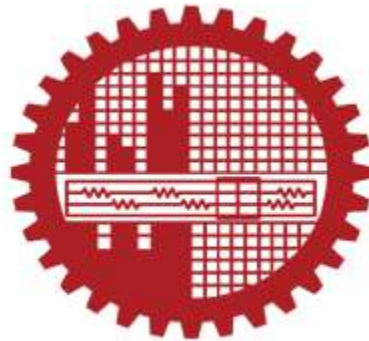# DEVELOPMENT AND CHARACTERIZATION OF CELLULOSE CRYSTAL REINFORCED BIODEGRADABLE COMPOSITE MATERIAL

By

Sharaban Tohora

Student Number: 0419112510

A thesis submitted in partial fulfillment of the requirements for the award of

MASTER OF SCIENCE IN MATERIALS SCIENCE

Department of Materials and Metallurgical Engineering

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

Dhaka-1000, Bangladesh

July 4, 2022.

DEVELOPMENT AND CHARACTERIZATION OF CELLULOSE CRYSTAL REINFORCED BIODEGRADABLE COMPOSITE MATERIAL

A Thesis submitted to Materials & Metallurgical Engineering Department, Bangladesh University of Engineering and Technology (BUET), Dhaka, in partial fulfillment of the requirements for the degree of **Master of Science** in Materials Science.

Submitted By:

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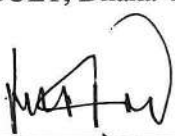Supervised By:

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Recommendations of The Board of Examiners

The thesis titled – "**Development and Characterization of Cellulose Crystal Reinforced Biodegradable Composite Material**"- submitted by Sharaban Tohora; Student number: 0419112510, Session- April 2019 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Science in Materials Science on July 4, 2022.

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Acknowledgments

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Dedicated to my beloved Parents

Abstract

Presently, development of biodegradable materials is one of the most popular topics in the field of materials science because of the adverse effects of plastics. Cellulose crystals (CC) as fillers in bio-composites have recently gained much interest amongst researchers for its promising qualities like improving elasticity and viscosity, rheological properties, and biodegradability. In present research, cellulose crystal has been extracted from jute using two steps of pretreatment. At first the raw jute fiber was ground and alkali treated with 15% sodium hydroxide for 1.5 hours. Then the resultant fiber was washed until neutral and bleached with 50% pure hydrogen peroxide for 1.5 hours. After the pretreatment, acid hydrolysis was done using 64% pure sulfuric acid for 15 minutes to produce pure cellulose crystal. The cellulose crystal was then freeze dried and used as reinforcement in a recently developed biodegradable composite from jute. The purchased jute polymer was dissolved and reinforced with cellulose crystal at 0, 0.1, 0.2, 0.3, 0.4 wt.% loading. The characteristics of the synthesized CC was studied using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. The results show that pure cellulose crystal was found, and micrographs showed presence of microscale particles with tear in the surface. For characterization of the films Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis was used. The results showed that the reinforcement did not introduce any new functional groups and did not help increase the crystallinity of the films. The SEM micrographs showed that CC loading up to 0.2% helped reduce the pore formation, however increasing the CC loading any further caused agglomeration and pores. Thermal characteristics of the reinforced composite films was tested using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and tensile properties were tested using UTM. The results show that the thermal and tensile properties increased up to 0.2% CC loading. The composites were tested for biodegradability and all the films degraded in soil after 100 days and the adding of cellulose crystal decreased degradation rate. Water absorption test revealed that the composites had a very high-water absorbance and the adding of cellulose crystal increased water absorption.

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CHAPTER 1
INTRODUCTION

Chapter 1

1. Introduction

One of the most widely discussed topics of the 21st century is biodegradable composites. We are striving to ensure the safety of the environment and the adverse effect of plastic packaging has emerged in front of our eyes like it had never before. Previously thought to be an invaluable gift to mankind, synthetic plastics are emerging as nothing short of a curse because of its indispensability in modern lifestyle. As of 2021, 60% of packaging materials come from plastics [1]. Common synthetic plastics such as low density polyethylene (LDPE), high density polyethylene (HDPE), polyethylene terephthalate (PET, PETE), polystyrene, polypropylene (PP) take 20 to 450 years to degrade under natural conditions [2]. These plastics are mainly being used for packaging purposes and they are being dumped into landfills, which occupy large areas and also emit methane and carbon dioxide gases after photodegradation [3]. People conscious about the environment are now raising awareness for using biodegradable materials instead of synthetic plastics. As a result, demand for sustainable biodegradable materials is increasing gradually and researchers are leaning towards this field to develop sustainable and economically feasible biodegradable materials.

1.1. Background

The history of biodegradable polymers goes way back to 1500 B.C when Meso-American cultures such as the Aztecs, the Mayans and the Olmecs used natural rubber and latex for various purposes. In 1862, Alexander Parkes created "Parkesine", the first man made biobased plastics but it was the 1980s when "biodegradable" polymers and plastics were first developed [4].

In 1907, worlds first synthetic polymer "Bakelite" was invented [5]. With advancement of technology, more synthetic polymers were invented and their popularity increased. Over the last two decades, approximately 140 million tonnes of synthetic polymers are being synthesized and used every year [6]. Surge in application of polymers in every sector of civilization, gave rise to the interest in polymer biodegradation as most of the synthetic polymers were not biodegradable [7]. Disposing of the polymer products after they were no longer useful, became a concern for everyone. In the years of 2005 to 2009, 20-25% of solid waste and 80% of marine debris were being generated from non-biodegradable polymers [7].

The importance of sustainable biodegradable polymers has been rising since the beginning of twentieth century and it can be evidenced by the investment of 1 billion dollars to promote recycling by the private sectors all over the world [6]. In addition, integration of processes like "composting" and "bio gasification" in the Solid Waste Management system has led to commercial interest in research in biodegradable materials.

Currently, several synthetic biodegradable polymers are being used to produce so called "environment-friendly" consumer products. Amongst them are starch based polymers such as poly lactic acid (PLA), polybutylene adipate terephthalate (PBAT), polycaprolactone (PCL), acrylic acid (AAc) blends, polyvinyl alcohol (PVA) etc [8]. However, the emergence of "biodegradable composites" has revolutionized the research in biodegradable materials.

Due to its biodegradability, availability, high strength-to-weight ratio, low cost, and low density, cellulose has garnered a lot of interest among natural renewable reinforcing materials. In polymer matrix composites, cellulose fibers can serve as reinforcement to enhance their mechanical and physical qualities. However, high moisture absorption rate and poor compatibility when combined with the hydrophobic polymer matrix, have reduced the potential for cellulosic materials to be used as a reinforcing agent in polymer matrices, especially for microscale materials [9].

In order to make biodegradable polymer composites, only natural fillers can be used. A common practice is to use nano or microscale fillers because the incorporation of non-degradable inorganic nanoparticles would nullify the sustainability of the polymer matrix. A lot of biodegradable polymers have been investigated as the matrix for CNC-incorporated nanocomposites such as poly(butylene succinate) (PBS), poly(lactic acid) (PLA), poly(caprolactone) (PCL), poly(butylene adipate-co-terephthalate (PBAT), and polyhydroxyl alkanoate. Cellulose crystals in nano scale have been effective as rheology modifier, elasticity and viscosity enhancer and has shown that the amount and blending method of CNCs when preparing nanocomposites primarily determine the viscoelasticity, processability, and final performance of the products [10].

In this study, to produce cellulose crystal (CC), a very unique set of steps have been followed because the process variables like concentrations of the chemicals used in pretreatment and processing time have not exactly been followed elsewhere, to the best of the author's knowledge.

Jute polymer-based packaging material developed in Bangladesh is a new product and to the best of the authors' knowledge, no studies have been conducted on composites created from dissolving the jute polymer based biodegradable packaging material and reinforcing it with jute produced cellulose crystal. These factors create the need for studying the mechanical, thermal, structural and biodegradable properties of the produced composite films.

1.2. Objectives

The main target of this research is to fabricate an environment friendly biodegradable composite material with cellulose crystal as reinforcement. A comprehensive study into the mechanical and structural properties of this material is to be conducted to discover the areas of usage. Following are the specific intentions of this research-

I. Synthesis of cellulose crystal from jute in a novel process.

II. Preparation of composite using jute produced biodegradable packaging material solution and cellulose crystal as reinforcement with a motive of increasing sustainability and strength.

III. Investigation of mechanical, thermal, structural, and biodegradable properties of cellulose crystal reinforced jute produced biodegradable composite material.

1.3. Scope of the thesis

This thesis has been organized in five chapters-

Chapter one	Introduction
Chapter two	Literature Review
Chapter three	Experimental
Chapter four	Results and Discussions
Chapter five	Conclusions and Future Work

Chapter one will introduce the concepts of the thesis. The main concepts along with the aims, objectives, scope of the thesis as well as the importance of the thesis will be justified.

Chapter two includes literature review. A summary and analysis of the previous work related to composites properties and types in general, cellulose reinforced composites, types of cellulose, biodegradable polymer and its uses, and justification of using jute polymer as research material has been presented.

Chapter three presents detailed outline of the process and experiments conducted during the preparation and characterization of cellulose crystal and cellulose crystal reinforced jute polymer composites.

Chapter four discusses the test results for characterizing the cellulose crystal and the cellulose crystal reinforced jute polymer composites.

Chapter five a conclusion is drawn from the experimental results which are novel to this field of study. Some recommendations are also enlisted in some future work proposals section.

CHAPTER 2
LITERATURE REVIEW

Chapter 2

2. Literature Review

In this chapter, composites, and their classifications, constituents of a composite, matrix, reinforcement, cellulose reinforced composites, biodegradable polymers, biodegradable packaging material, standpoint of Bangladesh in the biodegradable packaging production and use and justification of choosing Jute-polymer as the research material will be discussed.

2.1 Composite

In 2012 Olympics, Oscar Pistorius, known as "The Blade Runner," made history when he competed as the first double amputee athlete in the able-bodied Olympics. His prosthetic legs were made of carbon fiber composite material. This incident demonstrates the exploitation of medical uses of polymer matrix composites [11].

Composite materials can be defined as materials that are formed by combining two or more materials with different properties that do not dissolve or blend into each other. [12] Professor M. Balasubramanian in his book "Composite materials and processing" defines composite materials as- "a macroscopic combination of two or more distinct materials having a finite interface between them". Within the finished structure of a composite, the individual components remain separate and distinct [13].

First composites were used in 1500 BC when early Egyptians and Mesopotamians mixed straw and mud to create inhabitable structures [11]. As of the 21st century, composite materials have been introduced into almost every industry in some form or fashion. Sustainable composite materials result in better properties than those of the individual components used alone [14].

Composites make way for great design flexibility and offer a smaller number of separate parts for products. They also give the opportunity to select wide variety of constituents and tailor them to gain desired properties (Figure 2.1) [15].

Figure 2.1 Advantages of composite materials [1].

In addition to its properties, composites are fundamentally different in the way they are fabricated. The properties of composites vary largely based on their fabrication process. There are many options of how composites can be fabricated which depend on the form. Some of those options are summarized in Figure 2.2.
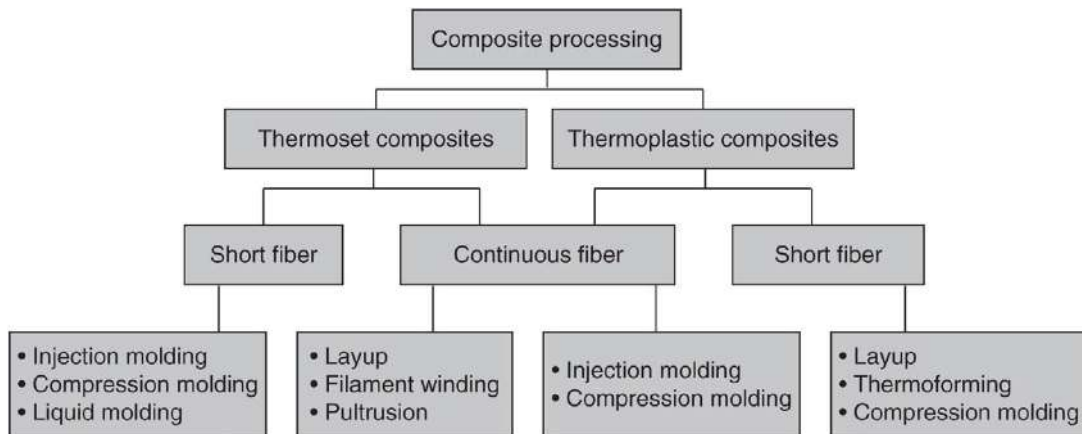
Figure 2.2 Fabrication processes of composites [4]

2.2 Types of Composites

Generally, composites can be classified into two types- natural composites and synthetic composites. Wood, bone, etc. are some of the examples of natural composites. In natural composites, the constituents are present in excellent scale, but it is very hard to customize the properties of natural composites. On the other hand, man-made composites can be easily tailored to have desired attributes [16]. However, composites can also be classified based on dispersed phases and matrix materials. These classifications have been discussed in the following sections.

2.2.1 Classification based on Dispersed Phase

There are two basic types of composites based on dispersed phase: fiber reinforced composites (FRCs) and particulate composites (Figure 2.3).

Fiber Reinforced Composite

According to Njuguna et al "The three main components of fiber reinforced composite are discontinuous phase grains, a continuous phase matrix and an interface region. The matrix component often contains epoxy or phenolic, which act as a corrosion prevention coating" [17].

In a fiber reinforced composite, there can be single or multiple layers. If the multilayered composite is made up of the same fiber, it is called a "laminate" and if two or more types of fibers are used for layering, it's called a "hybrid composite". For single layered composites, long or short fibers are used (Figure 2.4). The properties of the composites can vary with the direction of reinforcement loading. Single layered composites may be Isotropic or anisotropic.
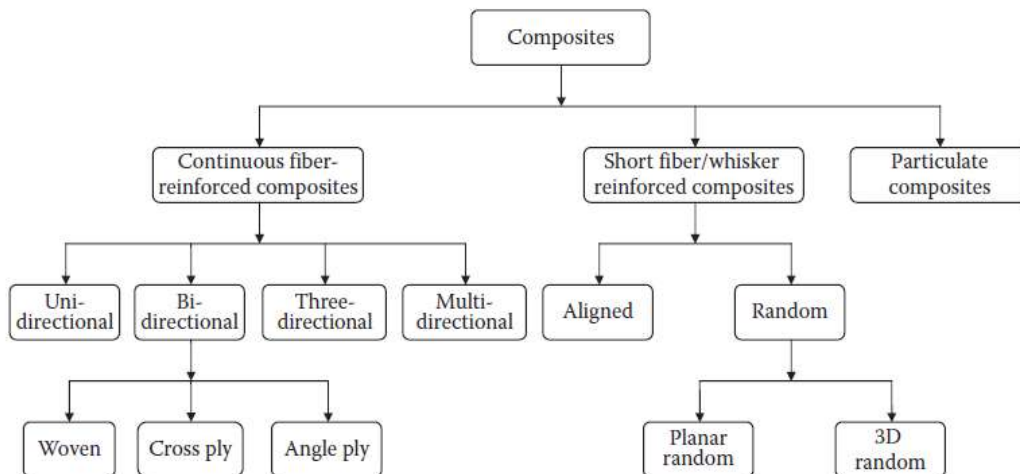
Figure 2.3 Classification of composites based on dispersed Phase [6].
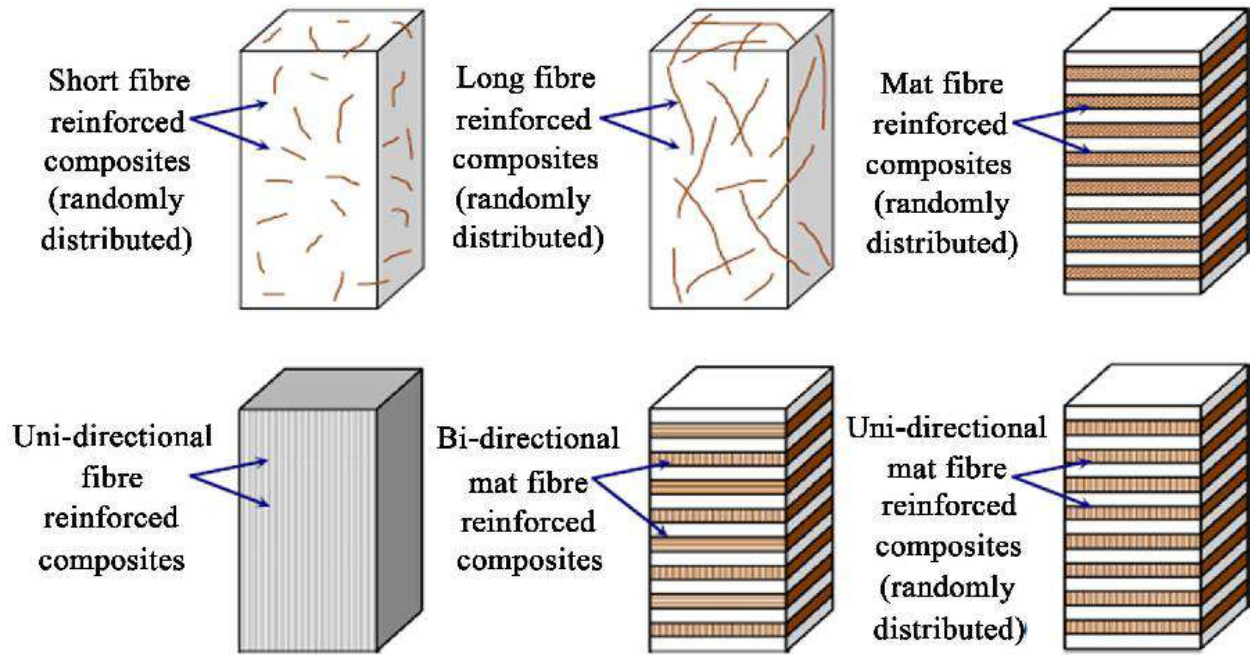
Figure 2.4 Different type of fiber orientation in laminate composites [8]

