to 8%. From the figure, (A) represents composite films with bagasse-PVOH 4%(w/w), (B) represents 0%(w/w) cellulose-PVOH, (C) represents 4%(w/w) cellulose-PVOH and (D) represents 8%(w/w) cellulose-PVOH composites films.

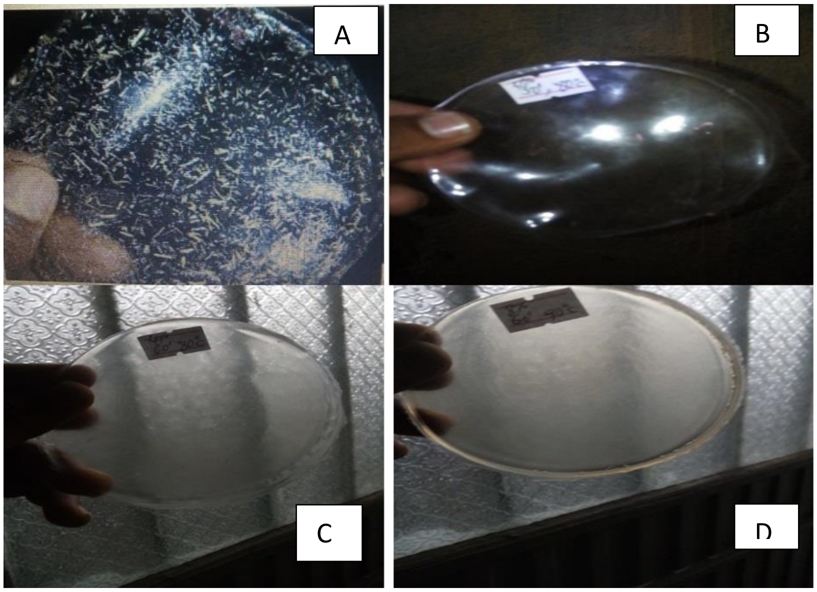


Figure 4.14 Composite films (A) bagasse-PVOH 4%(w/w) (B) 0%(w/w) cellulose-PVOH (C) 4%(w/w) cellulose-PVOH (D) 4%(w/w) cellulose-PVOH

1. Water Absorption

For the water absorption test, five samples were cut according to ASTM (American Society for Testing and Materials) ASTM D570, which describes several types of tests. Three specimens of every sample were submerged in distilled water at 25ºC. The specimens were removed from the water at different periods of time and weighted in a high precision balance and then submerged again in water. The content of water was calculated by the weight difference. When the content of water remained invariable in the specimens, they were removed and tests were finished and the result of measured percentage water absorption values of the films were listed in the following two tables. The values were the water absorption capacity of the bagasse and micro-cellulose reinforced biocomposite films. In all cases, the absorption capacity were reduced with increment of micro-cellulose percentage. (Table 4.9) and with the type of reinforcement (bagasse and cellulose) compared to the neat PVOH polymer (Table 4.10). The result shows, the reinforcement reduced the water absorption of the PVOH from 84% for neat PVOH to 62 % for 8% MCC composite and from 84 % to 75 % for 4% SCB, 69 % for 4% C.

Table 4.9 Water absorption capacity (%) of the PVOH films as function of cellulose amount.

Samples	**Water Absorption Capacity (%)**
0% MCC	84
4%MCC	69
8%MCC	62

Table 4.10 water absorption capacity (%) of the PVOH films as function of reinforcement type

Samples	Water Absorption Capacity (%)
Pure PVOH	84
4% SCB	75
4% MCC	69

Figure 4.15 and 4.16 are graphs which indicates percentage water absorption capacity of the films. The graphs clearly indicates that the neat PVOH film has higher water absorption capacity than the corresponding samples that were reinforced with MCC and SCB fibers and hence it implies that cellulose reinforced BCM is water resistant due to the structure or morphology of micro-cellulose which reduces diffusion of water molecules in the material. In case of reinforcement, water molecules do not directly diffuse into the material because of twisting pathway formation by micro-cellulose which results in improvement in water barrier property of the BCF. Fiber compositions such as hemicellulose and lignin plays important roles in reducing water absorption capacity of BCF if they were not completely removed during treatment. Fibers with higher content of hemicellulose absorb more water than fiber that partially or completely freed of hemicellulose by pretreatment.

Comparing the types of reinforcement (bagasse and micro-cellulose) reduction in water absorption capacity for cellulose reinforcement was high relative to that of the bagasse with equal fiber concentration which arises from the pretreatment used to remove hemicellulose and lignin, relative uniform distribution and the size aspects.

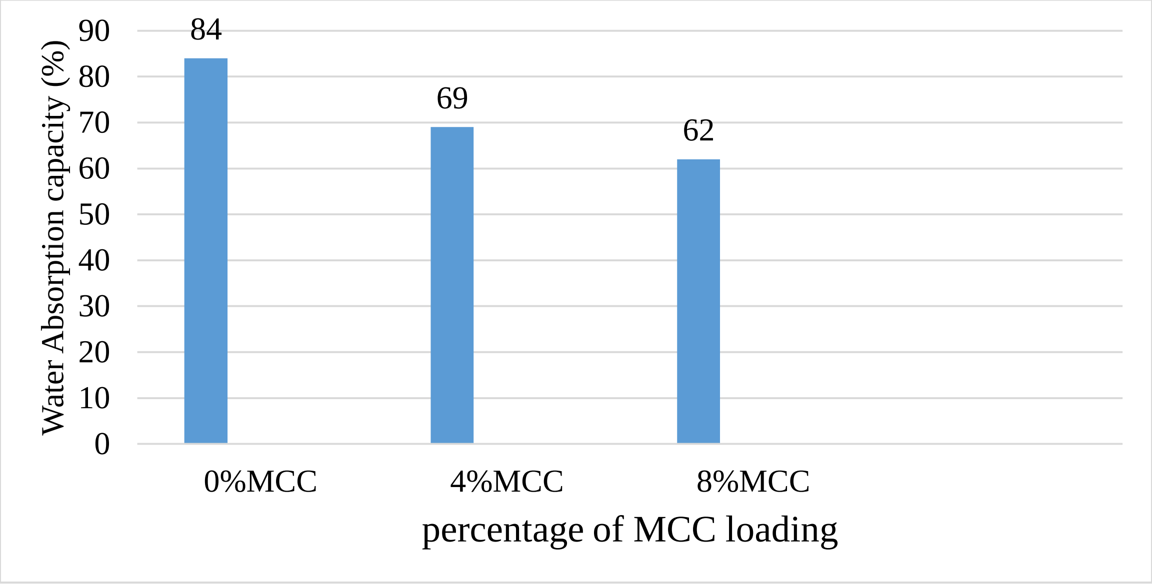


Figure 4.15 different micro-cellulose loaded biocomposite films water absorption

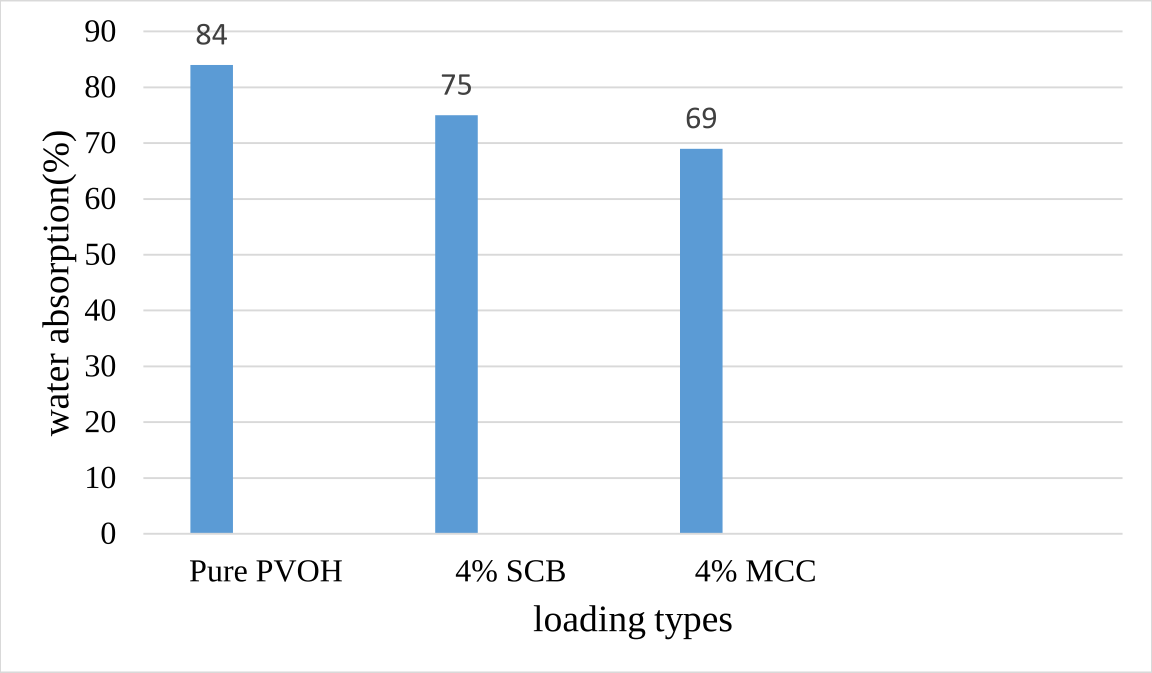


Figure 4.16 Biocomposite films water absorption capacity (%) based on types of loading.

2. Biodegradation Test

In this work, soil burial experiment were performed for all six samples(two samples for 0% fiber concentration, 4% fiber concentration and 8% fiber concentration). This test is extremely important to study biodegradation behavior which is fundamental for the application of biocomposites in environment. Weight loss of various films were calculated as a function of biodegradation periods. The result implies that weight loss shows an approximately linear relation with degradation(aging) time for all samples. For all the films weight decreases gradually as the time increases and after 18 days average weight decrease was 17%. Crystalline regions are more difficult to degrade. The ability of films to degrade depends greatly on physicochemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameter. All samples showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained herein reveal that the film composites will not cause any deleterious ecological impact. In other words, the film composites are fully biodegradable.