Particulate Composites

Particulate composites are composed of particles suspended in matrix [18]. The main advantage of particulate composites is that they offer tremendous flexibility in composition and component design. Particulate composites offer properties like load transfer between phases and a wide range of processing options [19]. The particles in a particulate composite can have any shape size or configuration. There are two subclasses of particulates: flake and filled/skeletal:

Flake: Flakes usually have large ratios of platform area to thickness. These flakes are suspended in a matrix material to form composites of this type. An example of this type of composite can be particle boards.

Filled Composites: A filled composite, also known as skeletal composites, is formed by a skeletal matrix filled by a second type of material. Examples include a honeycomb core filled with an insulating material. Particulate composites can be either anisotropic or orthotropic and

are used in cases where strength is not a significant component of the design. In the following figure, types of composites are shown [18]. Figure 2.5 shows types of particulate composites.
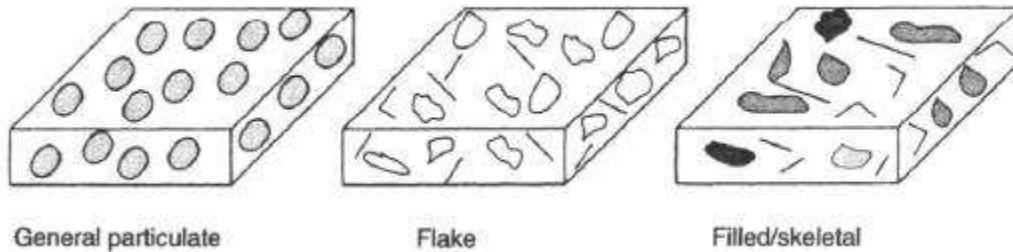
Figure 2.5 Schematic diagrams of types of particulate composite [77]

2.2.2 Classification based on matrix material

Based on the matrix material, the composites are classified into polymer matrix composites (PMCs), metal matrix composites (MMCs), and ceramic matrix composites (CMCs) (Figure 2.6). The classification of composites based on matrix material is shown in Figure- 1.3. The three types of composites differ in the manufacturing method adopted, mechanical behaviors, and functional characteristics. Since the matrix materials undergo physical or chemical change, the processing method to be used for making the composites has a direct bearing on the matrix system used. The temperature at which the matrix materials are processed determines the choice of the dispersed phase because the reinforcement should neither undergo any chemical reaction or physical change nor have any change in its properties. The temperature level at which a particular composite can be used is determined by the temperature resistance of the matrix material.
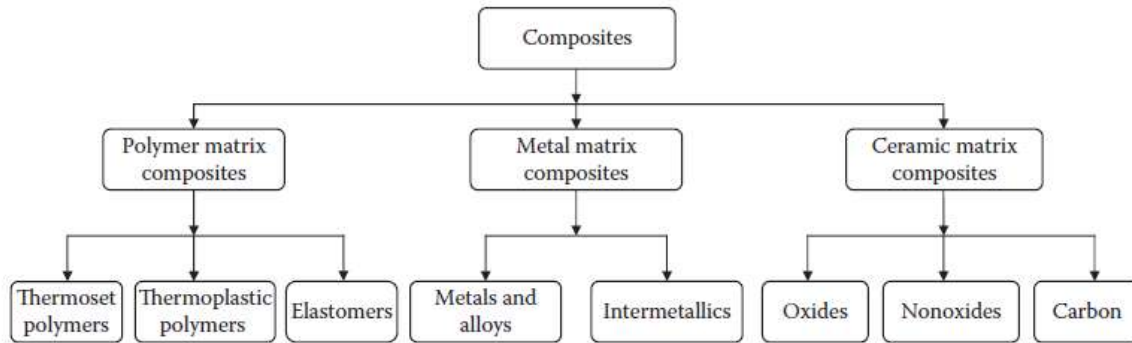
Figure 2.6 Classification of composites based on matrix material [6].

Metal Matrix Composites (MMC)

The class or materials where a metal is merged with another substance are called metal matrix composites. The components in a metal matrix composite appear in different phases that are physically and chemically different. Metal matrix composites are composed with a view to enhance the properties by adding supplementary features that the reinforcement provides [20]. To avoid chemical damage, the surface of the reinforcement material is sometimes coated with some inert material. Aluminum, magnesium and titanium are common metals used as matrix. Some of the less common matrix bases are copper, cobalt, nickel or alloys of metals that are highly useful. carbon fiber, silicon carbide, alumina, and boron are most common reinforcement material. Metal matrix composites are applied in the fields of aerospace and aircraft industry, sports, and automotive industries [21]. The major advantages of MMC's can be listed as follows:

- High Strength
- High Heat Resistance
- Fire resistance
- Inability to absorb moisture
- Radiation resistance
- Increased resistance to wear and tear
- High thermal conductivity
- Excellent abrasion resistance
- Good creep resistance

- High wear resistance
- High thermal stability

Ceramic Matrix Composites (CMC)

K.K Chawla describes ceramic matrix composites as "Ceramic matrix composites (CMC) are generally made from ceramic fibers or whiskers embedded in a ceramic matrix." Ceramics are inorganic materials These ceramics cover a varied range of inorganic, non-metallic materials and can be classified into two classes- ceramics that are in monolithic forms are conventional ceramics, such as- pottery, tiles, bricks etc. Ceramics that undergo chemical processing are advanced or high-performance ceramics such as silicon or aluminum. The main inspiration behind developing CMCs is to get rid of the problems such as low crack and fracture resistance and to increase toughness [22].

Some of the typical properties of Ceramic matrix composites are: [23]

- High thermal shock and creep resistance
- High temperature resistance
- Excellent resistance to corrosion and wear
- Inertness to aggressive chemicals
- High tensile and compressive strength, thus no sudden failure as compared to conventional ceramics
- Increased fracture toughness due to reinforcement
- Lightweight due to reduced density
- High strength retention at elevated temperatures

Polymer Matrix Composites (PMC)

The most common type of composites used in today's world are polymer matrix composites which are formed by a fibrous reinforcing material dispersed in a polymer matrix. They are low cost, require simple fabrication process, easily adopts any shapes, and thus have eared such popularity [13]. Based on their level of strength and stiffness, Polymer matrix composites are classified into two distinct types- Reinforced plastics offers increase in strength by adding embedded fibrous matter into plastics. Advanced composites consist of fiber and matrix combinations that facilitate

strength and superior stiffness. The 4 factors on which the strength of polymer composites depends on are: (1) the properties of the matrix, (2) the properties of the reinforcement, (3) the reinforcement–matrix compatibility and interaction, and (4) the dispersion of the reinforcement in the matrix for short fiber- or particle-reinforced systems [24].

Reinforcement of polymers by strong fibrous network permits fabrication of PMC characterized by the following properties [11]:

- High tensile strength
- High stiffness
- High fracture toughness
- Good abrasion resistance
- Good puncture resistance
- Good corrosion resistance
- Low cost

However, PMC has disadvantages like low thermal resistance and high coefficient of thermal expansion. Properties of the fiber and matrix and concentration and orientation of fibers are deciding factors in a polymer matrix. PMCs are used for automotive industry, aircraft and aerospace industry, biomedical applications, marine and sports goods and electrical and structural equipment.

Carbon-Carbon Composites (CCMs)

composite material consisting of carbon fiber reinforcement in a matrix of graphite are called Carbon-Carbon Composites [13]. These types of composites are like graphite/epoxy family of polymer composites. These materials can be made into one-dimensional to n-dimensional forms using unidirectional tows, tapes, or woven cloth and because of their multiformity, the mechanical properties of CC composites can be readily tailored. high strength and stiffness potential, high thermal and chemical stability in inert environments are common properties of carbon materials but they have to be insulated if used in oxidizing environment [25]. These composites are applicable in very high temperature environments and ate 20 times stronger and 3o times lighter than graphite fibers.

2.3 The Matrix

The monolithic and homogeneous material in which the fiber system is embedded is called the Matrix of a composite. "Monolithic" means formed or composed of material without joints or seams. The function of a matrix can be described as to provide a binding medium to hold reinforcements together [26]. There are three different types of matrices- Metal, Ceramic and Polymer.

2.3.1 Types of Matrices
Metal Matrix

Better than conventional materials in terms of enhanced mechanical and thermal properties, metal matrix composites are very popular as advanced materials. These materials show good wear resistance and exceptional thermal conductivity [27]. In the monolithic metal matrix the reinforcement is embedded, and it is continuous, meaning that, there is a path through the matrix to any point in the material which is absent in sandwiched materials [15]. Aluminum and it's alloys are commonly used as metal matrix composites. Other common metals are magnesium and titanium. cobalt and cobalt-nickel alloy matrices are common for high temperature cases. For several specialized application copper, zinc or lead matrix is also used [20].

Ceramic Matrix

Ceramic matrices are used for high temperature applications. According to Chawla "A ceramic is a material that is neither metallic nor organic. It may be crystalline, glassy or both crystalline and glassy. Ceramics are typically hard and chemically non-reactive and can be formed or densified with heat" [22]. In a CMC there are ceramic fibers embedded in ceramic matrix. CMCs are designed to overcome the major disadvantages such as low fracture toughness, brittleness, and limited thermal shock resistance, faced by the traditional technical ceramics [26]. Generally, ceramics are oxidation resistant, corrosion resistant, hard, strong, and able to withstand very high temperatures. The reinforcing material is usually selected to reduce brittleness.

Polymer Matrix

The substance in which a large number of atoms are bonded together to form a long chain are called polymers. Because of their light weight and easy fabrication, polymeric materials have become extremely popular [7]. There are two general types of polymers: The polymers which cure

into irreversibly hardened material are called thermoset polymers. The permanent state is caused by "crosslinking" which means the formation of bonds between polymer chains. These bonds fix the polymer in a three-dimensional array which causes the limited motion. The polymers that are capable of being repeatedly softened by adding heat and hardened by cooling are called thermoplastic polymers.

Thermosetting Polymers

Thermosetting Polymers are prepared combining chemical reactions of two or more materials. The monomer is used for forming the final chain of the polymer. The cross-linker helps in combining two or more strands related to monomers together [11]. Thermoset polymers differ from thermoplastics as they do not require heating to form the plastic material but utilize a curing process where a chemical reaction takes place, forming cross-links. Thermoset polymers could be cured to the desired shape and be as close to the finished product, as compared to thermoplastic polymers, which requires additional finishing [28]. Thermosets can be characterized by examples of polyesters, epoxies, polyurethanes, and silicones. Molding is a common way to give the thermosets the desired shape before solidifying and the common ways in which molding is done are: reaction Injection molding, compression molding, resin transfer molding , extrusion molding and spin casting [29]. Around 69% of the application of thermosets present in the construction and building industry, other uses of thermosets are in transportation, adhesives, and electrical equipment [30].

 Properties Associated with Thermosetting Polymers

Thermoset polymers have characteristics that enable the material to be more chemically or solvent resistant and high heat stability; hence it is notably used for applications with harsh conditions. These thermoset polymers are synthetically produced and not as recyclable as thermoplastics having remoldable/remelt characteristics [28]. The components which are used in a thermosetting plastic, effect its properties majorly. These types of plastics are brittle because they lose their elasticity when heated. They cannot be reshaped hence, they are not recyclable [29]. To apply recycling, it can be done chemically. As the processes enable the breakdown of thermoset polymer complex structure, chemical and thermal recycling may be considered as the recommended approach toward recycling thermoset polymers. Also, mechanical grinding can be done to turn the

thermosets into granules. These granules can then be depolymerized through chemical recycling. These small granules can also be used as reinforcements to form particulate composites [28].

Thermoplastic Polymers

Thermoplastic polymers melt from a solid to a liquid and then cool back to a solid without exchanging any electrons and so no crosslinking occurs. condensation or addition polymerization processes are used to make thermoplastic polymers. Thermoplastic bonds are covalent and they are called "heat- forming" [31]. According to Ibel et al. "A thermoplastic is a resin that is solid at room temperature but becomes plastic and soft upon heating, flowing due to crystal melting or by virtue of crossing the glass transition temperature (Tg)". Common processes to process thermoplastics include injection molding or blow molding. The thermoplastics can be reversible, can undergo reheating which gives it the quality of being recyclable. Because of its recyclability, thermoplastics can go under processes like extrusion, thermoforming, and injection molding etc. Examples of common thermoplastic materials include polyethylene (PE), polycarbonate (PC), and polyvinyl chloride (PVC). The downside of thermoplastics is that they can not be used for cases where extremely high temperatures occur.

2.4 The Reinforcement

Qin et al has described reinforcement materials as "Reinforcement materials usually add rigidity
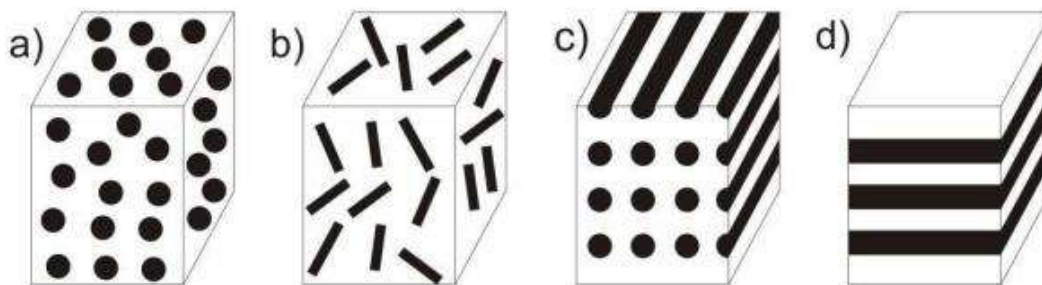
Figure 2.7 Various types of reinforcement in composites; a) particles, b) Short fibers, c) continuous fibers d) plates

and greatly impede crack propagation. They enforce the mechanical properties of the matrix and,

in most cases, are harder, stronger, and stiffer than the matrix" [32]. The reinforcement can be divided into four basic categories: fibers, particulates, fillers, and flakes (Figure 2.7).

Flakes:

Flakes are flat platelets with a two-dimensional shape that provides strength and stiffness in both directions. When suspended in glass or plastic, they can produce an effective composite material. Flakes are typically packed parallel to one another, resulting in a higher density than fiber-packing techniques. Mica, aluminum, and silver are common flake materials. Mica flakes incorporated in a glassy matrix produce easy-to-machine composites that are employed in electrical applications. Aluminum flakes, which are oriented parallel to the surface of paints and other coatings, are widely utilized [32].

Particles:

Small particles (less than 0.25 mm), hollow spheres, cubes, platelets, and carbon nanotubes can all be employed in composites. The particles give desirable material qualities in each case, while the matrix serves as a binding medium for structural purposes. The orientation of particulate elements might be random or with a preference. Particles are not particularly good in improving strength and fracture resistance in general. Lead, copper, tungsten, molybdenum, and chromium are common particle materials [32].

Fillers:

Fillers are granules or powders that are mixed into a material to alter or improve its physical and mechanical qualities. They are also employed to reduce the amount of pricey binder material used. Fillers are used to change or improve qualities including thermal conductivity, electrical resistivity, friction, wear resistance, and flame resistance, among others. Calcium carbonate, aluminum oxide, lime (also known as calcium oxide), fumed silica, processed clays, and hollow glass beads are examples of common fillers [32].

Fibers

A fiber is a rope or thread that is utilized as a component of composite materials and has a significant aspect ratio (length/diameter) (> 100). Circular, square, or hexagonal cross-sections are

possible. The following fibers are commonly used in composites: glass fiber, which is made by mechanically pulling molten glass through a small opening and contains mostly of silicon dioxide and metallic oxide modifying components. Because of their low cost and great corrosion resistance, they are widely used. aramid fiber, which has a greater specific strength and is lighter than glass, is more ductile than carbon and can be utilized in fishing rods, storage tanks, and aviation parts. Armor, protective garments, and athletic products are examples of industrial applications. Carbon fiber is frequently made from oxidized polyacrylonitrile or carbonized polymers pyrolyzed with low density, carbon fiber can have a modulus of up to 950 GPa. It has a diameter of 5–8 m, which is smaller than a human hair (50 m); and boron fiber, which has great stiffness, good compressive strength, and big diameters (0.05–0.2 mm) when compared to other types of fibers. silicon carbide fiber, which is commonly employed in high-temperature metal and ceramic matrix composites (CMC) because of its superior oxidation resistance, high modulus, and strength in a high-temperature environment [32].

2.5 Cellulose Reinforced Composites

2.5.1 Cellulose:

Cellulose is a polysaccharide containing a linear chain with hundreds to thousands of b-1,4 linked D-glucose units. Numerous intra and extra molecular hydrogen bonds are generated between hydrogen and oxygen on cellulose due to the presence of several hydroxyl groups. These bonds securely hold chains together to form microfibrils having exceptional tensile strength. The theoretically anticipated elastic modulus and tensile strength of a perfect crystal of cellulose are 150 and 10 GPa, respectively [24].

Cellulose is an intriguing biopolymer with almost limitless supply. While it is a lightweight material, it has exceptional strength and stiffness when used in its natural state. Unsurprisingly, cellulose fiber has been extensively researched as a bio-composites reinforcing component [33]. Cellulose has been used widely as alternative reinforcements in composite materials to replace inorganic fillers, like glass fibers and synthetic polymers. However, when utilized as reinforcing elements in composite materials, natural organic fibers have two fundamental drawbacks: (I) they have a high sensitivity to water and moisture; and (ii) they have poor compliance with the

hydrophobic polymeric matrices frequently used in this field. The repercussions of such characteristics are severe in the context of composite materials because moisture adsorption causes a loss of mechanical properties, and poor compatibility causes weak interfacial adhesion and dispersibility, resulting in low-performance composites [34]. Structure of cellulose is shown in Figure 2.8.
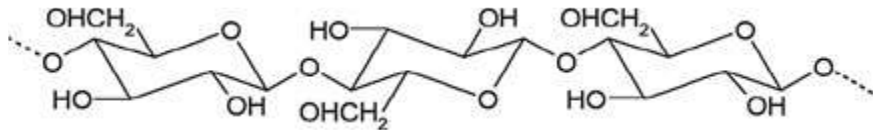
Figure 2.8 Structure of Cellulose [14]

Lignocellulosic fibers are made up of cellulose microfibrils encased in a matrix of other polymers, notably hemicelluloses and lignin. The natural fiber characteristics are substantially influenced by various variables, including chemical makeup and internal fiber structure, which varies by species plant parts as well as differences between plants. Microfibrils in most natural fibers position themselves at an angle to the fiber axis known as the "microfibril angle" [34]. Different plant fibers show a slight link between strength, cellulose concentration, and microfibril or spiral angle. In general, fiber strength rises as cellulose content rises and the spiral angle of the fiber axis decreases. This suggests that cellulose fibers with a high cellulose concentration and a low microfibril angle are the most efficient. Microfibril sizes range from roughly 2 nm to 20 nm, with lengths reaching several tens of microns, depending on their origin. Each microfibril can be thought of as a string of cellulose monocrystals linked along the microfibril by amorphous domains and having a modulus close to the theoretical limit for cellulose since they lack chain folding and have a minimal number of defects. The axial Young's modulus of the fundamental cellulose crystalline nanocrystal generated from theoretical chemistry is potentially stronger than steel and similar to Kevlar, which gives cellulose-derived composites their promise [34].

According to Chuanwei et. al. Cellulose has following properties: [24]

1. High specific strength and modulus—the maximum macroscopic Young's modulus of natural plant cellulose fibers is 128 GPa

2. Low density

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3. The fibers have hollow structure and so it has high sound proofing properties

4. Ease of surface modification due to reactive surface.

Although a range of other agri-fibers are available, wood is the most common source of cellulosic fibers, notably for the pulp and paper sector. The middle lamella, the primary wall, and the secondary wall are the three walls that define wood fibers. In all three locations, cellulose microfibrils and hemicelluloses can be found. Pectin in primary walls and lignin in secondary walls make up the third major component. Wood is a mixture of these components, with cellulose microfibrils contributing to its strength [24].

2.5.2 Cellulose Fiber Reinforced Polymer Composites
Cellulose fibers from a variety of sources are widely used and studied in composites. Polymers like high density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), low density polyethylene (LDPE), ethylene vinyl acetate copolymer etc. are used as matrix material [33].

Cellulose fiber reinforced composites have following disadvantages: (1) Because cellulose fibers are polar and hydrophilic, they are incompatible with non-polar and hydrophobic thermoplastics, resulting in inefficient reinforcement dispersion and weak matrix-reinforcement interaction; (2) processing temperature limits the compounding of cellulose fibers with major engineering plastics such as polyethylene, polypropylene, polystyrene, and poly(vinyl chloride); (3) cellulose fiber-reinforced composites can be made from cellulose fibers [24].

Processing natural cellulose fibers into a regenerated cellulose fiber such as rayon is one technique to avoid the uncertainty of characteristics. The raw material for rayon is extracted cellulose. After soaking in a caustic soda solution, cellulose is reacted with carbon disulfide to create a viscous material that is spun into rayon fiber. However, there are environmental issues with this method. A new type of artificial cellulose fiber, lyocell or Tencel, was first made two decades ago. Lyocell is made by dissolving cellulose directly in a non-toxic chemical solvent and spinning it. After that, the fibers are cleansed, and the solvent is recycled. It is environmentally friendly due to the closed-loop manufacturing method. Regenerated cellulose fibers have properties that are widely tunable. Traditional processing methods can be used to process fiber reinforced polymer composites. The

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drying of the fibers prior to processing is critical, since water in the fiber might cause weak adhesion between fiber and polymer, or even voids in the composite, when the water evaporates during processing [24].

Compatibility of cellulose fiber with polymer matrix is critical given the fact that cellulose fibers are highly polar and hydrophilic, and most polymers are non-polar and hydrophobic. This problem can be solved by physical, physio-chemical, or chemical pretreatment of the cellulose fibers to increase surface compatibility. The hydroxyl groups in cellulose can be exploited to make a number of cellulose derivatives. To retain the integrity of the fibers and consequently their mechanical strength, the changes should ideally be restricted to the surface hydroxyl groups [24].

Micro and Nano scale Cellulose Reinforcement in polymers

Pure cellulose microfibrils are widely recognized for their exceptional strength due to their highly crystalline structure and the presence of inter- and intramolecular hydrogen bonding. To fully utilize the qualities of cellulose, researchers have attempted to generate cellulose microfibrils with unique properties, particularly high strength, through controlled disintegration of natural fibers or the growth of cellulose from bacterial sources. Cellulosic structures are typically millimeter or nanometer scale, and when utilized as reinforcement in polymer composites, they can exhibit unique features [24]. There are several forms of extracted pure cellulose used and amongst them, micro fibrillated cellulose, microcrystalline cellulose, bacterial cellulose, and nanocrystalline cellulose are discussed in detail in the following sections. SEM micrographs of various cellulose are shown in Figure 2.9.
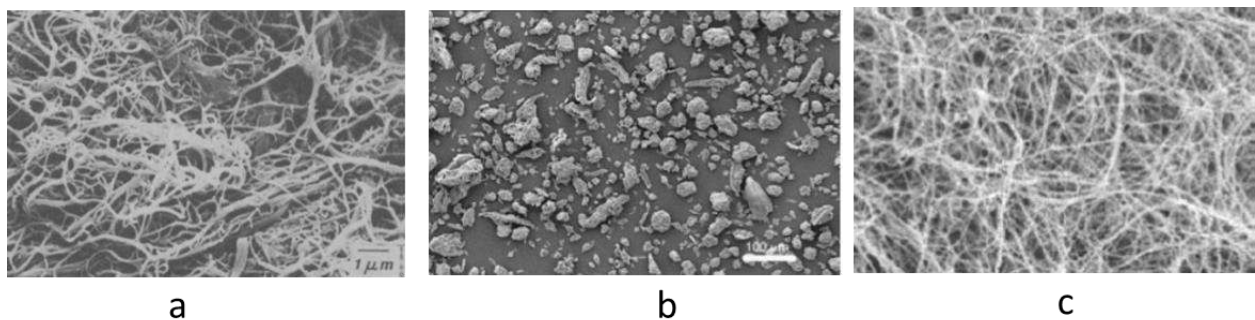
Figure 2.9 SEM micrograph of a) Microfabricated Cellulose b) Microcrystalline Cellulose c) Bacterial cellulose. [24]

Micro Fibrillated Cellulose

Despite its fibril-like appearance, MFC is made up of fragmented cell wall material rather than pure cellulose fibrils. MFC always has a net-like arrangement of microfibrils. Microfibrillated cellulose nanofibers (MFC) degraded from wood pulp can be used to make high-performance polymer nanocomposites. The Young's modulus of these composites approaches 20 GPa. The claimed strength is also high, albeit the findings should be interpreted with caution because brittle material flexural strength is highly dependent on specimen shape. Because the Young's modulus of the cellulose crystal is as high as 134 GPa. MFC nanofibers are expected to be stiff. During biosynthesis, its polymer molecules crystallize in extended-chain conformation, forming microfibrils with a lateral dimension of roughly 4 nm. The preferred orientation of cellulose microfibrils in wood is often close to the axial fiber direction. In cellulosic wood pulp fibers, wood microfibrils form 15–18 nm thick aggregates [35].

Micro Crystalline Cellulose

Microcrystalline cellulose (MCC), in contrast to MFC, is a commercial product with a history of almost half a century. Surprisingly, the finding of MCC is the result of an unsuccessful experiment. In that experiment. Presently, extensive research has been done in using MCC as reinforcement. MCC was synthesized from wood pulp by Laka et al. (2003), and MCC/Na-carboxymethylcellulose (Na-CMC) composites were formed by film casting an aqueous mixture of the two components. The MCC used in the studies was generated by grinding bleached wood pulp in a ball mill. 60% of the particles had a longitudinal size of 3–20 lm, while 80% of the particles had a transverse size of 3–20 lm. The mechanical properties of the film did not alter when the MCC dry weight content was less than 43%, according to the testing findings. MCC was created in the experiments using bleached wood pulp and then ground in a ball mill. 60% of the particles had a longitudinal size of 3–20 lm and 80% of the particles had a transverse size of 3–20 lm. When the MCC dry weight concentration was less than 43%, the film's mechanical characteristics remained unchanged. After then, the composite's tensile strength and elastic modulus rose, peaking at 42 and 30%, respectively, at 70 percent MCC (dry weight) content. [24]. Borges et al. (Borges et al. 2004) examined the tensile characteristics of MCC (Avicel) fiber-hydroxypropyl cellulose (HPC) composite films cast from HPC acetone solution. The MCC particles used in their trials were 30 micrometers in size on average. At 5:1 aspect ratio at 20 wt. percent MCC, the composite's tensile stress and Young's modulus were raised two and three times,

respectively, above MCC-free HPC. When 1,4-butyldiisocyanate (BDI), a crosslinking agent that can react with the hydroxyl groups on HPC and MCC, was used to process films, the maximum strength was achieved at 10 wt.% MCC content, and the values were 15–20 percent greater than the uncross linked ones. This was explained in terms of improved MCC packing in the composite films, i.e., better distribution, which was backed up by AFM findings [34].

Mathew et al. (2005) investigated the mechanical characteristics, crystallinity, and biodegradation of PLA and MCC composites made by directly compounding them using a twin-screw extruder. PLA composites reinforced with wood pulp (WP) and wood flour were compared to the outcomes (WF). PLA/MCC composites were shown to be the least effective of the three types of composites. Despite being well disseminated in the composite, SEM images revealed that MCC had weak adhesion with the PLA matrix. Because of its particle shape, MCC had a substantially lower aspect ratio than WP and WF, which contributed to its worse performance compared to other fillers. Another aspect contributing to the poor mechanical characteristics of PLA/MCC composites, according to the scientists, is their decreased crystallinity. Degradation tests found that wood flour composites degrade at the fastest rate. Finally, they postulated that high-performance bio composites may be obtained if MCC in composites could be dissolved further into whiskers [24].

Nano Crystalline Cellulose

Nanocellulose as a nanocomposites reinforcing material has been a popular study topic. Nanocellulose has various advantages, including low cost, low density, renewability, low energy consumption, high specific characteristics, biodegradability, and relative ease of manufacture. Because of its high surface reactivity, it performs better as a reinforcing phase in nanocomposites. Compared to cellulose composites made of micro- or macro-cellulose Customization, design flexibility, and the processability of nanocellulose–polymer composites allow for widespread use. Among them are the automobile, packaging, electronics, and biotechnology industries. Some, however, Nanocellulose's usage as a reinforcing material has drawbacks, mainly its expensive cost. Moisture absorption, poor wettability, and incompatibility with most polymeric matrices are all issues. Processing temperature constraints These disadvantages have prompted scientists to concentrate on these challenges; several approaches, such as nanocellulose or polymer matrices alteration or novel processing strategies to manufacture high-performance nanocellulose reinforced composites with good characteristics have been proposed [36].

Nanocellulose modification should ultimately improve the characteristics of composites. Different processing processes can be used to make nanocellulose particles and related materials, all of which have an impact on the final material qualities. First and foremost, regardless of the processing method used, the quality of particle dispersion is the most difficult aspect of nanocomposite synthesis. Despite significant progress in recent decades, combating agglomeration remains a challenge. It's been incredibly difficult to obtain a fully homogenous dispersion of individual nanoparticles . This is due to nanoparticles' natural inclination to clump together, which is not unique to cellulose nanoparticles. The innate tendency of nanoparticles to agglomerate is aided by certain physical features. Almost half of the constituent atoms in a nanoparticle can be found on the particle surface, which has a large specific surface area and surface energy present on the cellulose surface. These forces are generated by the presence of surface hydroxyl groups in nanocellulose, which can reach areal concentrations of up to 7.2 groups/nm2 in CNCs. The hydrogen bonds (H-bonds) between two parallel CNCs in contact have an estimated energy of 7.5 1016 J. This number is nearly two orders of magnitude greater than the van der Waals energy in colloids [36].