Table 4.11: Biodegradable studies of six film composites(three dublicates).

days	**0% MCC**	**0% MCC**	**Average loss (%)**	**4% MCC**	**4% MCC**	**Average loss (%)**	**8% MCC**	**8%MCC**	**Average loss (%)**
3	1.50	1.40	1.90	1.60	1.60	1.60	1.90	2.01	3.96
6	1.80	1.78	1.78	2.45	2.44	2.45	4.60	4.80	4.70
9	2.42	2.42	2.42	7.00	7.02	7.01	9.00	8.99	9.00
12	2.90	3.00	2.95	9.00	9.10	9.05	13.00	12.50	12.75
15	4.00	4.00	4.00	12.8	13.00	12.90	15.00	16.00	15.50
18	6.00	5.99	6.00	15.20	15.00	15.10	17.50	16.50	17.00

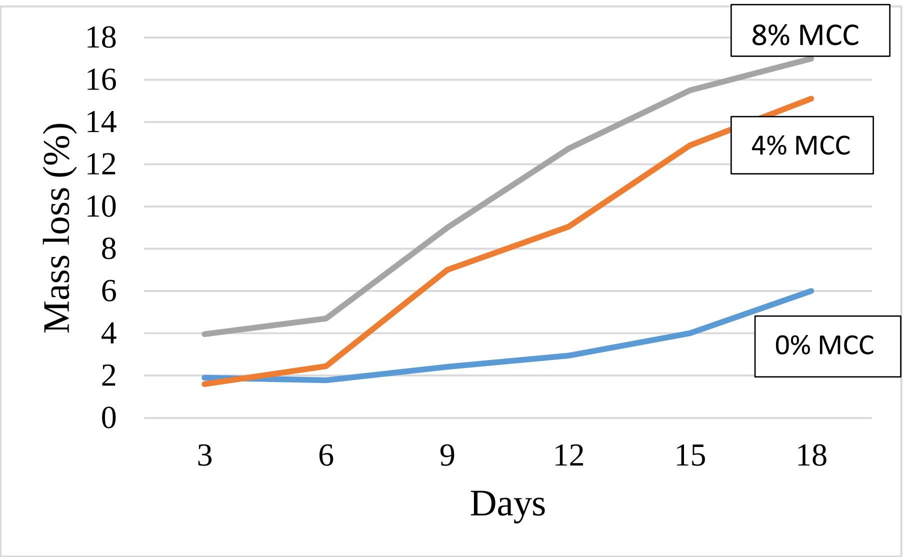


Figure 4.17 Biodegradable studies of three film composites blended with different cellulose loads.

3. Morphology analysis

Scanning electron microscopy (SEM) was used for the evaluation of the film microstructure. Before the analysis, the samples were sputter coated with a thin layer of gold to avoid electrical charging. The surface morphology of the sample films were evaluated using field emission scanning electron microscopy (FESEM), Each sample was put on a holder before being coated with a thin platinum layer to avoid the charging effect. Scanning electron microscopy(SEM) is one of the instruments used for morphology/structure testing for BCF and dispersion analyzer for distribution of fibers in the continues phase(matrix). The picture of 8%MCC loaded BCF was shown below figure 4.18 (a) which indicates that the morphology of the film has web like networked structure between PVOH matrix that represents the interaction between PVOH and micro-cellulose through hydrogen bonding whereas figure 4.18 (b) shows a uniform dispersion of the MCC within the PVOH matrix. As it can be seen from the picture, it is clear that the fiber dispersion is uniform (figure 4.18b) with a defect of existence of some sort of white dotted signs resulted from inefficient removal of bubbles(degassing) during preparation of suspensions as well as at the time of blending which can be reduced by proper ultrasonication.

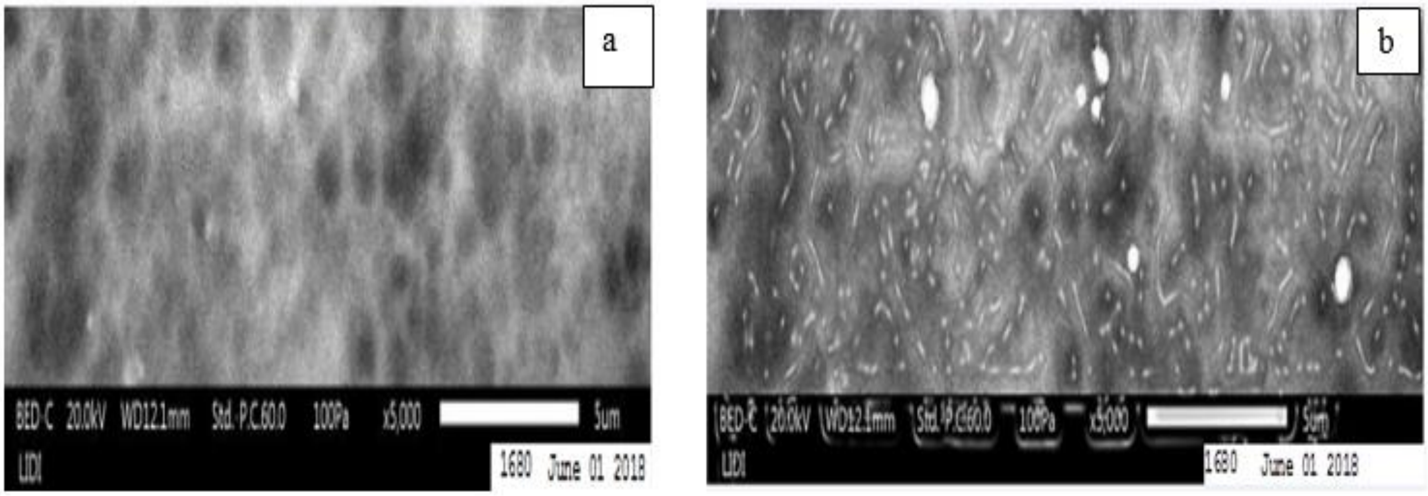


Figure 4.18 BCM film images from SEM

Figure 4.18 shows 8%wt MCC loaded BCF image from SEM with web like bonding between MCC and PVOH matrix(a) and 8%wt MCC loaded BCF image from SEM with the homogenous distribution of MCC (b).

4. Mechanical properties

The tensile strength (TS) and elongation at break (Eb) of the films were measured as per ASTM D 882 test methods, using an Autograph AGS-X Universal Tester at LIDI. The samples were cut into rectangular shapes with dimensions of 100 mm in length and 10 mm in width. The gauge length was fixed at 50 mm and the speed of the moving clamp was 5 mm min^{-1}. The results from mechanical property tests for tensile strength and elongation at break of composite film shows that as far as the micro-cellulose weight percent increase in the composite, tensile strength and elongation at break of the composite films were increased (table 4.12 and figure 4.19 and 4.20). The increment in tensile strength and elongation at break was due to strong interaction between the matrix and micro-cellulose resulting in high stiffness and strong linkage through H-bonding which leads to improved composite properties. Uniform dispersion and percolation phenomena are also the main parameters for mechanical properties improvement. Comparing the two properties of for different reinforcement types(bagasse and micro-cellulose) the result was not the same for the same or equal percentages of fibers loading. Compared to the neat PVOH all the reinforcement used were improved both tensile and elongation at break which was due to high surface area, aspect ratio, high uniform dispersion, tensile strength and young´s modulus of micro-cellulose compared to bagasse. 4% loadings both in bagasse and the micro-cellulose reinforcement resulted in about 1.5 fold increment with respect to bagasse and 1.4 folds increment with respect to cellulose. On the other micro-cellulose, and, the elongation at break was decreased from 355 for pure matrix to 280 for 4%B and to 199 for 4%C. All the results were achieved as expected which means they are as per the literature.

Table 4.12: The tensile strength and elongation at break test results done at LIDI for pure matrix, cellulose and bagasse reinforced films.

Composite	Tensile strength (MPa)	Elongation at break (%)
0%MCC	31	355
4% MCC	43.35	199
8% MCC	54	132
4%B	36.4	280

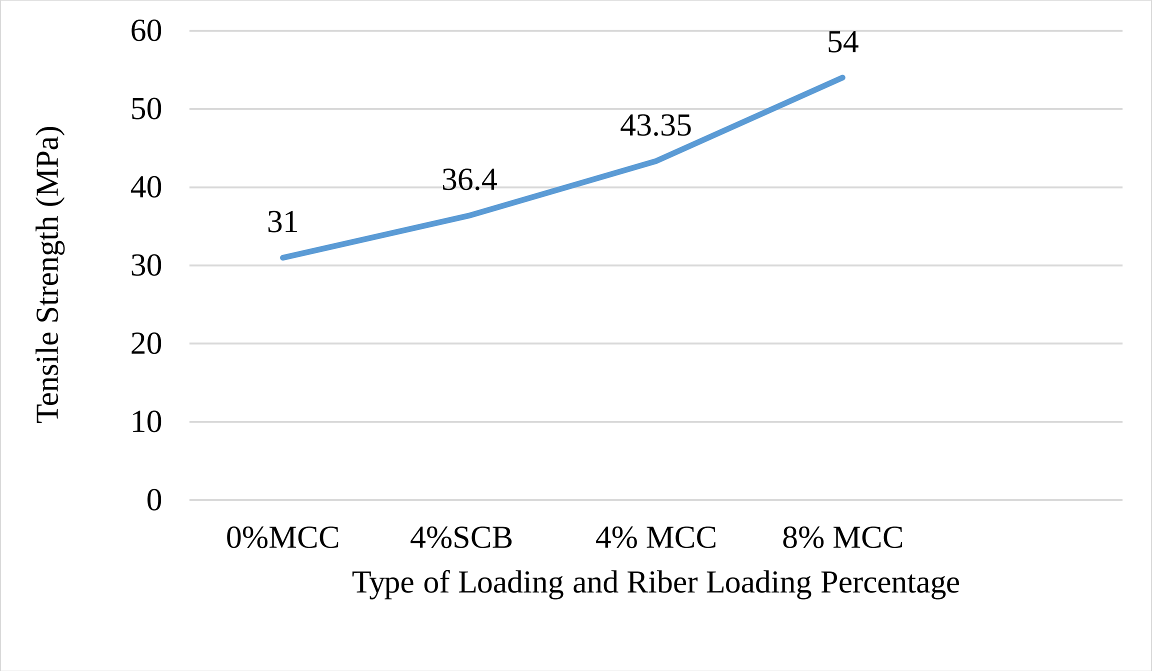


Figure 4.19: Composite films tensile strength based on reinforcement type

It is simple to understand the effect of both treatment and amount of fiber reinforcement in the polymer. Pure polymer microcomposite has the least or the minimum value of tensile strength whereas eight percent reinforced microbiocomposite film has the maximum value of tensile strength due to higher amount of fiber. Four percent bagasse reinforced sample has tensile strength value of greater amount when compared with the respective amount of microcellulosse reinforced sample because of the existence of lignin and hemicellulose in the bagasse. Therefore as the amount of microcellulose increases, tensile strength also increases until the thresh-hold value is achieved.