When cellulosic materials are dried, they go through irreversible agglomeration, reorganisation, and co-crystallization processes produced by attraction forces (Figure 2.10). The distance between CNC particles in a film swollen by water was calculated by Reid et al. to be 1.2–1.6 nm (corresponding to 4–6 layers of water molecules). The authors argue that the swelling of the film began with the filling of the film's pores, followed by the wetting of individual particles. The CNC–CNC interactions (i.e. H-bonds) are replaced by solvent–CNC interactions during this wetting. Many solvents were investigated, and the results were consistent: van der Waals forces kept the films together and stable. These findings revealed that dispersing CNC in solvents or polymers requires both polar components and external energy to disrupt the CNC–CNC H-bonds.
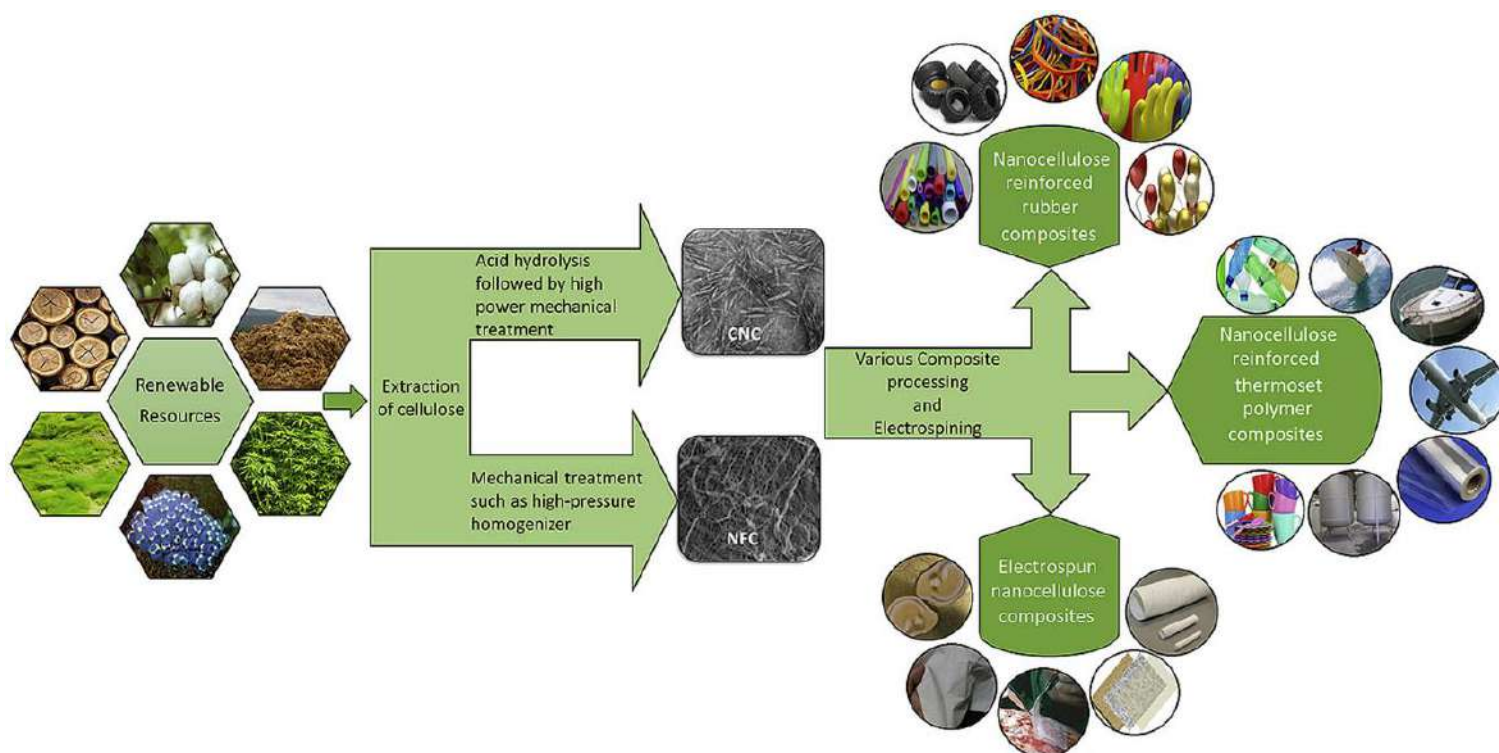
Figure 2.10 Life of Cellulose from extraction to composites [27].

Attempts to avoid agglomeration are centred on maintaining a particle suspension in a suitable solvent for as long as possible. Suspension maintenance can sometimes be carried over into the processing stage by using a suitable water-soluble matrix or performing a solvent exchange from water to an organic solvent. Alternatively, by grafting long molecular chains between nanoparticles, it is feasible to improve polymer–filler compatibility, so boosting particle dispersibility within a hydrophobic matrix, or to generate steric barriers among nanoparticles, thereby increasing interparticle distances. Chemical changes can be used to conduct both of these strategies (improving polymer–filler compatibility and establishing steric barriers among cellulose nanoparticles). In the last five years, a particularly "green" strategy has been created. Several studies have employed lignin, a natural polymer found in plants, to improve the compatibility, crystallinity, barrier characteristics, and other features of cellulose nanocomposites and nanopapers [37]

2.6 Biodegradable polymers

The various definitions of biodegradation differ depending on the polymer's application (biomedical or natural environment). Many distinct definitions have been officially adopted,

depending on the background and goals of the defining standard groups. Van der Zee and Seal has studied every definition available in various standards. Albertsson and Karlsson described biodegradation as the process of living organisms and their secretory products decomposing through the action of enzymes and/or chemical disintegration. Abiotic factors must also be considered. Photodegradation, oxidation, and hydrolysis are examples of reactions which could change the polymer before, during, or after Environmental variables induce biodegradation. So, "Biodegradation of a polymer" is rigorously defined as – "the deterioration of its physical and chemical properties and a decrease of its molecular mass down to the formation of CO_2, H_2O, CH_4 and other low molecular-weight products under the influence of microorganisms in both aerobic and anaerobic conditions aided by abiotic chemical reactions like photodegradation, oxidation and hydrolysis" [38].

Bioplastics are polymers obtained from renewable sources (bio-based) or designed to be biodegradable. Bioplastics are bio-based but non-biodegradable [1]. Hori et al. have also discussed the method for creating novel biodegradable polymers. It is feasible to create biodegradable polymers for a specific purpose based on polymer structure, physical properties, and environmental conditions. The following are some guidelines: Fully carbon chain polymers are less likely to degrade than hetro atom containing polymers, chain branching is detrimental to biodegradation, condensation polymers are more likely to undergo biodegradation, lower molecular weight oligomers are more susceptible to biodegradation, crystallinity reduces biodegradation, lower surface area reduces biodegradation, and so on. The biodegradability of water is enhanced by its solubility and cleanliness. Temperature, pH, moisture, oxygen, nutrients, an appropriate microbial population, concentration, and test length are all factors to consider while evaluating the environment. In short, chemical structure, chemical composition, distribution of repeat units, presence of functional groups, presence of chain defects, configurational structure, molecular weights and polydispersity, presence of low molecular weight compounds, processing
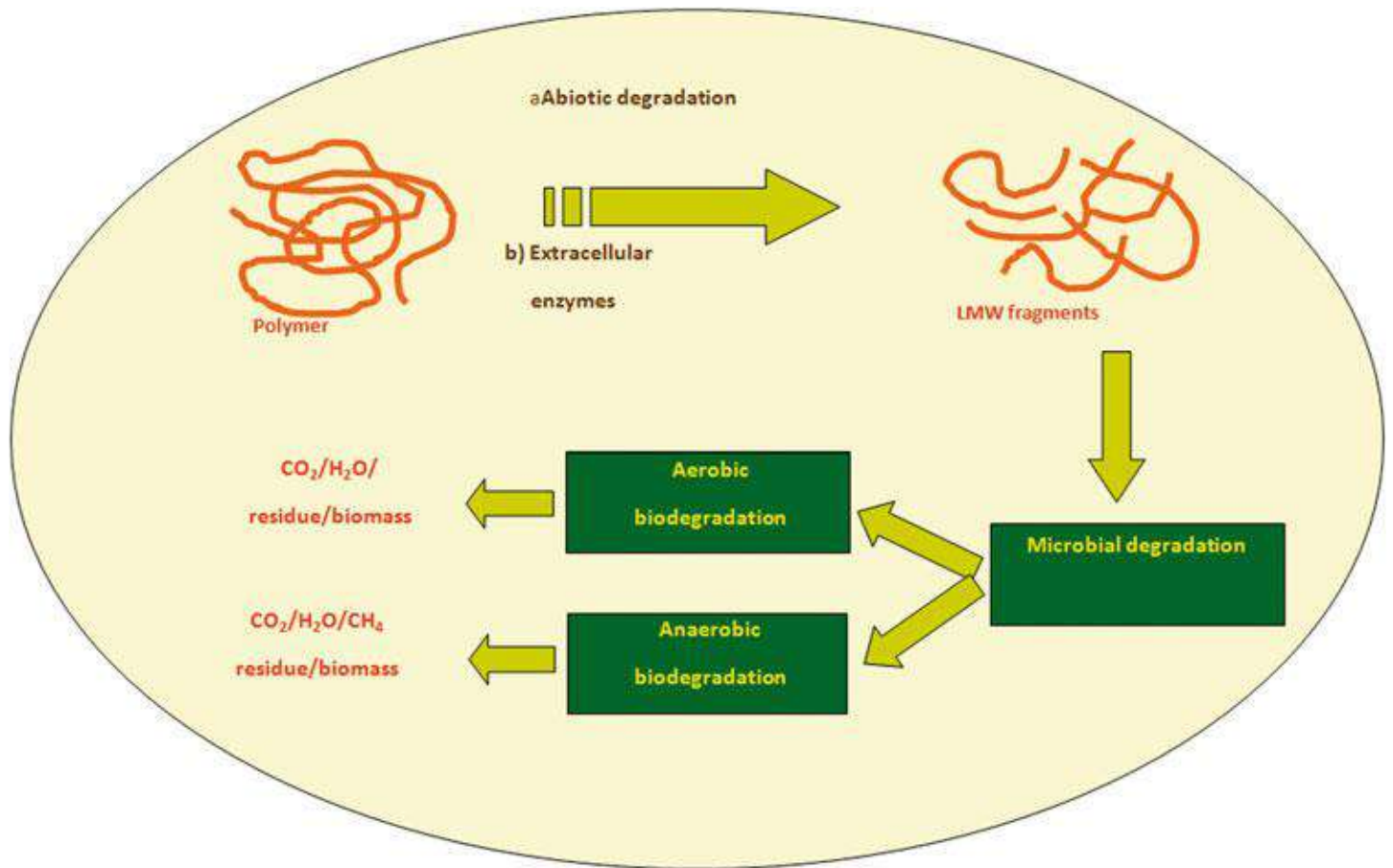
Figure 2.11 Diagrammatic representation of the chemistry of biodegradation [1].

conditions, shape, sterilizing conditions, morphology, annealing effects, storage history, and so on may all be taken into account when choosing a biodegradable polymer (Figure 2.11) [1].

Plastics' biodegradability is determined by the chemical structure of the substance. Plastics biodegrade at a rapid rate under various soil conditions, depending on their characteristics. Enzymatic assault at the glucosidic connections caused biodegradation of starch-based polymers between the sugar groups, resulting in a reduction in chain length and the splitting off mono-, di-, and oligo-saccharide units.

2.7 Biodegradable Packaging Material

Synthetic plastics are widely utilized in medical devices, packaging, building materials, and packaging, among other applications. Almost all ordinary consumer goods come with packaging that performs at least one of the following tasks. - to guard from physical harm, pollution, and degradation.

- to entice customers to buy.
- to ensure that the brand identity of the product is easily identifiable.
- to provide product-related information.
- to reduce the cost of distribution and storage.
- to ensure consumer comfort and safety.

With the rise of ready-to-eat meals in our modern industrial civilization, food packaging has become a significant portion of the packaging market, with global sales expected to reach USD 411.3 billion by 2025. Because of its strong barrier and gas selectivity, plastic packaging provides food with a long and stable shelf life, as well as safety and protection during transportation and storage. Biodegradable polymers may be degraded/composted after use, making them an appropriate solution for non-biodegradable packaging as indicated above. It can also provide qualities like working as a barrier or selective functional membrane to gas, moisture and aroma. Despite extensive scholarly attempts to promote the use of biodegradable polymers in packaging, there are few bio-based/biodegradable polymers on the market that can match modern society's high demand for food packaging. This is due to difficulties in achieving similar oxygen/water vapor barrier performance to classic petroleum-based polymers or their mixtures. A thorough understanding of the oxygen/water vapor barrier for various biodegradable polymers, as well as the barrier-structure relationship, is critical for academic and industry design of high-barrier sustainable packaging to meet future market demands [1].

Biodegradable packaging material from various sources

Biodegradable packaging materials made from renewable natural resources have received widespread government support in recent years. The goals of biodegradable packaging development are twofold: (1) to use renewable and potentially more sustainable raw materials (crops rather than crude oil); and (2) to promote integrated waste management systems to reduce landfill. To date, significant scientific progress has been made in producing biodegradable packaging materials with functions comparable to those of typical oil-based plastic packaging. Commercially available materials based on or derived from starch include Mater-BiTM, NatureWorksTM Polylactide, BioskaTM , BioplastTM, SolanylTM, PotatopacTM, GreenfilTM. Despite their greater costs than standard plastics, many have found increasing commercial applications in packaging [1, 4].

Depending on whether the dominant constituent is a synthetic oil-based polymer or a biologically produced polymer, biodegradable packaging materials can be divided into biodegradable polymers and biopolymers. Synthetic polymers with varying degrees of intrinsic biodegradability, such as polycaprolactone, polyhydroxybutyrate, and poly(vinyl alcohol), and chemically modified plastics to aid biodegradation are the former. Biopolymers are long-chain compounds that arise naturally. Typical examples include cellulose, polysaccharides etc. Materials manufactured or derived from these natural polymers are included in this definition. Unlike synthetic polymers, the majority of them are biodegradable, meaning they may be decomposed by biological activity such as bacteria or fungi to produce natural metabolic products.

Polysaccharides (starch) based biodegradable packaging materials are most popular amongst commercially available biodegradable packaging materials that are available commercially at present. This is mainly attributable to the facts that starch is annually renewable, abundant and inexpensive. Because of its poor mechanical qualities like brittleness and hydrophilic nature, starch is rarely used as a packaging material. They are frequently altered mechanically, physically, or chemically, as well as coupled with plasticizers or polymeric additions [8].

Biodegradable Packaging in Bangladesh

Many Bangladeshi organizations are now getting invested in research, development, and manufacturing of biodegradable packaging material. According to International Finance Corporation (IFC) – "Bangladesh earns most of its foreign currency by exporting apparel items. In the last 7 years Bangladesh has increased its annual revenue from $19 billion to $34 billion- which makes it the second largest exporter of garments in the world, with the sector accounting for 80 percent of Bangladesh's total export earnings." New initiatives in several Bangladeshi textile companies support improved environmental practices in addition to better worker conditions. The environmental practices involve ensuring the use of biodegradable material for packaging, use of chemicals that are not harmful for the environment, operational efficiency, and resource consumption and so on [39].

In this spirit, biodegradable packaging materials have gained more and more interest in the past few years. Expo Accessories Ltd is producing Corn based biodegradable packaging material aiming Bangladesh's garment industry and has the potential to manufacture 800,000 pieces per day [40].

Another biodegradable and compostable packaging material manufacturer in Bangladesh is Trims Sourcing who source their raw material from cassava roots (South American plant). Trims Sourcing claims that their packaging material- "look and weigh like poly bags, but they are not made of polythene. They are in fact organic bags made from biodegradable materials like corn or roots of cassava. Our bags are totally non-toxic and don't cause the environment any harm. We use Biodegradable ink to confirm our bags are fully biodegradable and compostable in earth" [41].

Another prospective alternative to plastic packaging in Bangladesh is a new packaging material invented from Jute cellulose by a team of Bangladeshi scientists of Bangladesh Jute Mills Corporation (BJMC). BJMC has been developing protocols and has already established a Jute-polymer" unit in Latif Bawani Jute mills located in Demra. The production capacity is currently only 2000 pieces per day but fund are being allocated by the Bangladeshi government for the mass production of this product. This Jute-polymer has proven to have 1.5 times more tensile strength than low density polyethylene. It degrades within three months of soil burial [42].

Justification of choosing Jute-polymer as the research material:

If this research results in developing the characteristics of jute-polymer using jute derived cellulose crystal, then the lost glory of jute industry of Bangladesh will be renewed. Jute production will increase, and Bangladeshi farmers will benefit. Global demand of sustainable biodegradable polymer will be met. Increase of jute production will increase jute farming which will eventually help the environment by releasing oxygen and taking in carbon-di-oxide. Jute plantation is also good for the soil.

2.8 Economic Aspects

Jute is grown abundantly in Bangladesh. According to Bangladesh Investment Development Authority (BIDA), Bangladesh is the second-largest jute producer in the world, producing an estimated 1.6 million tonnes of jute annually (2019, FAO) [43]. Currently, 220-245 private jute mills in Bangladesh. In addition, there are around 700 diverse jute producers in the nation that employ 50,000–100,000 people. 1.16 million tonnes of raw jute are typically consumed domestically each year (BJSA). With typical annual exports of over $1 billion USD, Bangladesh is also the world's biggest exporter of jute and items made from it [44]. It can be said that the jute frown in Bangladesh is abundant for producing more than enough cellulose for jute has almost 70% cellulose and this can be extracted very efficiently.

CHAPTER 3
EXPERIMENTAL

Chapter 3

3. Experimental

In this chapter, experimental procedures of present research will be introduced. Cellulose was extracted from raw Jute. Jute-polymer was collected from Bangladesh Jute Mills Corporation (BJMC). pH balanced water was used to make a solution of jute polymer into water. The extracted cellulose crystal was used as reinforcement in the jute-polymer matrix which was dried into films. Characterization of both the crystalline cellulose and the composite films were done. FTIR was done for compositional investigation. To know the crystallographic properties, XRD was conducted. Thermal properties were investigated using DSC and TGA. SEM was used to observe morphological properties. The tensile properties of the films were determined using a universal testing machine (UTM).

3.1 Materials

3.1.1 Raw Jute

Raw jute (Corchorus capsularis) fiber was collected from local market of Demra, situated on the banks of river Shitalakhsa near the city of Dhaka. While collection the fibers, thorough visual inspection was conducted to make sure that they had not gone through any previous surface treatment and that there was no waxing material present. This fiber was then washed and dried and cut into small pieces for use. Picture of jute fiber is shown in Figure 3.1.

Figure 3.1 Raw Jute

3.1.2 Jute polymer

Jute polymer was bought from BJMC. The bags were available in transparent, green, pink, yellow and blue color (Figure 3.2). The transparent ones were chosen to avoid the presence of any dyeing agent. The bags cost tk 10 each.

Figure 3.2 Jute Polymer

3.1.3 Chemicals

Several other chemicals were required for this research. Those are: hydrogen peroxide, sodium hydroxide and sulfuric acid (Figure 3.3). These chemicals in industrial grade were bought from local vendors of Sigma-Aldrich, Merk, Germany.
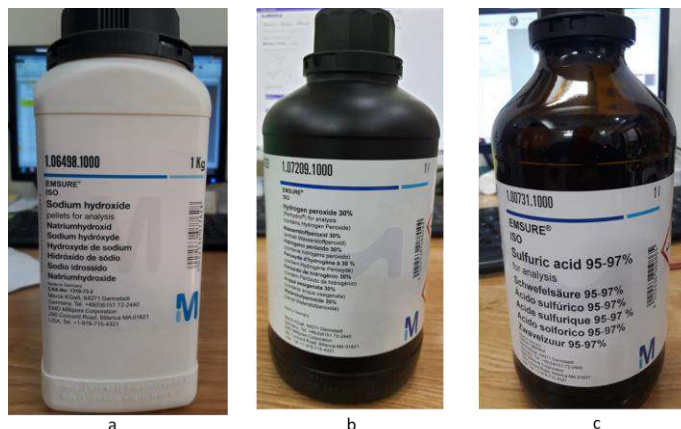
Figure 3.3 : Pictures of bottles containing (a) sodium hydroxide, (b) hydrogen peroxide and (c) sulfuric acid.

3.2 Methods

3.2.1 Extraction of Cellulose from raw Jute

The extraction of cellulose was done in several steps. These steps are demonstrated in the following chart (Figure 3.4).

Jute fiber cut into small pieces and washed thoroughly

Grinding of washed jute fiber

Alkali treatment with 15% NaOH

Bleaching with 50% H_2O_2

Washing thoroughly until the bleached jute was free from bleaching agent

Acid Hydrolysis with 64% pure H_2SO_4

Centrifuge to separate the crystalline cellulose from the acid
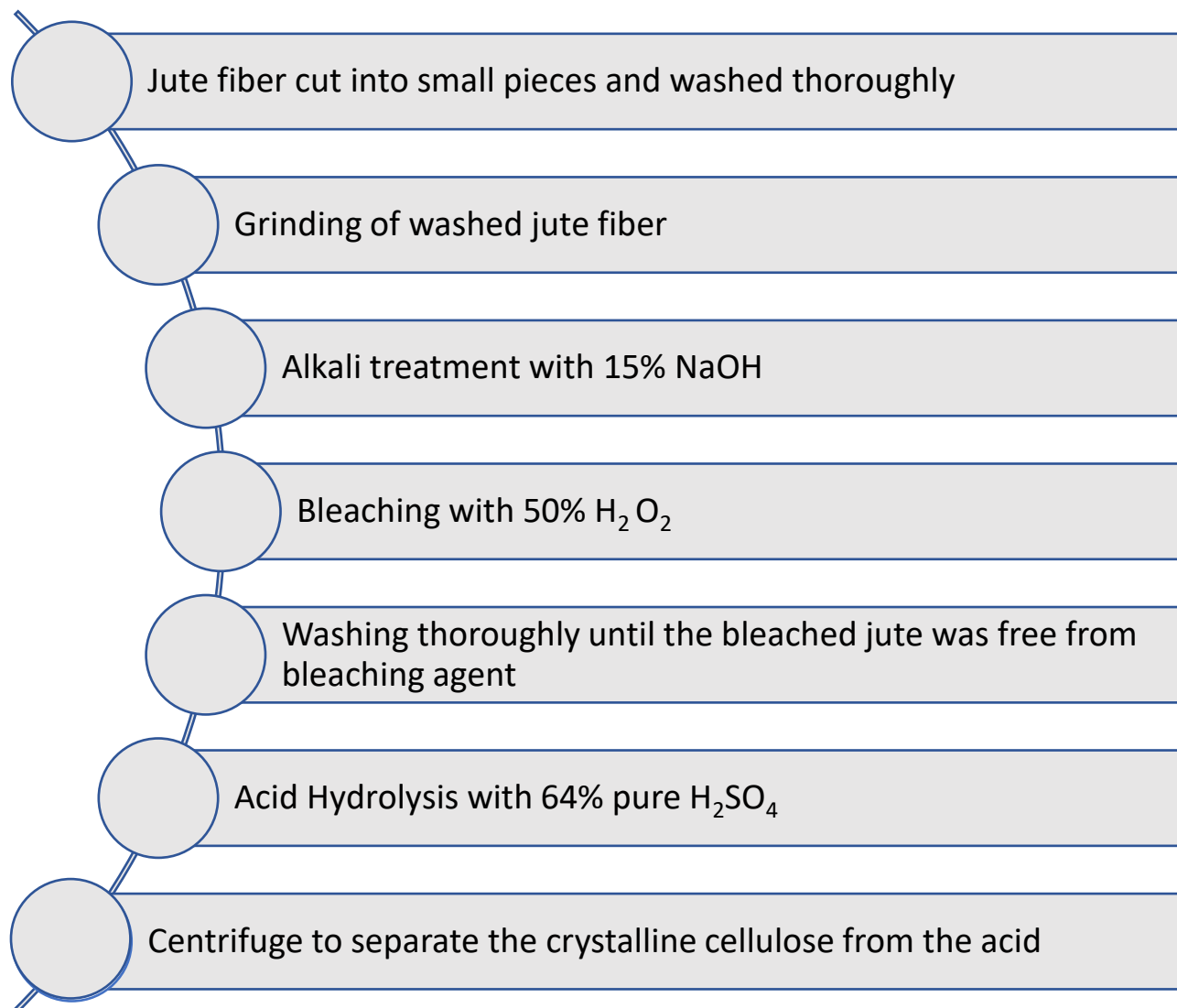
Figure 3.4 Flow Chart for cellulose extraction process.

3.2.2 Preparing Jute fiber for pretreatment

The collected jute fiber was dirty and needed to be washed thoroughly. The jute fiber was washed with clean tap water and then left to air dry for 3 days. After the drying process the jute was then cut into small pieces and then they were ground using a grinding machine (Figure 3.5).

Figure 3.5 Picture of ground raw jute

3.2.3 Alkali treatment of ground jute

The alkali treatment (also known as mercerization when treated with caustic soda) causes fatty acids and other lignin components from jute strands to leach out, increasing the amorphous region. In this research, ground jute was mercerized in 15% caustic soda (NaOH) for 1.5 hours. The temperature was raised to 100°C. Picture of mercerized just is shown in Figure 3.6.

Figure 3.6 Alkali treated jute

After the alkali treatment, the mercerized jute was thoroughly washed with distilled water to get rid of any extra caustic soda. After several washing, the pH of the water was tested using a litmus paper and when the paper showed neutral, the jute was oven dried.

3.2.4 Bleaching of alkali treated jute

Bleaching jute fiber results in loss of lignin, weight, breaking strength and the loss of color [45]. After drying the alkali treated jute fiber, it was bleached using hydrogen peroxide. Hydrogen peroxide is environment friendly in a sense that it breaks into hydrogen and oxygen. 50% pure H_2O_2 was used.

Figure 3.7 Picture of bleached Jute fiber.

The peroxide was kept in a beaker which was placed on a hot clave magnetic stirrer and was kept until the temperature rose to 120°C. After the desired temperature rise, the jute fiber was added. The fiber to peroxide ratio was kept 1:20. It was kept for 1.5 hours for the completion of the bleaching process. After the bleaching was done, the bleached jute was washed several times with distilled water to get rid of all the residual peroxide. Picture of bleached just is shown in Figure 3.7.

3.2.5 Sulfuric Acid Hydrolysis

For Acid hydrolysis of bleached jute, 64% dilute sulfuric acid. The jute to acid ratio was 1:35 and the temperature was 37.8°C. The mixture was stirred for 15 minutes and then it went through centrifugation. The suspension was then diluted with distilled water to stem the hydrolysis reaction. The suspension was centrifuged at 6000 rpm for 15 minutes. This was done to separate the cellulose by concentrating it and also to remove excess acid. The solution was further

centrifuged for 7 days until constant pH was achieved. Picture of hydrolyzed cellulose crystal is shown in Figure 3.8.

Figure 3.8 Acid hydrolyzed cellulose crystal in wet form.

3.2.6 Freeze drying of wet cellulose Crystal

After the centrifugation process was complete, cellulose was obtained in crystalline form. This cellulose was then freeze dried to get powdered cellulose crystal (Figure 3.9).

Figure 3.9 Cellulose crystal in powdered form

3.2.7 Preparation of composite films using Jute polymer and Cellulose Crystal

To prepare the biocomposite films, the jute-polymer bags collected from BJMC were first cut into very small pieces and dissolved into alkaline water. The pH of the water was 9. It took 48 hours

for the polymers to completely blend into the water. After 48 hours the solution was put on a magnetic stirrer for 15 mins at 1000 rpm to make an even solution.

In this stage the prepared cellulose crystal was added. Five different concentrations were used: Those are 0, 0.1, 0.2, 0.3 and 0.4 wt%. Solutions containing five different concentrations of cellulose crystal was then sonicated to make sure that the cellulose particles were properly mixed. Each mixture was at first sonicated for 2 minutes. And then checked if there was an even solution. If not, the sonication time was increased.

It was observed that initially there were no precipitates. With increasing concentrations of cellulose crystal, precipitates were seen even after increasing the sonication time to 4 minutes.

Table 3-1 Concentrations and Sonication time of composites

CC concentrations in wt%	Sonication time	Precipitate
0	2 minutes 44 seconds	none
0.1	2 minutes 50 seconds	none
0.2	2 minutes 48 seconds	none
0.3	4 minutes	present
0.4	4 minutes	present

The mixture of cellulose crystal and jute polymer solution was then poured on a film casting machine and heat dried. The solution took approximately 1 hour to dry. Picture of prepared dried film is shown in Figure 3.10.

Figure 3.10 Picture of dried film

3.3 Characterization of Cellulose Crystal

3.3.1 Fourier-transform infrared spectroscopy (FTIR)

The Perkin Elmer FT-IR Spectrum Two machine was used to identify the functional groups present in crystalline cellulose. The powdered cellulose crystal sample was heated at 60°C overnight to get rid of the absorbed moisture from the atmosphere. The sampling plate was at first cleaned with isopropyl alcohol cleaner using a chem wipe which is a disposable wiper without any cleaning fluid in it. A dry cleaning chem wipe was used to dry the area. After cleaning the sample plate, the powdered sample was directly taken from the desiccator and put directly onto the sample plate and the compression clamp was tightened. After that the scan was run from the software.

3.3.2 Scanning Electron Microscopy (SEM)

SEM was used to perform morphological examination on the cellulose crystal. This is the most commonly used surface analytical method. The study of Surface topography and failure analysis have benefited greatly from high-resolution SEM. Although the technology allows for qualitative three-dimensional (3-D) imaging of surface characteristics, it is not well suited for quantitative surface roughness characterization. The surface morphology of cellulose crystal was investigated by Phenom World SNE-3200M Tabletop scanning electron microscope.

3.3.3 X-ray Diffraction (XRD) analysis.

Crystallographic investigation of cellulose crystal was conducted using Rigaku Smartlab SE X-ray diffraction (XRD) machine. This machine is equipped with 3 kW Cu X-ray tube with a semiconductor hybrid pixel array detector that was specifically designed for multipurpose X-ray diffractometers. Scans were carried out over the range of 5-90°, using a step size of 0.01 and scan speed of 15.00°/min. Samples were oven dried overnight at 60°C to get rid of the moisture content.

3.4 Characterization of Cellulose Crystal Reinforced Composite Films

3.4.1 Tensile Test

Tensile strength of the composite films was measured using Zwick Roell Z010. Test specimens were cut of the required shape (Figure 3.11). The tensile test was carried out according to ASTM D 882 standards. Teat speed was 125mm/min. At least Five samples were tested for each specimen and each test was continued until tensile failure.