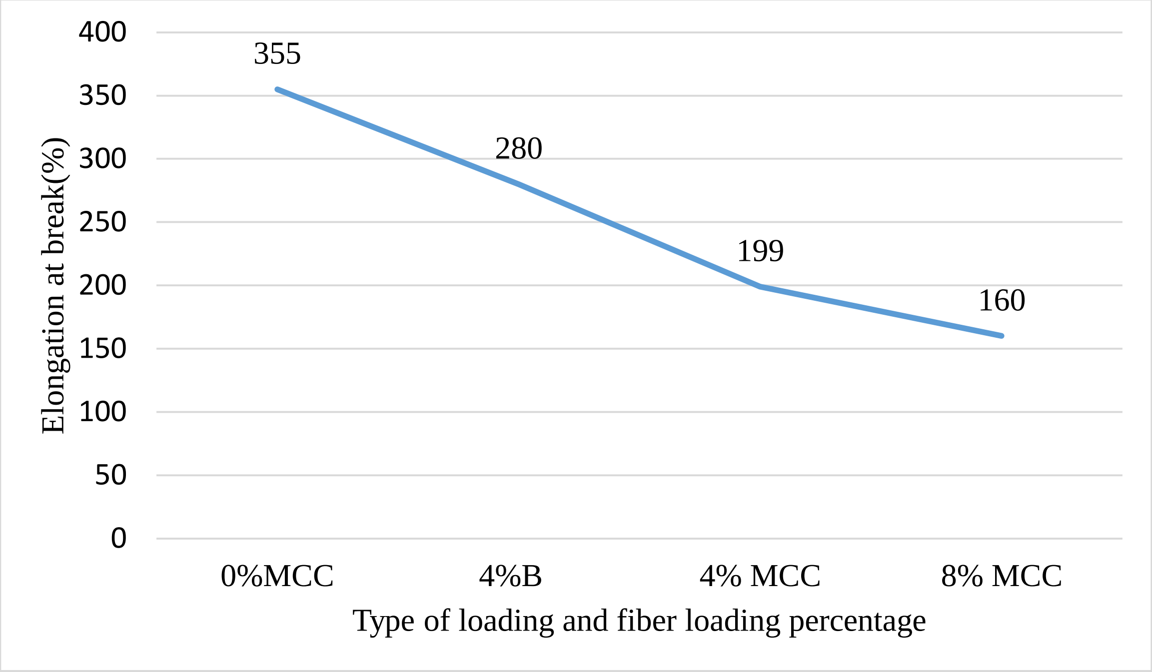


Figure 4.20: Composite films elongation at break based on reinforcement type

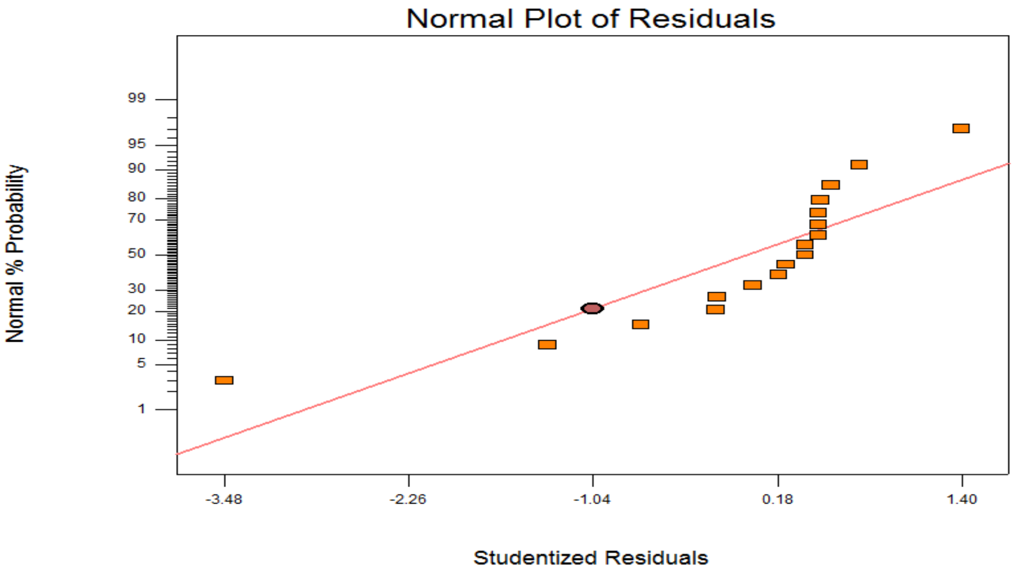


Figure 4.21diagnosis graph: normal plot versus studentized

The residual is defined as the difference between the observed and fitted value of the study variables. Therefore, it is the deviation between the data and the fit. Hence it is a measure of the variability in the response variable that is not explained by the regression model. Residuals can be thought as the observed values of the model errors. Graphical analysis of residuals is very effective way to investigate the adequacy of the fit of a regression model and to check the underlying assumption. So it is expected that if there is any departure from the assumptions on random error, then it should be shown by the residuals. Analysis of the residuals help to find the model inadequacies. Studentized residuals use the exact variance which is constant. From the graph it is clear that the deviation is very small and hence the model is good.

One factor effect analysis and variables interaction:

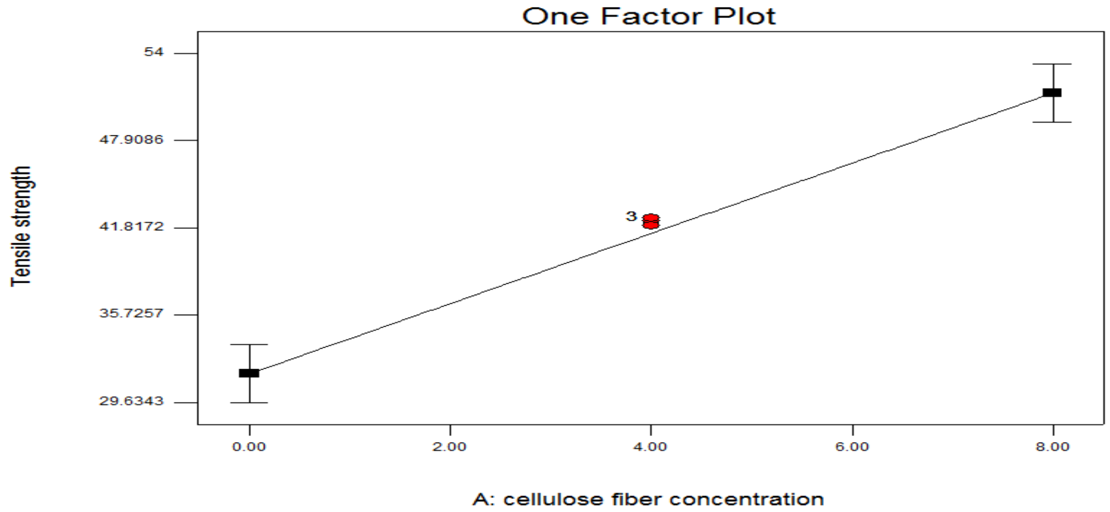


Figure 4.22 Effect of cellulose fiber concentration on tensile strength

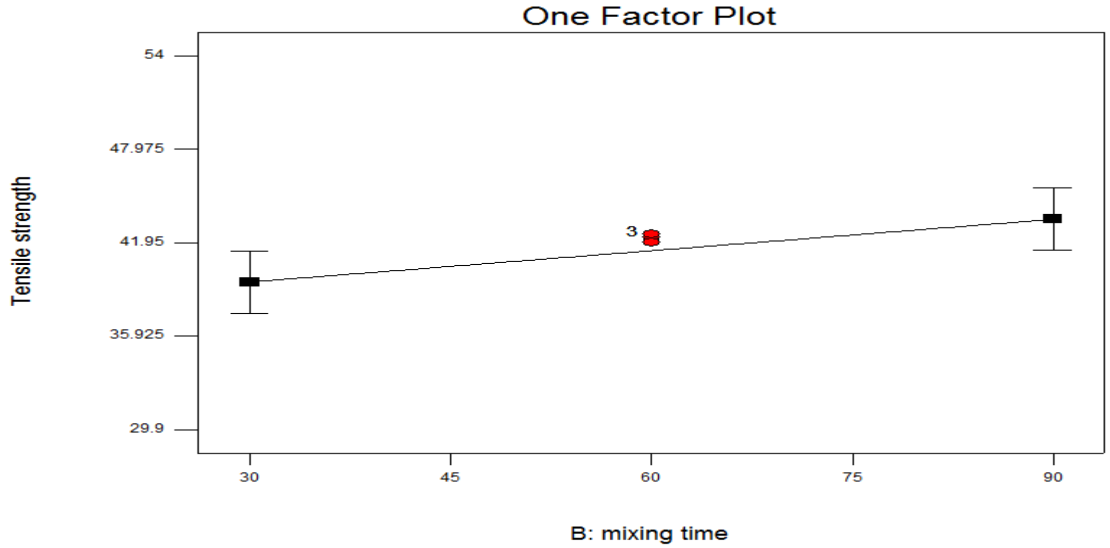


Figure 4.23 Effect of mixing time on tensile strength

From the two plots it is observable that the slop of tensile strength versus micro-cellulose concentration is very steep where as that of tensile strength versus mixing time is relatively not. The steepest slop indicates that the particular variable has significant effect on the response variable. The effect of mixing temperature is shown by the following plot that its slop is almost horizontal indicating that temperature has no much effect on tensile strength in the specified range.

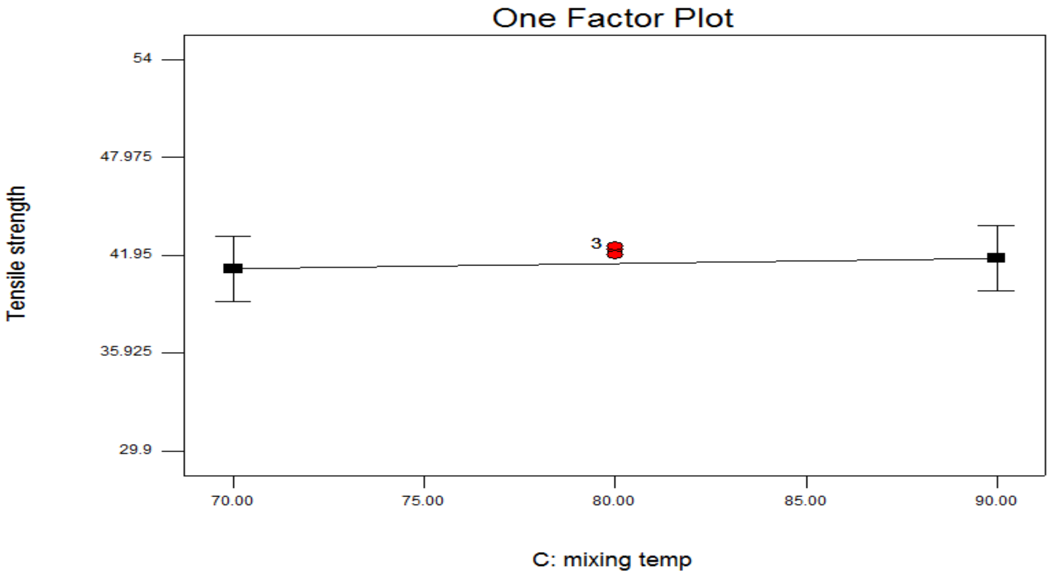


Figure 4.24 Effect of mixing temperature

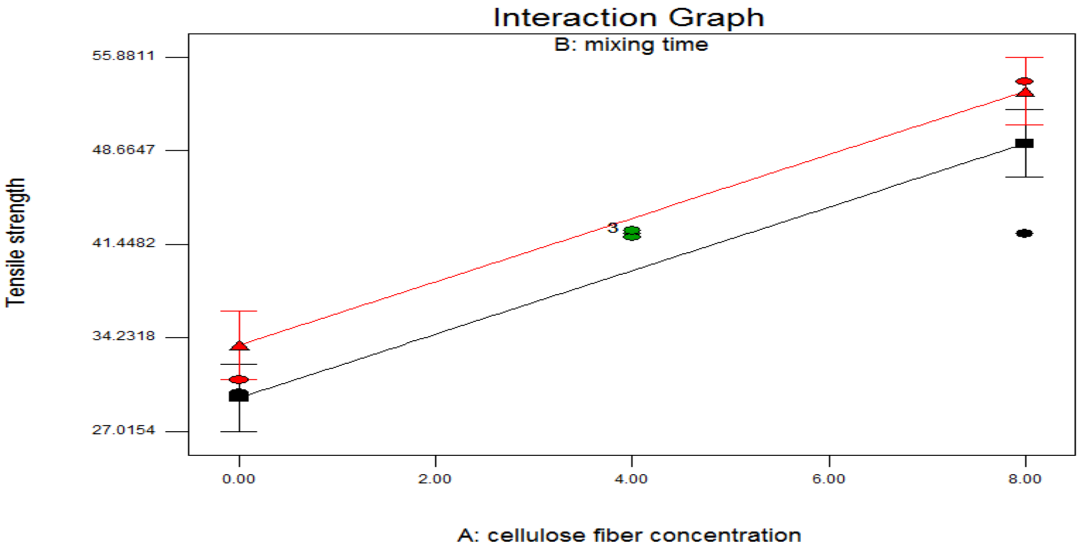


Figure 4.25 Interaction effect of mixing time and cellulose fiber concentration on tensile strength

As it can be seen from one factor effects and interaction effect, the mechanical property is highly dependent on fiber concentration and mixing time.

Ts = 25.08324 + 2.45000**F** + 0.067417**t** + 0.031500**T** Where Ts is tensile strength, F is fiber concentration, t is mixing time and T is mixing temperature.

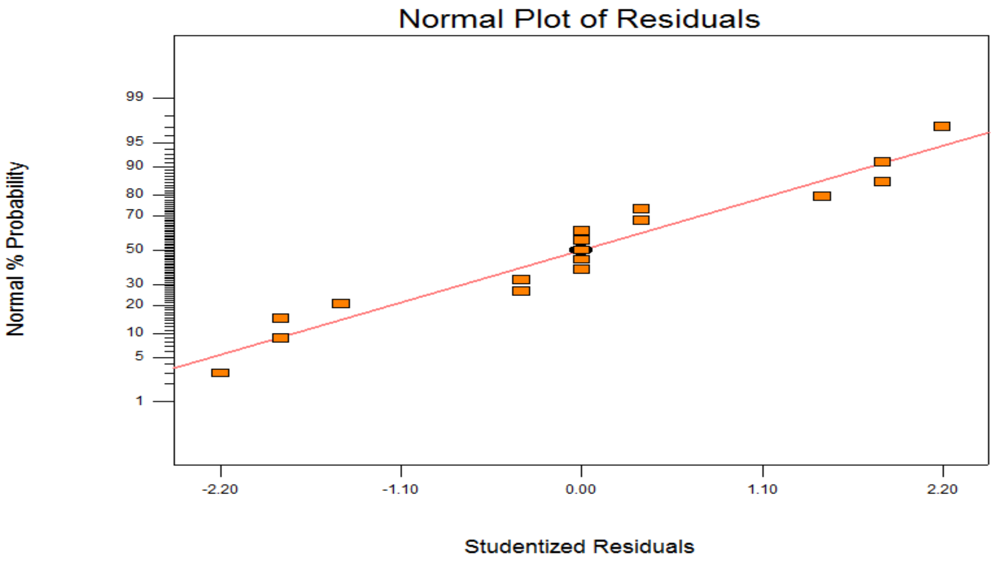


Figure 4.26 diagnosis graph: normal plot versus studentized

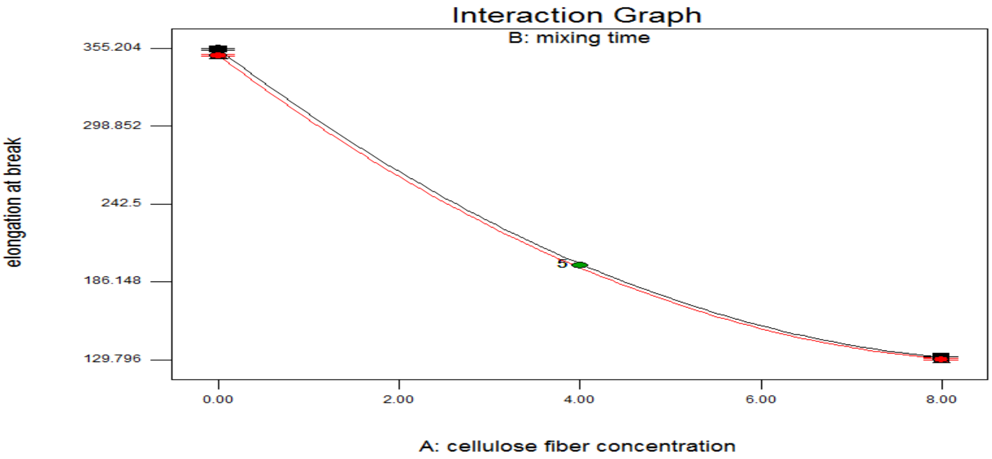


Figure 4.27 Interaction effect of mixing time and cellulose fiber concentration on elongation

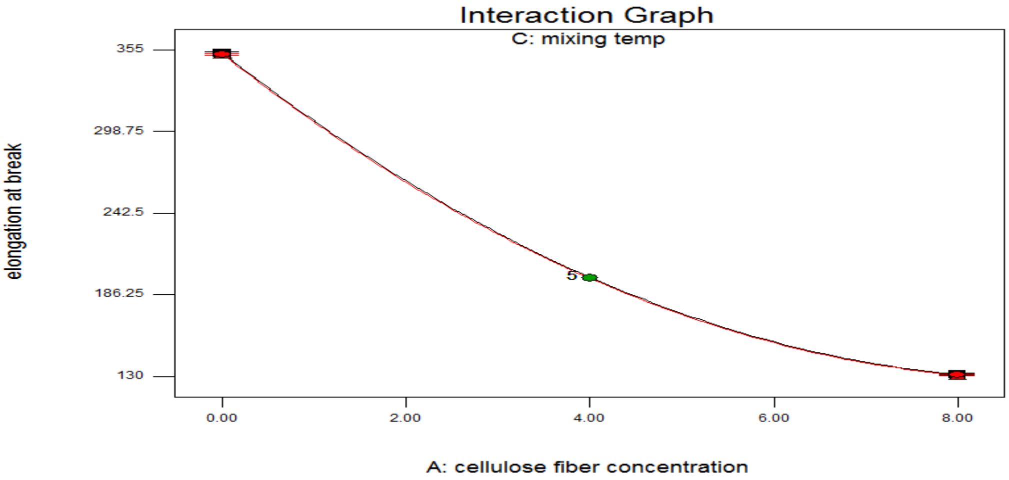


Figure 4.28 Interaction effect of mixing temperature and cellulose fiber concentration on elongation

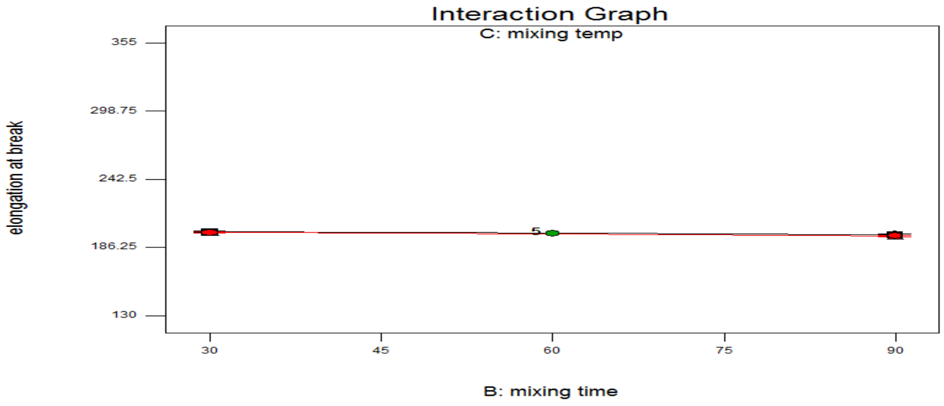


Figure 4.29 Interaction effect of mixing time and cellulose fiber concentration on elongation

The mechanical property is highly dependent on fiber concentration and mixing time.

$$Eb = 350.06250 - 50.29687\mathbf{F} - 6.25000E\text{-}003\mathbf{t} + 0.17500\mathbf{T} + 2.75000\mathbf{F}^2 - 2.77778E\text{-}004\mathbf{t}^2 - 1.25000E\text{-}003\mathbf{T}^2 + 6.25000E\text{-}003F\mathbf{t} + 3.12500E\text{-}003F\mathbf{T} - 4.16667E\text{-}004\mathbf{t}T$$

Where Eb is elongation at a break.