Figure 3.11 Schematic diagram of the specimen used for tensile test A=40mm B=10mm C=25mm D=6.25mm

3.4.2 Fourier-transform infrared spectroscopy (FTIR)

The Perkin Elmer FT-IR Spectrum Two machine was used to identify the functional groups present in the polymer composite films. The polymer composite film samples were cut into $10mm \times 10mm$ sheets. The sampling plate was at first cleaned in the same way with isopropyl alcohol. The films were placed on the sample plate and the compression clamp was tightened. After that the scan was run from the software.
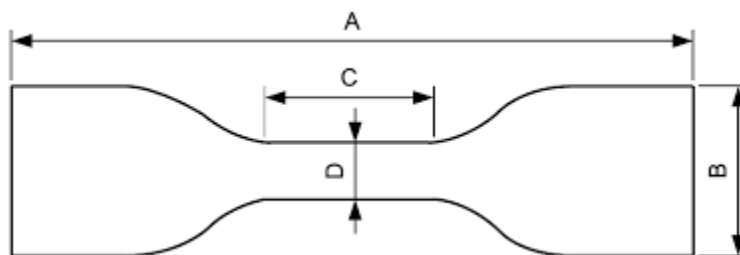
3.4.3 X-ray diffraction (XRD) analysis

Crystallographic investigation of cellulose crystal was conducted using Rigaku Smartlab SE X-ray diffraction (XRD) machine. This machine is equipped with 3 kW Cu X-ray tube with a semiconductor hybrid pixel array detector that was specifically designed for multipurpose X-ray diffractometers. Scans were carried out over the range of 5-90°, using a step size of 0.01 and scan speed of 15.00°/min. Samples were oven dried overnight at 60°C to get rid of the moisture content. The crystallinity was determined based on the ratio of crystalline region's area to the total area in the XRD spectra.

$$Crystallinity\ Index\ (CrI) = 100 \times \frac{I_{Total} - I_{Am}}{I_{Total}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where I $_{total}$ is the maximum intensity of the lattice diffraction peak corresponding to the plane in the sample and I$_{am}$ represents diffraction of the non-crystalline phase [46-48]. The crystallite sizes were estimated using the Scherrer's equation:

$$\beta = \frac{0.9\lambda}{\tau\cos\theta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where β is the full width at half maximum (FWHM) of XRD peaks, λ is the wavelength of incident X-rays, τ is the crystallite sizes, θ is the diffraction angles corresponding to the planes. [46-49]

3.4.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique that monitors the weight change that occurs as a sample is heated at a constant pace to assess a material's thermal stability and fraction of volatile components. It contributes to the understanding of structure-property correlations and the management of molecular design technology with the goal of industrial production of various polymeric materials, particularly fiber reinforced composites. Furthermore, it is a good tool for determining the materials' thermal stability. It also allows for the quantification of potentially detrimental, deteriorating volatiles, such as moisture uptake during a hydrothermal treatment, which can induce composite deterioration. In this research, Thermogravimetric analysis was done using TGA Q50 V6.4 Build 193 instrument. The heating rate was 5°C/sec and the temperature range was 25-400°C.

3.4.5 Differential scanning calorimetry (DSC)

Differential scanning calorimetric investigation was done were performed on a DSC 131evo thermal system with a sealed thermal aluminum capsule. Each test specimen weighed between 18

and 22 mg. Each sample was heated at a constant rate of 5°C/min while being scanned at temperatures ranging from 30-600°C.

3.4.6 Scanning electron microscopy (SEM)

The surface morphology of the polymer composite films was investigated by Phenom World SNE-3200M Tabletop scanning electron microscope.

3.4.7 Biodegradability Test

The biodegradability was tested using the soil burial method. Biodegradation studies under real soil burial conditions were carried out. The biodegradability of prepared cellulose crystal reinforced composites was measured. The soil biodegradation test lasted for three months (100 days). The film samples were cut into 40 mm $\times$ 40 mm pieces (approximately, 1.2-1.6 g). All the samples were buried 0.15-0.40 m under the soil. 42[50] pH of soil was neutral, and moisture was 20%. The percent degradation was measured after 15, 30, 45, 60, 75 and 90 days interval. After each sample was retrieved, it was cleaned and dried at room temperature before measuring. The degree of soil degradation (DSD) was calculated by using following equation

DSD= [(W_0 -W_d) x 100 %]/ W_0

Where W_0 and W_d are the initial and final dry weight (before and after degradation) respectively of the blend sheets.

3.4.8 Water Uptake test

The water absorption test specimens were 20mm$\times$20mm in size. The weights of all the specimens were taken and recorded after oven drying. Following that, the specimens were submerged in distilled water as per ASTM D 570-99 [51]. The % increase in weight during immersion was estimated using Equation after 2 min, 5 min, 10 min, 20 min and then 24 hours.

Increase in weight, % = [(weight $_{wet}$ – weight $_{dry}$)/ weight $_{dry}$] $\times$ 100

CHAPTER 4
RESULTS AND DISCUSSION

Chapter 4

4. Results and Discussion

4.1 Characterization of Cellulose Crystal

For characterization of cellulose crystal, FTIR, X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) were conducted. Results obtained from those analysis are described below.

4.1.1 Fourier-transform infrared spectroscopy (FTIR)

The aim of using FTIR is to measure the change of surface composition of the fibers after treatment. In this study, the changes in the chemical properties of raw and treated jute were determined by FTIR analysis and shown in Figure 4.1. These changes were accounted for by the disappearance or reappearance of functional groups made obvious by the IR spectrums of raw jute, alkali treated jute, bleached jute and acid hydrolyzed jute (pure cellulose).

In raw jute, the broad peak in the range of 3316 cm^{-1} appears due to O-H stretching vibrations, and the peaks at 2927 cm^{-1} and 2855 cm^{-1} appear due to C-H stretching vibrations in cellulose and hemicellulose. The sharp peak at 1746 cm^{-1} for C-O stretching gives evidence of carboxylic acid and ester group present in the hemicellulose, which entirely disappears in the treated samples. The peaks near 1642 cm^{-1} arise due to absorbed water. Peaks near 1590 cm^{-1} and 1504 cm^{-1} appear in raw jute samples and alkali treated jute due to lignin components. Peaks in these positions disappear in bleached jute and acid hydrolyzed pure cellulose, which prove the removal of lignin. Disappearance near peak at 1458 cm^{-1} is also evident of removal of lignin. Due to CH$_2$ Bending of pyranose rings, there appears peaks near 1429, 1424, and 1420 cm^{-1}. Deformation vibration frequency for C-OH and CH groups causes peaks near 1316 cm^{-1}. The peak for C-H and C-O vibrations contained in the polysaccharide rings of cellulose is around 1370 cm^{-1}.
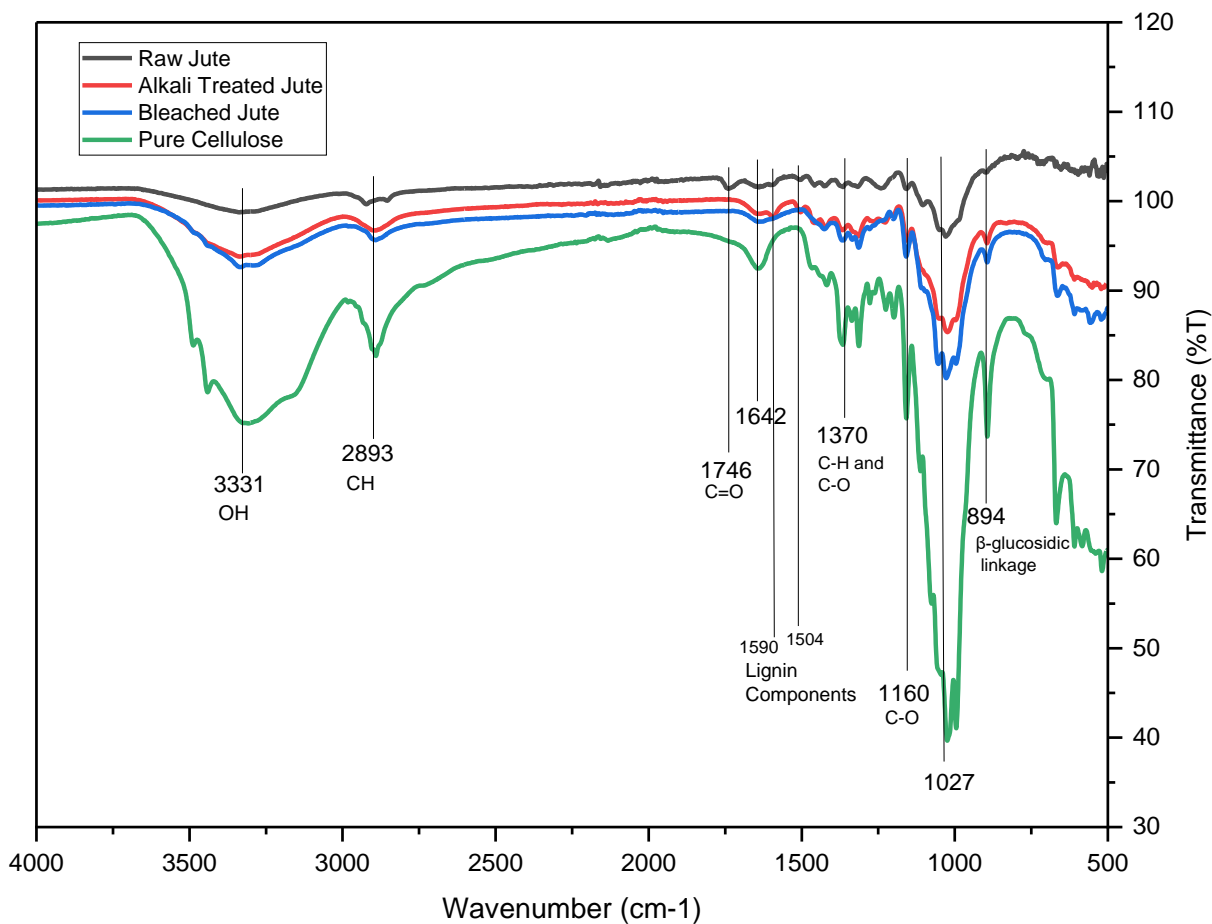
Figure 4.1 FTIR spectra of raw jute, alkali treated jute, bleached jute, pure cellulose

There is a medium peak in raw jute samples near 1245 cm^{-1} caused by C-O stretching of ether linkage for lignin. This peak completely disappears in the further treated samples. There are peaks visible near 1162 cm^{-1} in raw jute, near 116 cm^{-1} in alkali treated jute, near 116 cm^{-1} in bleached jute and 1159 cm^{-1} in pure cellulose due to C-O stretching.

The peak at 890 cm^{-1} and 890 cm^{-1} confirms the presence of ß-gluocosidic linkage. The peak at 1030 cm^{-1} corresponds to C-O and C-C stretching vibrations [52].

The FTIR spectra for raw jute, alkali treated jute, bleached jute and pure cellulose can be found in Figures 4.2- 4.5 and the peaks and their possible assignments can be found in Table 4.1.

Table 4-1 FTIR Peaks and possible functional group assignments.