4.5 Evaluation of Effectiveness of Reinforcement

Water absorption capacity, mechanical properties and morphology are used for comparison to indicate the difference between reinforced and neat PVOH biocomposite films. **I**mprovement in mechanical properties, decrement in water absorption and, bagasse and cellulose uniform dispersion were used as effectiveness of reinforcement evaluated. Comparing the neat PVOH film with bagasse and cellulose reinforced film, cellulose micro-composite has improved properties and hence shows effectiveness of reinforcement because of high surface area, aspect ratio, high tensile strength and young`s modules of micro-cellulose.

4.5.1 Improvement in Water Absorption

Comparing the result data gained from the experiment indicates that reinforcing decreases water absorption capacity of the films. On the other hand, reinforcing lowers the absorption capacity which results in lower absorption when compared with the neat polyvinyl alcohol composition. This reduction in water absorption capacity shows that polymer matrix that contain micro-cellulose fibers and bagasse has good preventive ability against water. The films reinforced with micro-cellulose was more water preventive than the neat matrix and bagasse reinforced composite which indicates the effectiveness of cellulose reinforced PVOH polymer matrix in reduction of water absorption capacity.

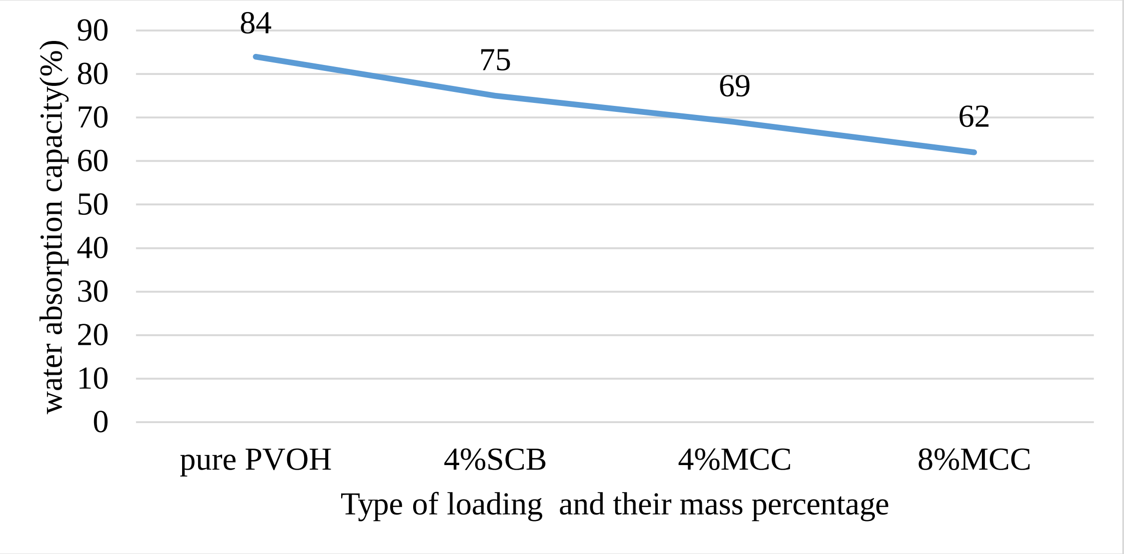


Figure 4.30 percentage water absorption capacity for BCF of various fibers with different loadings.

4.5.2 Improvement in Mechanical Properties

Compared to neat PVOH film, mechanical properties of reinforced composites films were improved as shown by the measured parameters and result data(table 4.15 and figure 4.23 and 4.24). The values shown clearly indicated the variation appeared on the films by micro-cellulose reinforcement resulted in higher tensile strength and lower elongation at break compared to neat PVOH film. This is an indication of using micro-cellulose for polymer reinforcement improves the mechanical properties of the biocomposites. From table 4.15 and figure 4.23 and 4.24 we can clearly observe that the tensile strength increases as a function of reinforcement loading values but bagasse reinforced film has less value than corresponding values of micro-cellulose whereas elongation at break decreases as a function of reinforcement loading values. It is lower for corresponding loading values for micro-cellulose as compared to that of bagasse.

4.6 Effectiveness Evaluation by Clustering Analysis

Cluster based analysis of composite films in terms of mechanical properties and water absorption capacity improvement and morphological properties of the films were necessary for determining the effectiveness of the reinforcement. As it can be seen from the following graph it is clearly observable that the values for the properties shows three visible regions which are for neat PVOH composite, bagasse reinforced composite and micro-cellulose reinforced composite. Neat PVOH composite has largest values for elongation and water absorption but smallest value for tensile strength, bagasse reinforced composite has medium properties value compared to neat PVOH composite and micro-cellulose reinforced composite whereas micro-cellulose reinforced composite has smallest values for elongation and water absorption and largest values for tensile strength. Elongation and water absorption decreases with increasing loading percentage. These results indicates that, micro-cellulose reinforced composites of PVOH has better results than those reinforced with bagasse and that of neat PVOH composites.

which in turn much better than those neat PVOH films. Therefore, reinforcement of the matrix by micro-cellulose was effective in improving both the mechanical properties and water absorption capacity of the host matrix.

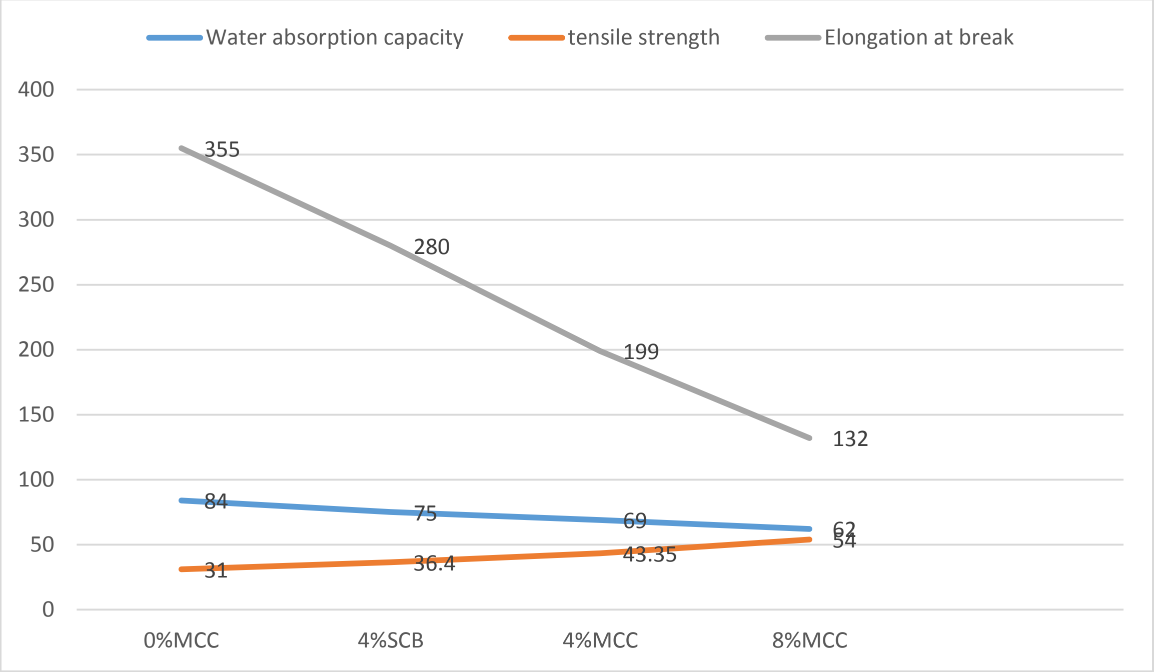


Figure 4.31: water absorption, tensile strength and elongation comparison for neat PVOH, SCB and MCC reinforced composites.

5. Conclusions and Recommendations

5.1 conclusions

Biodegradable film composites were successfully prepared using micro-cellulose fibre-reinforced with polyvinyl alcohol. Composites produced by this method show very good biodegradation behavior that the percentage of mass loss after aging for 18 days were 6%, 15.10% and 17% respectively for reference, for 4%MCC/PVOH and 8% MCC/PVOH micro-biocomposites. The observation of the surface morphology of the micro-biocomposite film shown that micro-cellulose was homogeneously dispersed at low filler loading and started to agglomerate as concentration of cellulose increases. Water absorption capacity of microcellulose reinforced PVOH films were shown an improvement of from 84% for neat PVOH to 69 % for 4%MCC/PVOH and to 62 % for 8%MCC/PVOH composite films. 4%SCB/PVOH water absorption capacity was 75% which is greater than the corresponding value of 4%MCC/PVOH. Therefore, micro-cellulose reinforced films shown better result in reduction of water absorption capacity because of micro scale size, chemical composition (hemicellulose, lignin), interaction between the polymer matrix and the reinforced materials.

Mechanical testing was used for characterizing the effectiveness of the micro-biocomposites and the overall results revealed that the micro-cellulose reinforced composites have much better and improved properties when compared with that of neat polyvinyl alcohol composites and equally loaded corresponding bagasse reinforced composites. The tensile strength for 0%MCC/PVOH, 4%SCB/PVOH, 4%MCC/PVOH and 8%MCC/PVOH was 31MPa, 36.40MPa, 43.35MPa and 54MPa respectively whereas elongation at a break was 355%, 280%, 199%, 132% respectively. Improvements in mechanical properties were because of chemical composition (hemicellulose, lignin) difference and as a result different interaction between the polymer matrix and the reinforced materials (Percolation phenomena and strong hydrogen bonding). The improvement increased with increment in cellulose concentration. In contrast, the flexibility of MCC/ PVOH composite films was reduced as filler amount increased.

Scanning electron microscopy (SEM) was also used for characterizing the effectiveness of micro-biocomposites and the results indicated that the micro-cellulose reinforced composites have 3D interwoven network of micro-fibrils, very fine, pure and dimensionally uniform. In conclusion, the current outcomes will give an advantageous insight of developing biodegradable and renewable bio-micro-composite and bio-nano-composite films that will be highly useful for a wide range of applications. The films were appeared transparent, suggesting uniform dispersion.

The overall results shown that the micro-cellulose reinforcement resulted in higher improvement of properties of the matrix.

5.2 Recommendation

I would like to recommend that it is better if standard procedures for extraction and testing processes of micro-cellulose and composites are developed so that to achieve the targeted goals. It is strongly recommended that micro-cellulose reinforcement is very essential especially for non-degradable and hydrophobic synthetic polymers which are environmentally unfriend. In addition to consuming bagasse as energy source it is recommended to consumed it for other applications and hence requires further intense researches. Extracting and consuming micro-cellulose and nano-cellulose from sugar cane bagasse being at infant stage provided a new area for research development and it is better if provoked for further works. Finally it is recommended that development of biocomposites from other abundant biomasses for replacement of synthetic components contributes for healthy environment and therefore it must be encouraged. Intensively using certified and internationally accepted reference materials for comparisons of results would also be useful for quality assurance.

References

Aboody, M. H. (2013). Extraction of Cellulose from some Industrial and Plant ' s Waste and its hydrolysis using new heterogeneous catalyst, (September).

Acharya, S. K., Mishra, P., & Mehar, S. K. (2011). Effect of Surface Treatment on the Mechanical on the Mechanical Properties of Bagasse Fiber Reinforced Polymer Composite. *Bioresources*, *6*, 3155–3165. https://doi.org/10.1177/0021998302036008180

Anggono, S. & S. (2015). Alkali Treatment on Sugarcane Bagasse To Improve Properties of, 1–11. https://doi.org/10.1002/9781119031192.ch14

Arsène, M-A Savastano Jr, H. Allameh, S. M. Ghavami, K., & Soboyejo, W. O. (2003). Cementitious composites reinforced with vegetable fibers. *Proceedings of the 1st Interamerican Conference on Non-Conventional Materials and Technologies in the Eco-Construction and Infrastructure (IAC-NOCMAT)*, (November 2003), 13–16. Retrieved from http://www.nku.edu/~allamehs1/Arsene-Natural Fibers fianl IAC NOCMAT.pdf

Balaji, A., Karthikeyan, B., & Sundar Raj, C. (2015a). Bagasse fiber ??? The future biocomposite material: A review. *International Journal of ChemTech Research*, *7*(1), 223–233. https://doi.org/10.1016/j.jclepro.2007.11.001

Balaji, A., Karthikeyan, B., & Sundar Raj, C. (2015b). Morphological and mechanical behavior of sugarcane bagasse fibers reinforced polyester eco-friendly biocomposites. *Journal of Chemical and Pharmaceutical Research*, *7*(8), 573–577.

Borsa, J. (2014). Synthesis of cellulose derivative based superabsorbent hydrogels by radiation induced crosslinking. Cellulose, 21, 4157–4165.

Cannazza, G., Cataldo, A., Benedetto, E. De, Demitri, C., Madaghiele, M., & Sannino, A. (2014). Experimental Assessment of the Use of a Novel Superabsorbent polymer (SAP) for the Optimization of Water Consumption in Agricultural Irrigation Process. Water, 2056–2069.

Capanema, N. S. V., Mansur, A. A. P., de Jesus, A. C., Carvalho, S. M., de Oliveira, L. C., & Mansur, H. S. (2018). Superabsorbent crosslinked carboxymethyl cellulose-PEG hydrogels for potential wound dressing applications. International Journal of Biological Macromolecules, 106, 1218–1234.

Capitani, D., Alessandro, M., Nobile, D., Mensitieri, G., Sannino, A., & Segre, A. L. (2000). 13 C Solid-State NMR Determination of Cross-Linking Degree in Superabsorbing Cellulose-Based Networks. Macromolecules, 33, 430–437.

Chang, C., Duan, B., Cai, J., & Zhang, L. (2010). Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery. European Polymer Journal, 46(1), 92–100.

Chang, C., Lue, A., & Zhang, L. (2008). Effects of Crosslinking Methods on Structure and Properties of Cellulose / PVA Hydrogels. Macromolecular Chemistry and Physics, 209, 1266–1273.

Chang, C., & Zhang, L. (2011). Cellulose-based hydrogels : Present status and application prospects. Carbohydrate Polymers, 84(1), 40–53.

Corradini, E., Ito, E. N., Marconcini, J. M., Rios, C. T., Agnelli, J. A. M., & Mattoso, L. H. C. (2009). Interfacial behavior of composites of recycled poly(ethyelene terephthalate) and sugarcane bagasse fiber. *Polymer Testing*, *28*(2), 183–187. https://doi.org/10.1016/j.polymertesting.2008.11.014

Gupta, G., & Bhatnagar, R. (2015). A Review on Composition and Properties of Bagasse Fibers. *International Journal of Scientific & Engineering Research*, *6*(5), 143–148.

Harja, M., & Arbut, M. B. (2008). Properties of fiber reinforced polymer concrete, 1–10.

Kalia, S.; Kaith, B.S., Kaur, I. (2011). *Cellulose Fibers: Bio- and Nano- Polymer Composites*. *Media*. https://doi.org/10.1007/978-3-642-17370-7

Kalia, S., Dufresne, A., Cherian, B. M., Kaith, B. S., Njuguna, J., & Nassiopoulos, E. (2011). Cellulose based biocomposites and nanocomposites – a review, *2011*, 1–103.

Kargarzadeh, H., Ioelovich, M., Ahmad, I., Thomas, S., & Dufresne, A. (2017). Methods for Extraction of Nanocellulose from Various Sources. *Handbook of Nanocellulose and Cellulose Nanocomposites*, 1–49.

Kumar, A., Negi, Y. S., Bhardwaj, N. K., & Choudhary, V. (2013). Synthesis and characterization of cellulose nanocrystals/PVA based bionanocomposite. *Advanced Materials Letters*, *4*(8), 626–631. https://doi.org/10.5185/amlett.2012.12482

Lu, J. Z., Wu, Q., Negulescu, I. I., & Chen, Y. (2006). The influences of fiber feature and polymer melt index on mechanical properties of sugarcane fiber/polymer composites. *Journal of Applied Polymer Science*, *102*(6), 5607–5619. https://doi.org/10.1002/app.24929

Marcicano, J. P. P., & Jr, A. P. (2013). Textile Fiber Produced From Sugarcane Bagasse Cellulose : an Agro-Industrial Residue, *3*(2), 15–28.

Menezes, F. F. de, Maciel Filho, R., & Rocha, G. J. de M. (2016). Obtainment and characterization of lignin from enzymatic hydrolysis of sugarcane bagasse of 2G ethanol process in pilot scale. *Chemical Engineering Transactions*, *50*, 397–402. https://doi.org/10.3303/CET1650067

Muniyasamy, S. (2015). Development of Sustainable Biobased Composite Products from Agricultural Biomass, (October), 1–53.

Muniyasamy, S. (2016). Contents Development of Sustainable Biobased Plastics and its Green Composite Products from South African Agricultural Waste / Crop Residues : Opportunities and, (January).

Nallappan, M. L. (2011). Developement of virgin polypropylene composites by sugarcane bagasse reinforcement, (April).

Ni, N., & Zhang, D. (2017). Synthesis and characterization of zein-based superabsorbent hydrogels and their potential as heavy metal ion chelators. Polymer Bull.

Nnadi, F., & Brave, C. (2013). Environmentally friendly superabsorbent polymers for water conservation in agricultural lands, 1(5), 94–98.

Onofrei, M., & Filimon, A. (2012). Cellulose-based hydrogels : Designing concepts, properties, and perspectives for biomedical and environmental applications. In polymer science (pp. 108–120).

Pan, S., & Ragauskas, A. J. (2012). Preparation of superabsorbent cellulosic hydrogels. Carbohydrate Polymers, 87(2), 1410–1418.

Peppas, N. A., Bures, P., Leobandung, W., & Ichikawa, H. (2000). Hydrogels in pharmaceutical formulations. European Journal of Pharmaceutical and Biopharmaceutics, 50, 27–46.

Raafat, A. I., Eid, M., & El-arnaouty, M. B. (2012). Radiation synthesis of superabsorbent CMC based hydrogels for agriculture applications. Nuclear Inst. and Methods in Physics Research, B, 283, 71–76.

Rimmer, S. (2011). Biomedical Hydrogels: Biochemistry, manufacture and medical applications. Materials. Cambridge: Woodhead Publishing Limited.

Ryan, J., Estefan, G., & Rashid, A. (2001). Soil and Plant Analysis Laboratory Manual(Second). Aleppo, Syria: International Center for Agricultural Research in the Dry Areas (ICARDA)

S.NAGAKALYAN1 .ANOOPISAN . B.VIJAYKIRAN. (2015). Interfacial Behaviour of Composites of Polymer and Sugarcane Fiber, *2*(7), 53–61.

Sahari, J., & Sapuan, S. M. (2011). Natural fibre reinforced biodegradable polymer composites. *Rev.Adv.Mater.Sci*, *30*, 166–174.

Verma, D., Gope, P. C., Maheshwari, M. K., & Sharma, R. K. (2012). Bagasse fiber composites-A review. *Journal of Materials and Environmental Science*, *3*(6), 1079–1092.

Wirawan, R., Sapuan, S. M., Yunus, R., & Abdan, K. (2012). Density and Water Absorption of Sugarcane Bagasse-Filled Poly (vinyl chloride) Composites, *20*(7), 659–664.