| Samples				Possible assignments
Raw Jute	Alkali Treated Jute	Bleached Jute	Cellulose	
3316	3337	3334	3318	OH stretching in H-bonded hydroxyls groups of cellulose and hemicelluloses etc.
2927, 2855	2891	2892	2893	C–H functional group.
1746	---	---	---	C=O groups of carboxylic and ester groups of hemicelluloses present in the jute fibers
1642	1642	1642	1642	Absorbance of water
1590	1587	--	--	Lignin components
1504	1500	--	--	Lignin components
1458	--	--	--	Lignin components
1429	1424	1424	1420	CH_2 Bending of pyranose rings
1370	1370	1370	1370	C-H and C-O vibrations contained in the polysaccharide rings of cellulose
1316	1316	1316	1316	Deformation vibration frequency for C-OH and CH groups
1245	--	--	--	C-O stretching of ether linkage for lignin (Rosa et al., 2012)
1162	1160	1161	1159	C-O stretching
1108	-	--	--	C-O/C-C stretching vibration for ring
1051	-	--	--	C-O/C-C stretching vibration (C3 O3)
1030	1014	1027	1028	C–O in the alcohol hydroxyl group [53] or C-O/C-C stretching vibration (C6 H2 O6) [52] or C-O-C pyranose ring vibration
894	890	894	890	β-glucosidic linkages present between various sugar components.
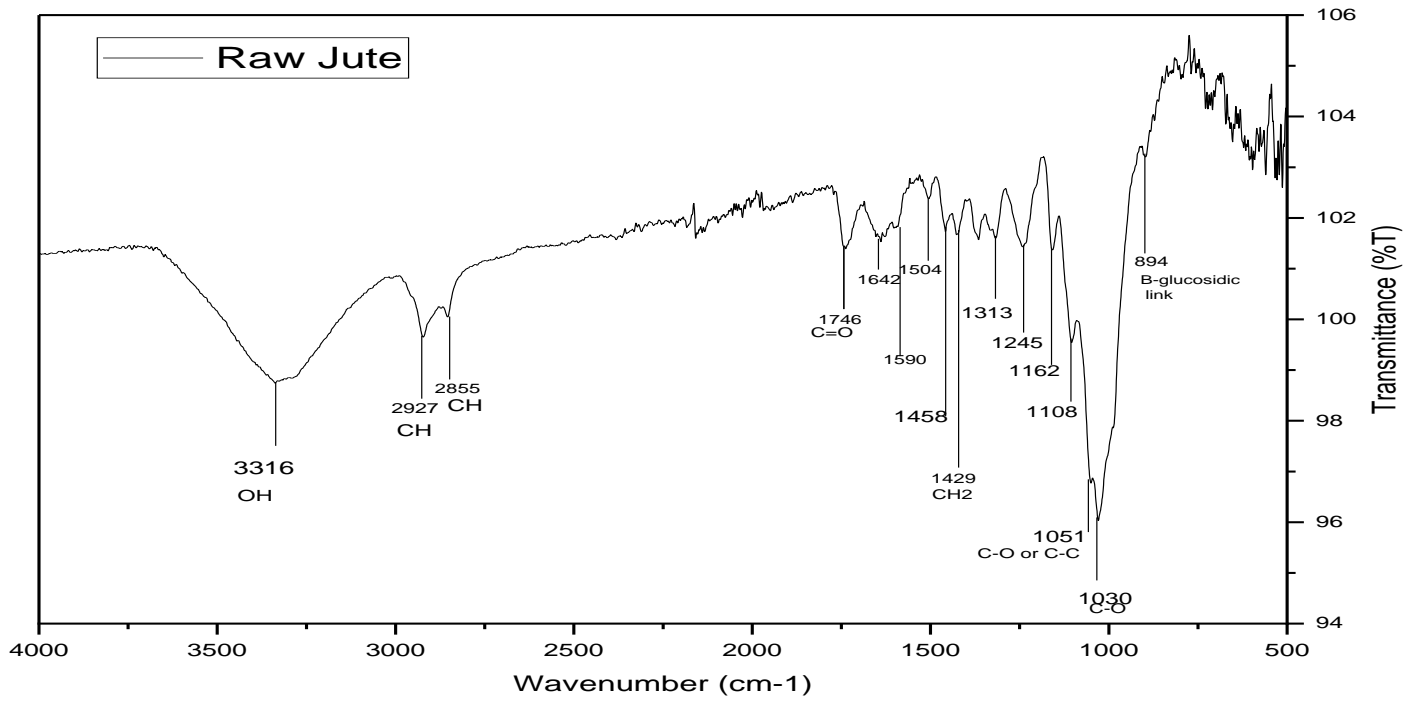
Figure 4.3 FTIR Spectra of raw jute fiber.
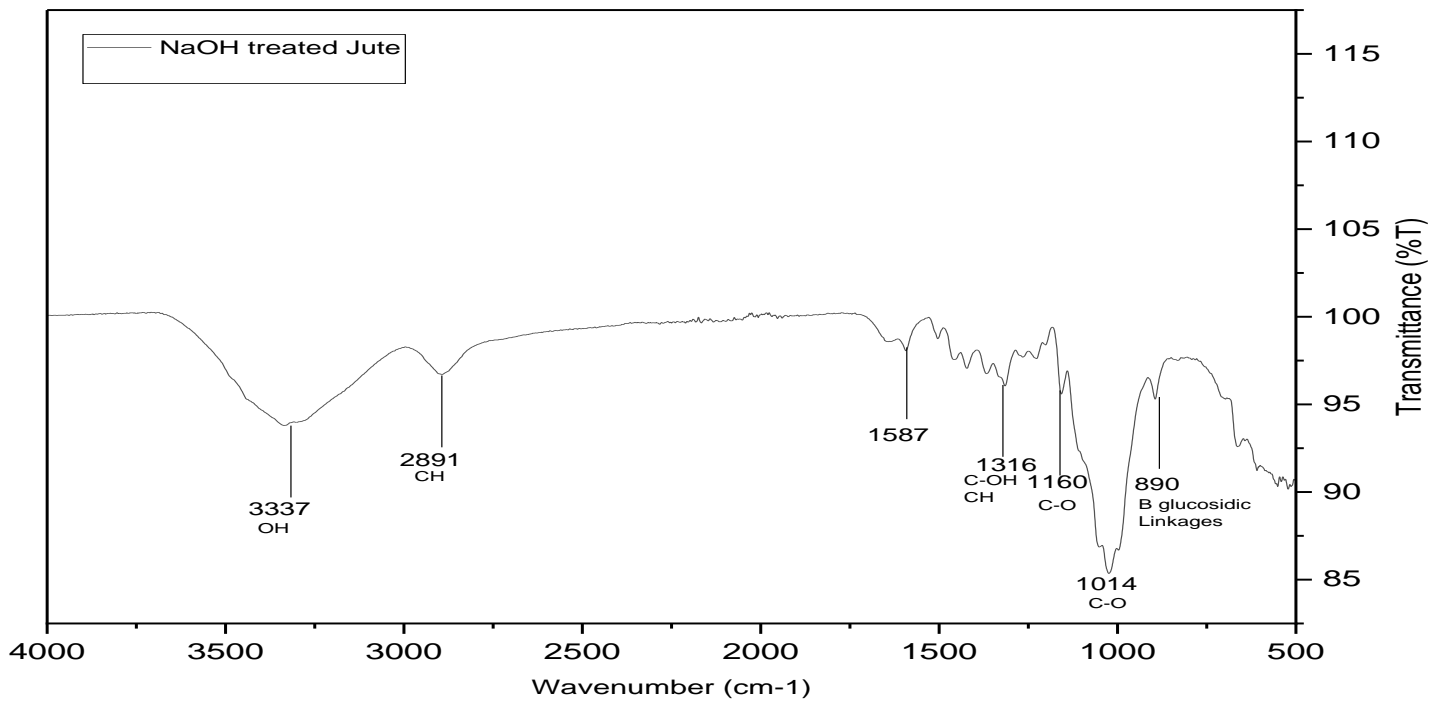
Figure 4.2 FTIR Spectra of alkali treated jute.
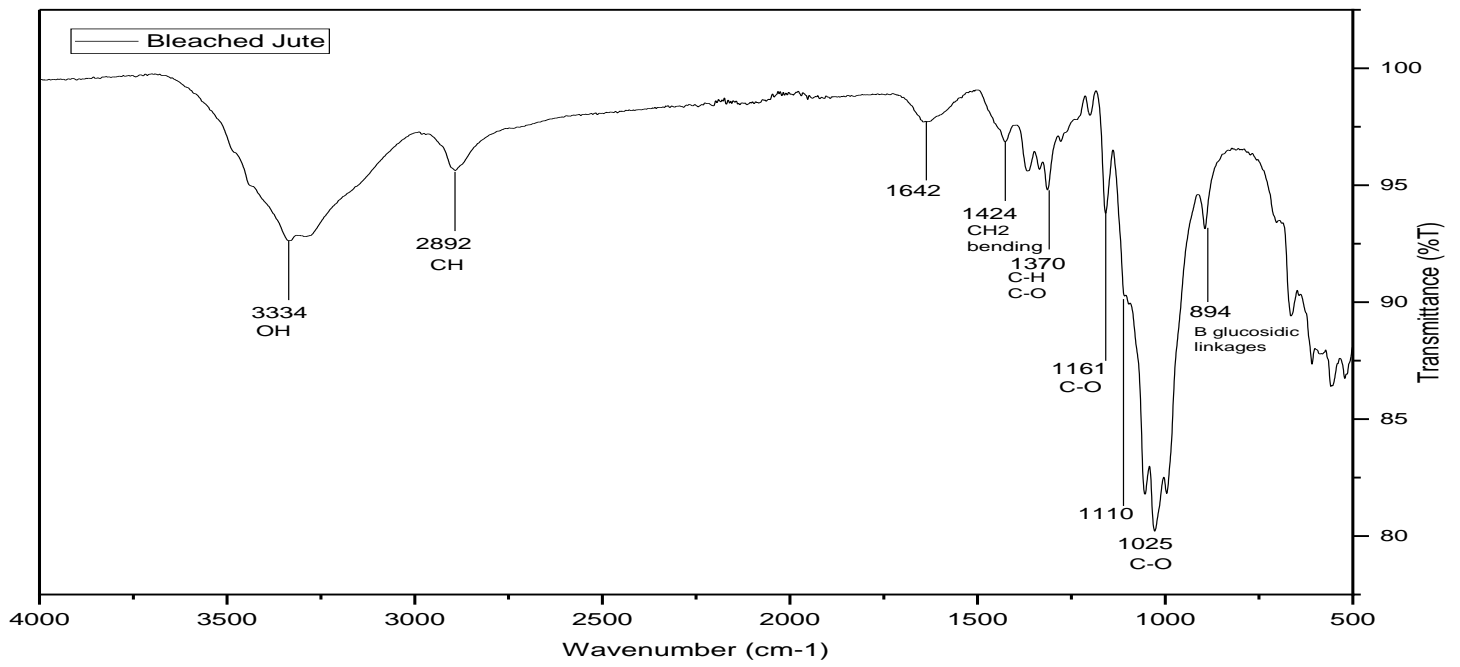
Figure 4.5 FTIR Spectra of bleached jute.
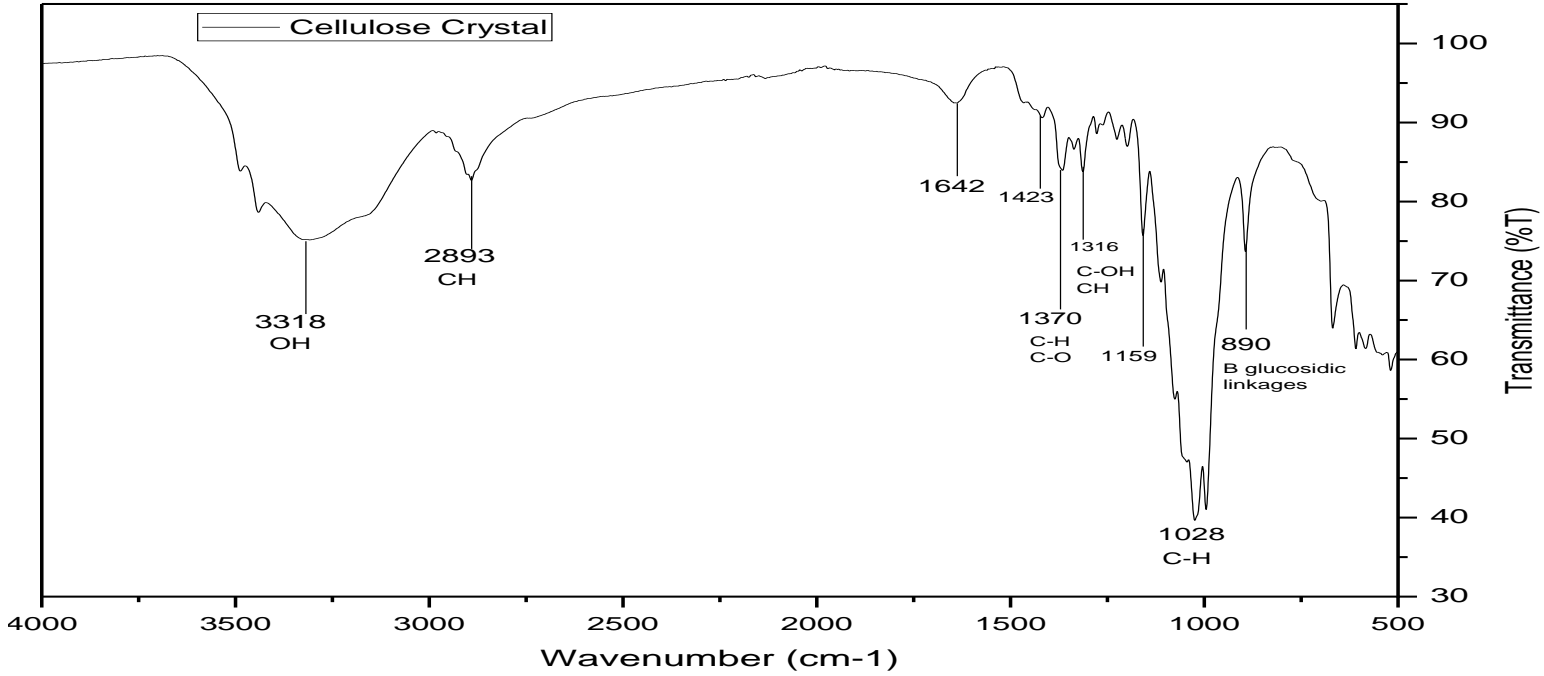
Figure 4.4 FTIR for pure cellulose.

4.1.2 X-Ray Diffraction

To explore the crystallinity of jute cellulose crystal, XRD was conducted. XRD patterns help understand the formation and change in crystal structure, which is shown in the **Figure 4.6** as counts against degrees 2-theta (2θ) graph.
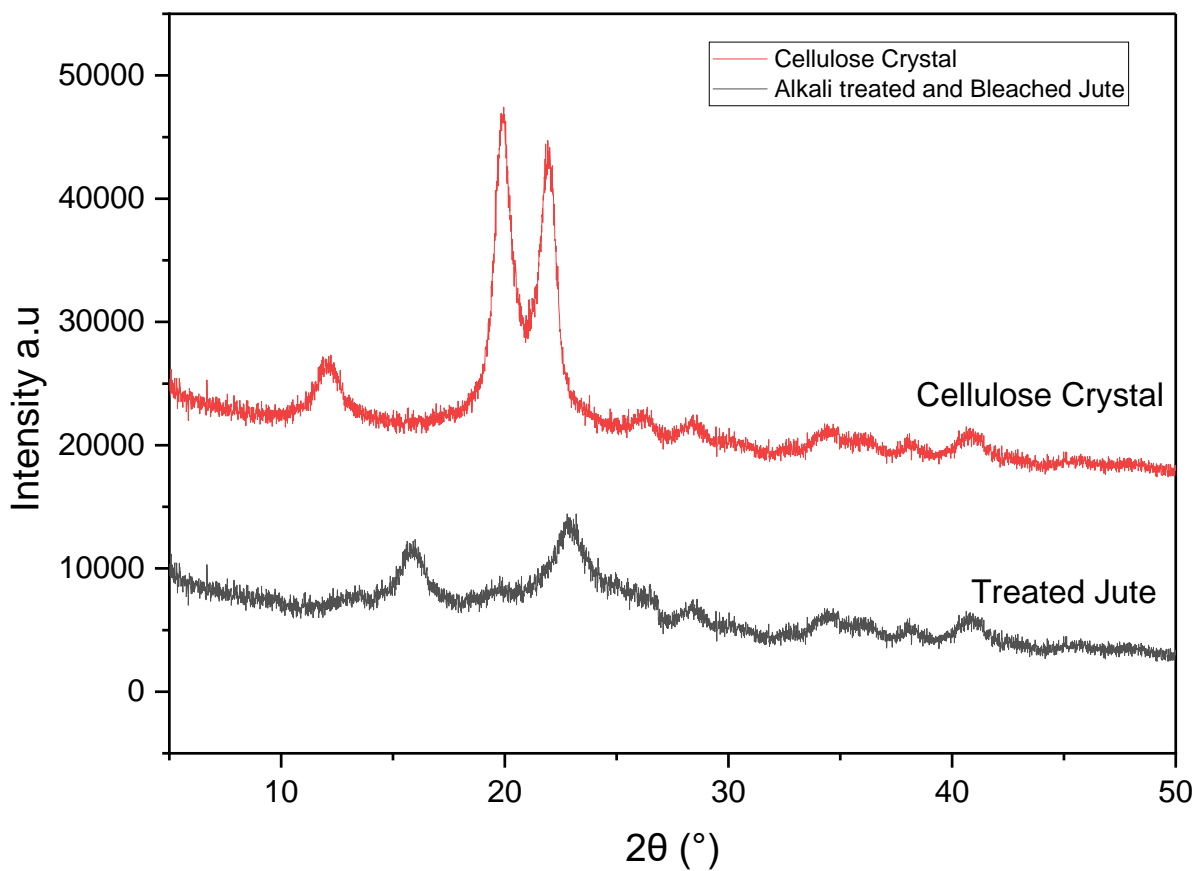
Figure 4.6 X-ray diffraction (XRD) pattern of jute after alkali treatment and bleaching and cellulose crystal.

Alkali treatment and bleaching removes all lignin and hemicellulose from the raw jute leaving pure cellulose. This cellulose has both amorphous and crystalline regions. The molecular orientation can vary widely in the crystalline regions, and this causes emergence of various polymorphs [49]. The ability of a solid material to exist in more than one form or crystal structure is called polymorphism [54]. There can be found 4 different polymorphs of cellulose- cellulose I, cellulose II, cellulose III, and cellulose IV [49].

XRD result analysis data has been summarized in Table 4.2. In this research, for treated jute, peaks were found near 2Θ= 16.08° and 22.68° confirming the presence of cellulose I [37, 46, 49, 55]. After acid hydrolysis (64% sulfuric acid), only cellulose crystal is left, which gives peak around 2Θ= 12.18°, 20.01° and 22.06° that is consistent with peak patterns of Cellulose II [56]. These peaks are corresponding to planes 1$\bar{1}$0, 110 and 200. It can be said that upon hydrolysis, the crystal pattern of cellulose has changed. Similar results have previously been reported [46]. Probable explanation of this phenomena can be explained by the fact that during acid hydrolysis, the amorphous regions are attacked first. In the meantime, The crystalline region swell up and the crystalline structure is reorganized resulting in different polymorph [49].

Table 4-2 Peak positions, crystallinity index, crystal size and polymorph type of Treated jute and Cellulose crystal.

Sample	Peak Positions (2Θ°)	Crystallinity (%)	Crystal size	Cellulose Type
Treated jute	16.08, 22.68	30.92	14.6 nm	Cellulose I
Cellulose Crystal	12.18, 20.01, 22.06	69.25	7 nm	Cellulose II

Due to acid hydrolysis, crystallinity has significantly increased from 42.92% to 69.25% and crystal size has reduced from 14.8nm to 7nm. The cause of increased crystallinity is that in treated jute, the cellulose has tightly packed crystalline region and stabilized by complex hydrogen bond network. During acid hydrolysis, the amorphous region is attacked first and are removed by acid hydrolysis. With the use of high concentration sulfuric acid, the crystalline regions can be attacked and rearranged.

4.1.3 Scanning Electron Microscopy

Scanning electron microscopy was conducted to determine the surface morphology of cellulose crystal. The images are shown in **Figures 4.7-4.9**. The Average particle size was found to be 3 micrometers. The particles are irregularly shaped. The particles have tear in their surface which is caused due to sulfuric acid hydrolysis. The rough surface is also a result of acid hydrolysis [57]. Agglomeration is visible (Figure 4.7). Compact agglomeration in some regions of cellulose crystals shows that cellulose chains have an intermolecular hydrogen bonding and a strong hydrophilic interaction in between the cellulosic chains. The agglomeration can also be caused by

the freeze drying [58]. The images show that the fiber like structure found in raw cellulose is no more present. Moreover, individual particles show absence of lignin [37, 55, 58]. Raw cellulose was crushed into individualized micro-sized particles under acid hydrolysis. Compact agglomeration in some regions of cellulose crystals shows that cellulose chains have an intermolecular hydrogen bonding and a strong hydrophilic interaction in between the cellulosic chains [57].