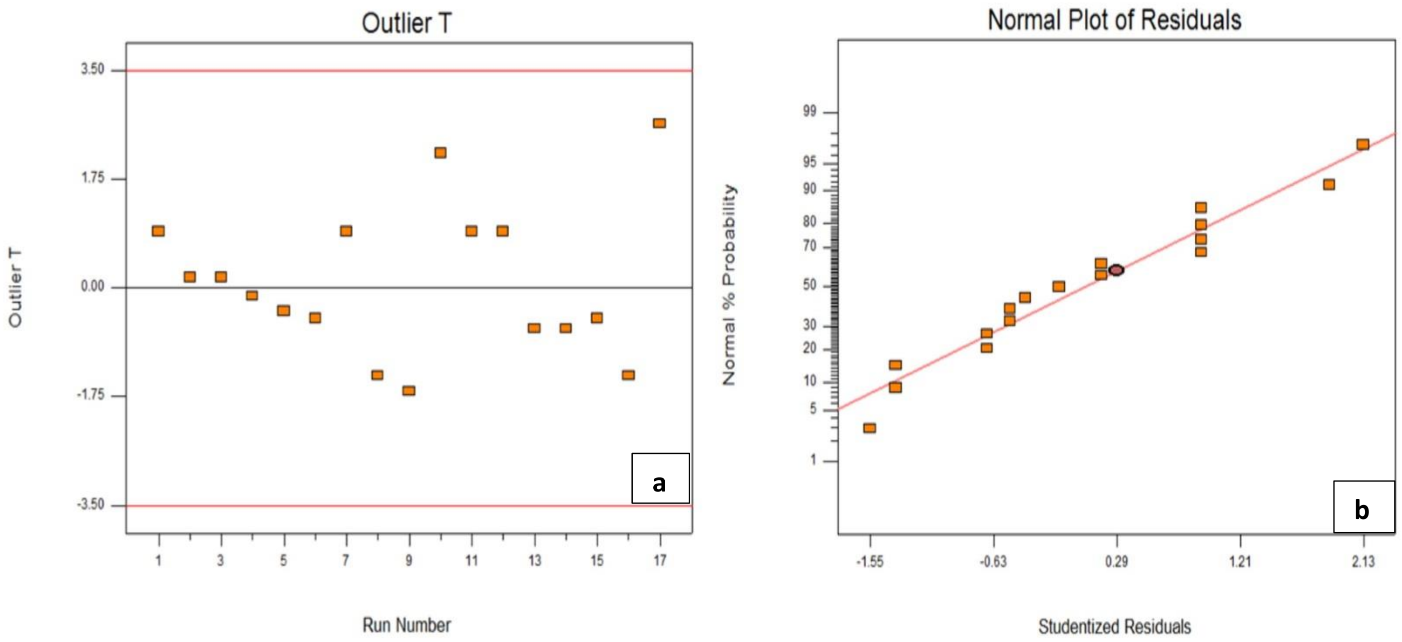
Wulandari, W. T., Rochliadi, A., & Arcana, I. M. (2016). Nanocellulose prepared by acid hydrolysis of isolated cellulose from sugarcane bagasse. *IOP Conference Series: Materials Science and Engineering*, *107*, 12045. https://doi.org/10.1088/1757-899X/107/1/012045

Appendices

Appendix A

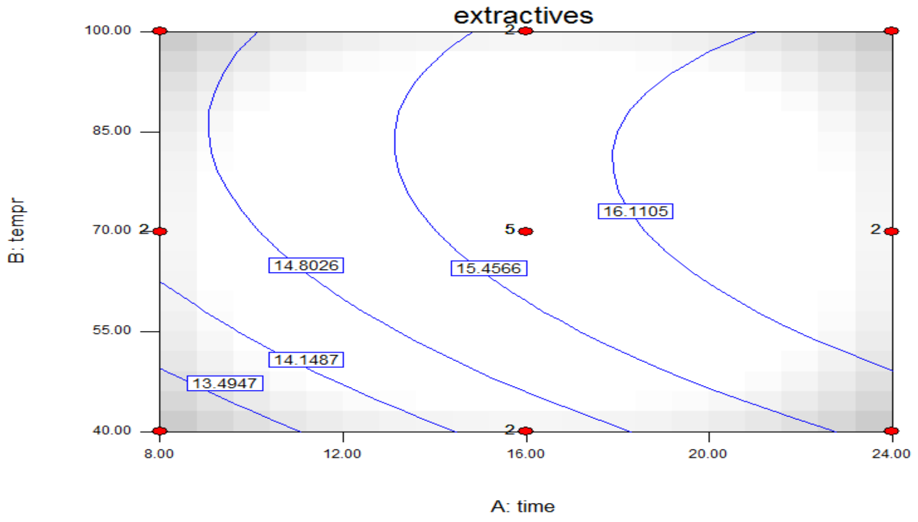
Contour, outlier, normal residual and interaction plots

1. Design expert results for removal of extractives



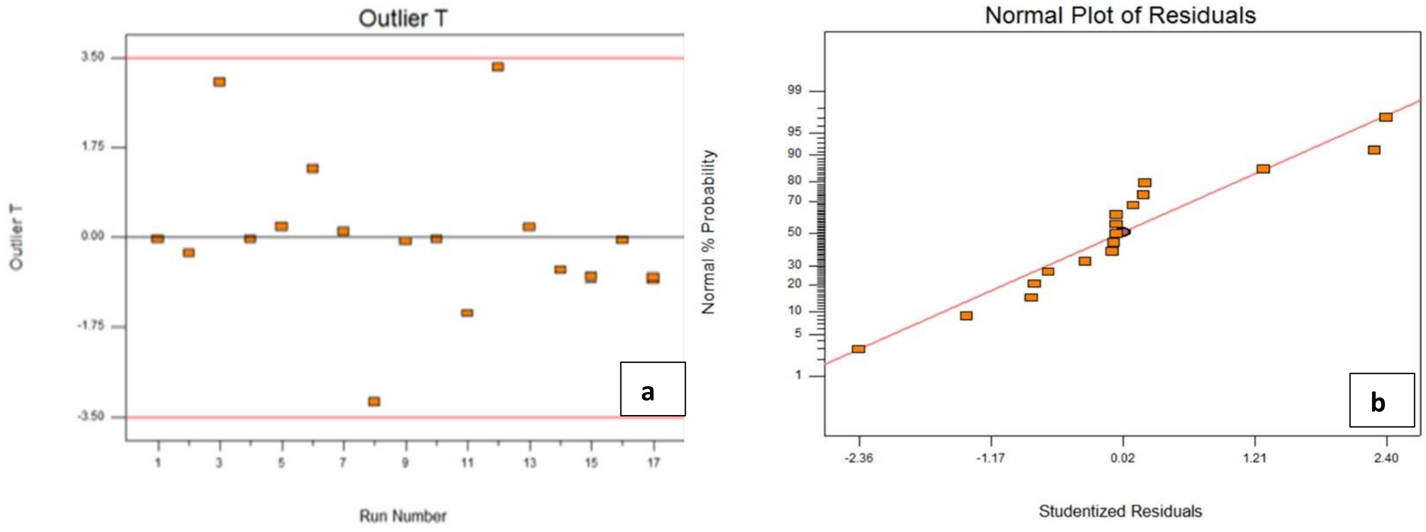
A₁: Outlier T(a) and normal plots of residuals(b) for diagnosis test.

Both the above plots show that the data taken and the results achieved are in the required range(there is no element outlier)

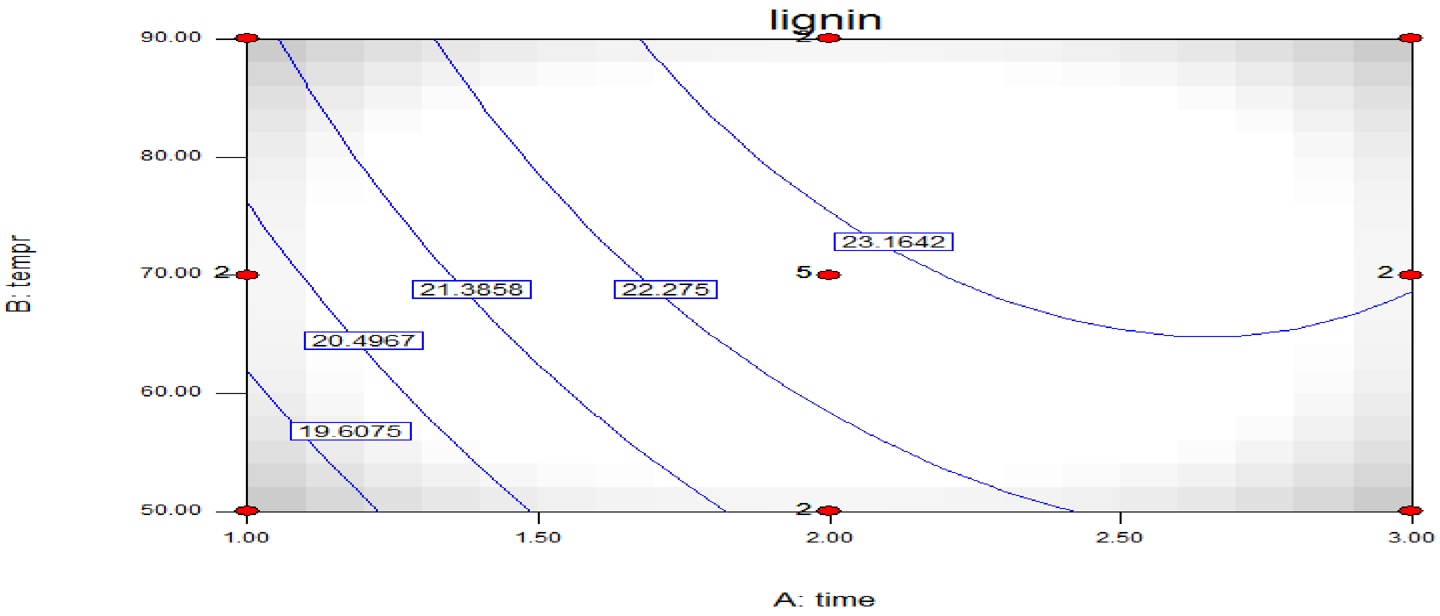


A₂: Contour plot of extractives vs temperature and time

2. Design Expert Plots for Delignification

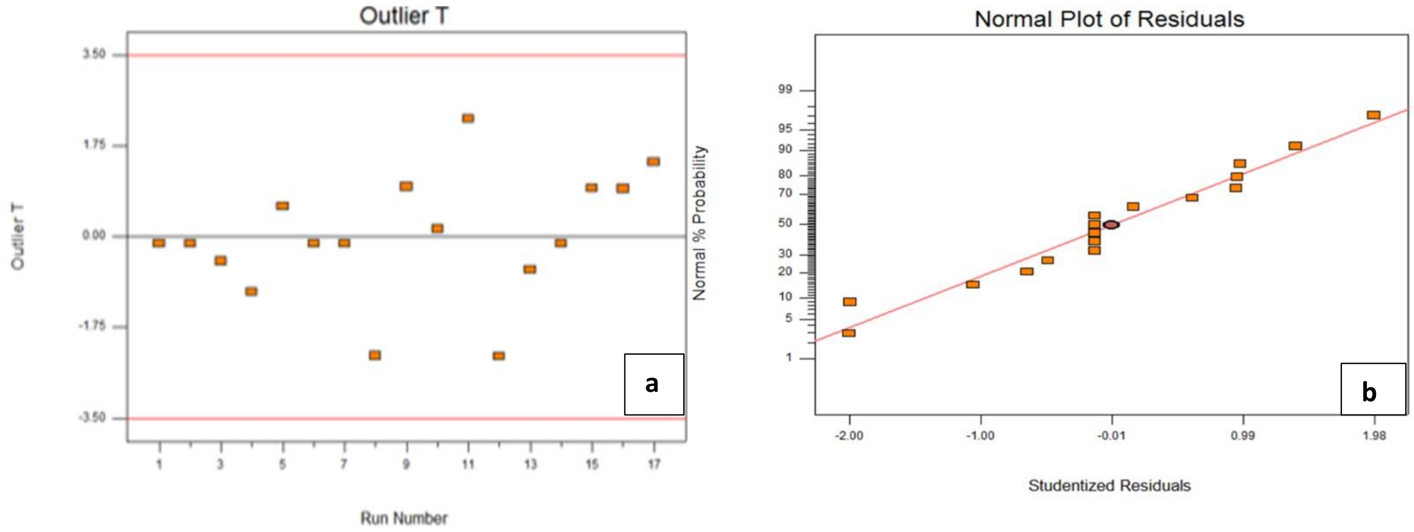


A3: Outlier T(a) and normal plots of residuals(b) for diagnosis test.

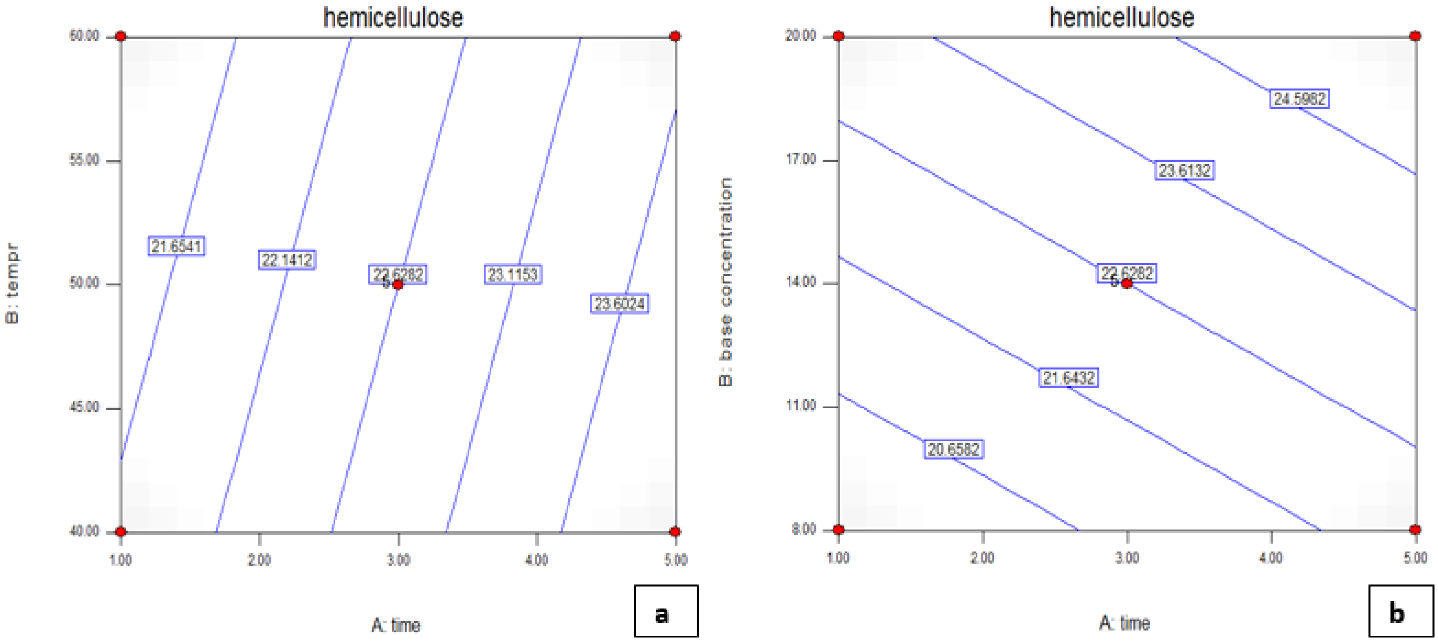


A4: Contour plot of lignin removal as a function of mixing temperature, time

3. Design Expert Plots for Hemicellulose Removal



A5: Outlier T(a) and normal plots of residuals(b) for diagnosis test.



A6: Contour plots: temperature vs time(a),base concentration vs time(b).

A7: hemicellulose removal variables interaction plot: base concentration vs time(a) temperature vs time(b).

The above figures show that there is no any interactions between the variable.

Appendix B

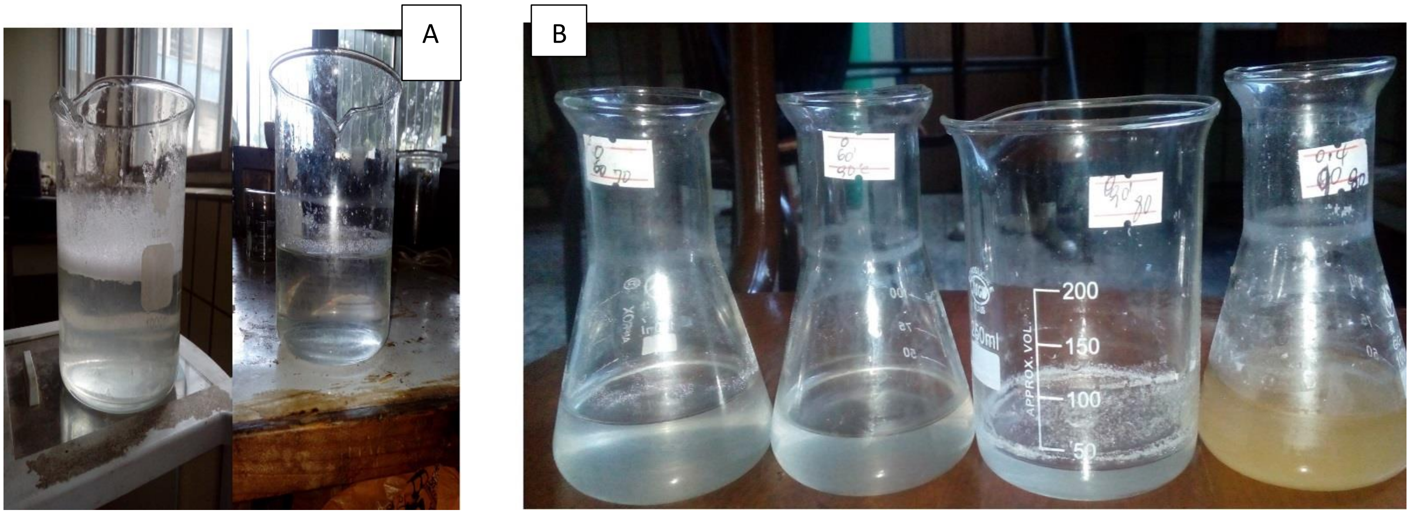
Some pictures from laboratory work

1. Pictures from bagasse processing and cellulose extraction:

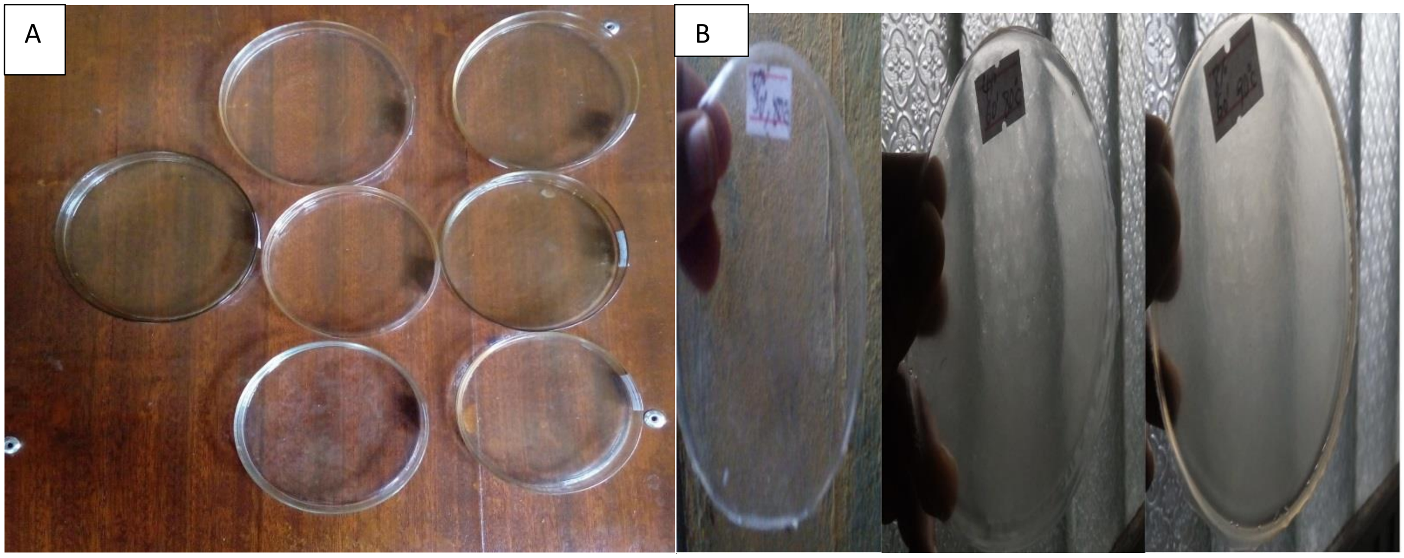
A) bagasse as it was brought from wonji showa sugar factory B)size reducing unit operation c) size reduced bagasse under washing

A) samples from extractives removal, delignification and hemicellulose removal B) extracted micro-cellulosse: drying and packaging

2. Pictures from biocomposite fabrication:



A) PVOH solution before and after sonication B) Neat PVOH and blended suspension of cellulose in PVOH solution



A) Casted samples of biocomposites B) Peeled biocomposites