Alkali treatment causes "axial splitting" of the fiber structure. Bleaching and alkali remove lignin content. Jute fibers are bundles of individual strands held together by lignin. So, removing lignin by pretreating the cellulose has caused the fiber like structure to disappear [57, 59].
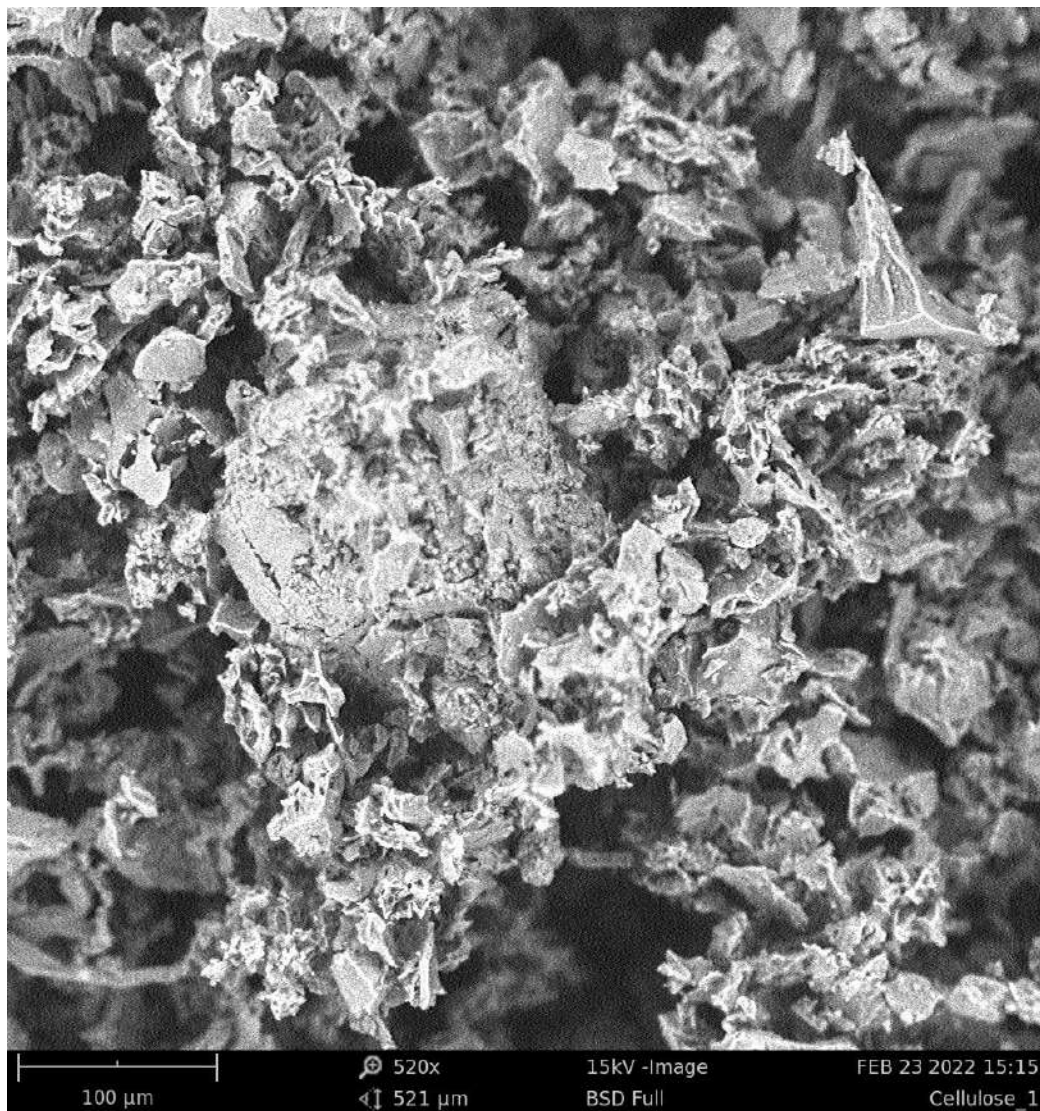
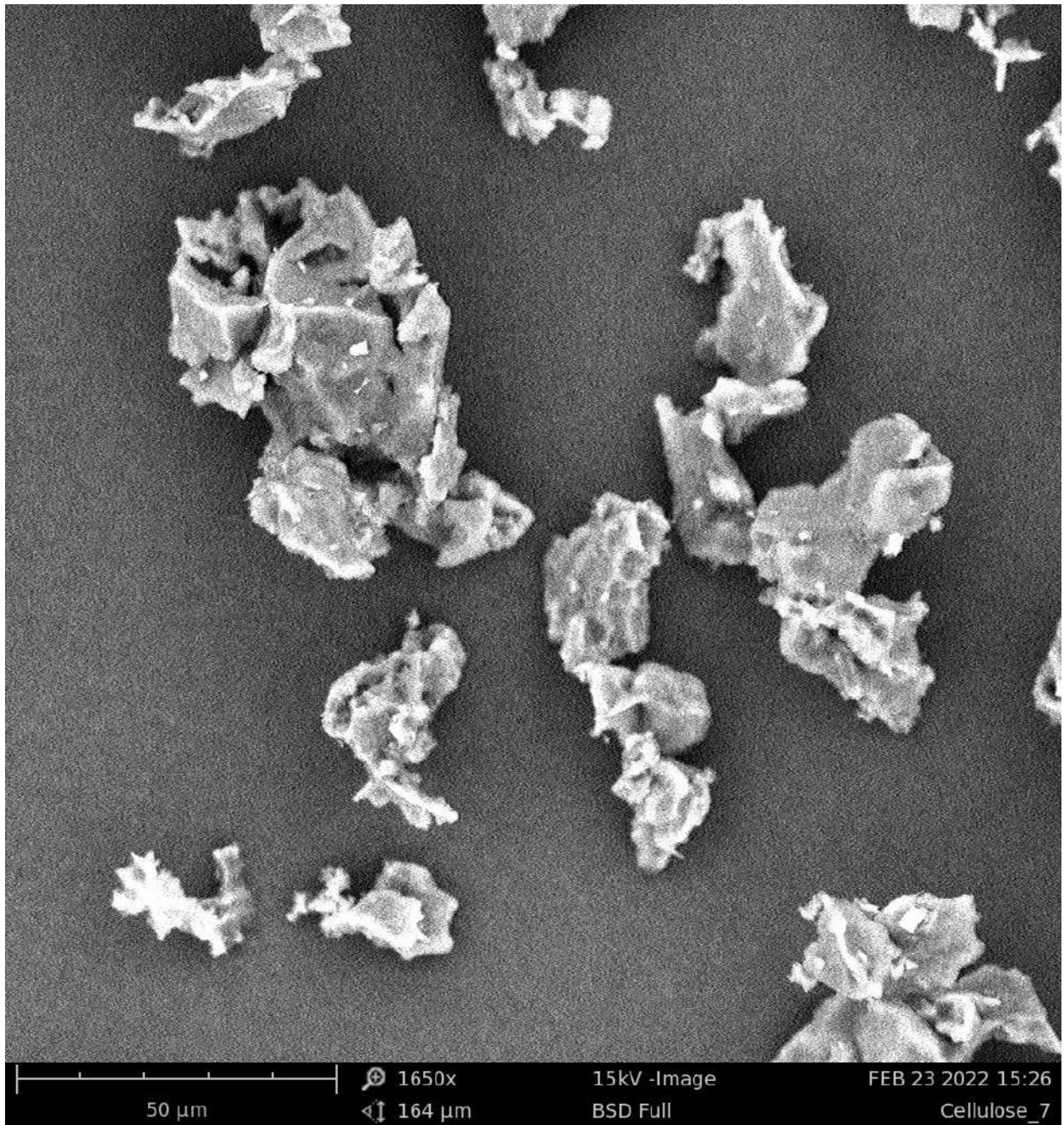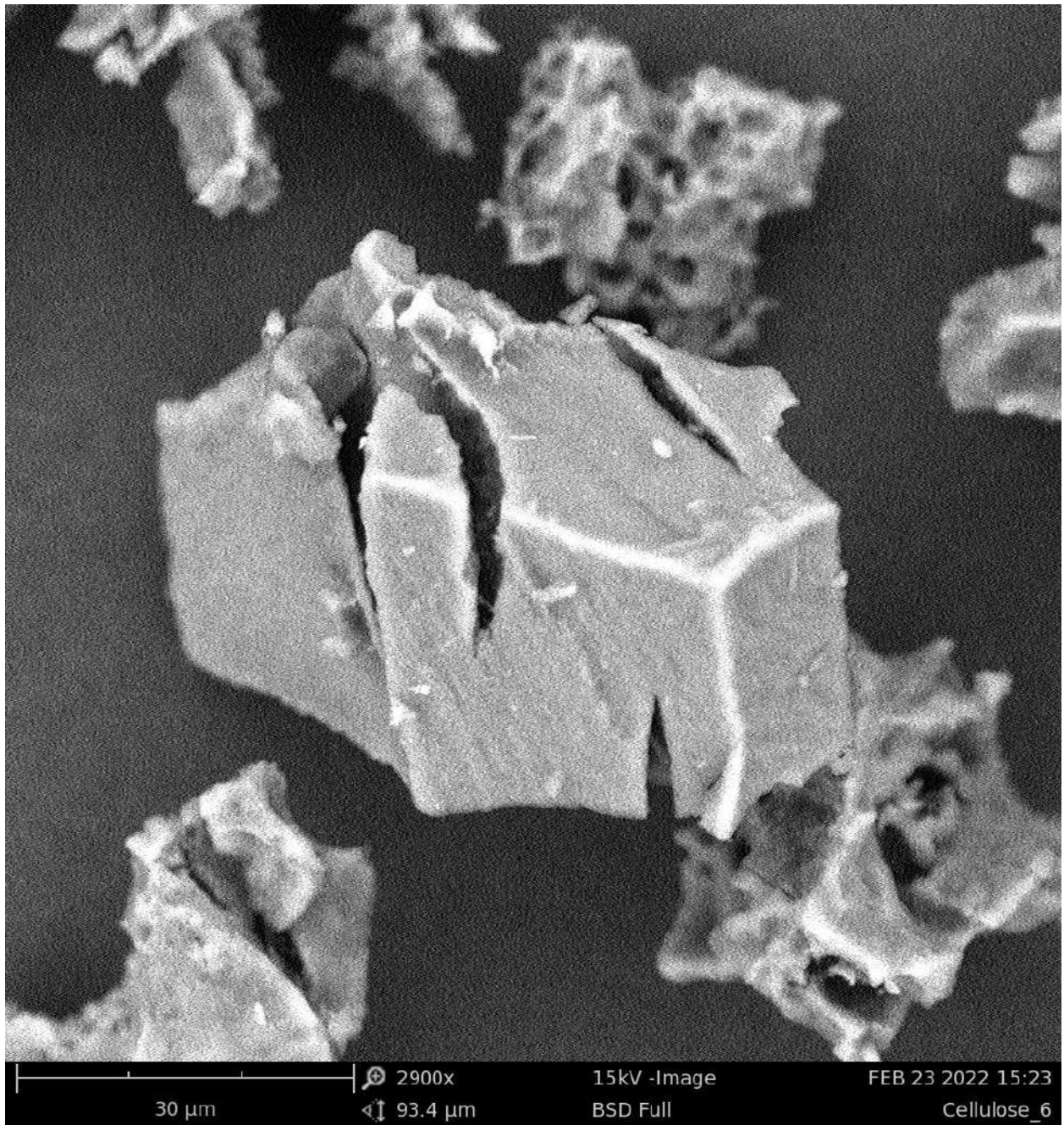*Figure 4.7 : Scanning electron microscopic image for cellulose crystal at magnification of 520.*

Figure 4.8 Scanning electron microscopic image for cellulose crystal at magnification of 1650.

Figure 4.9 Scanning electron microscopic image for cellulose crystal at magnification of 2900.

4.2 Characterization of Composite Films

4.2.1 Fourier-transform infrared spectroscopy (FTIR)

FTIR analysis was conducted on the bio composite films prepared using varied concentrations of cellulose crystal (CC). Figure 4.10 shows that all the variations show the exact same peaks in the spectra. Figure 4.10 proves that there has not been any chemical reaction for adding cellulose crystal to the solution of jute polymer.
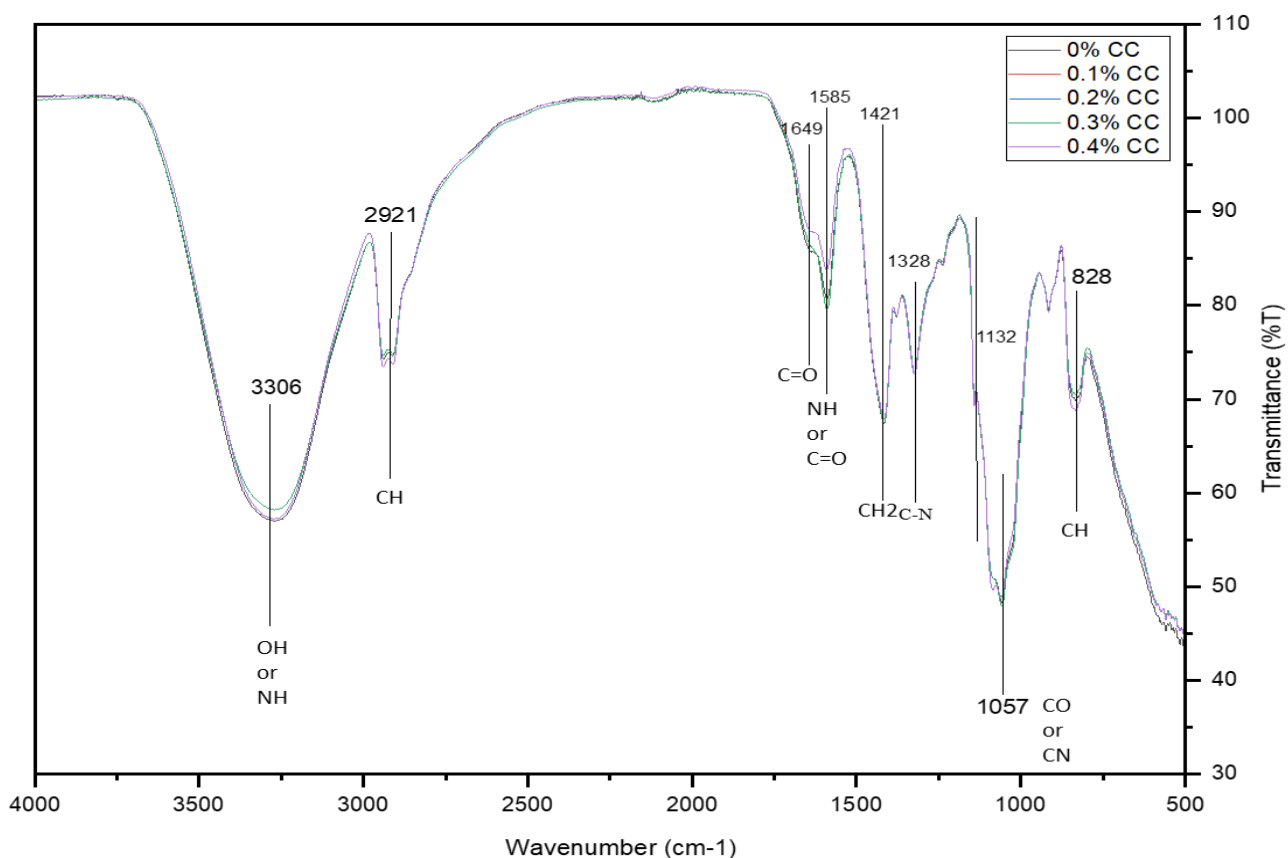
Figure 4.10 FTIR spectra for 0% CC 0.1% CC and 0.2% CC 0.3% CC and 0.4% CC reinforced bio composite films.

For the composite, the large band observed between 3650 cm^{-1} and 2980 cm^{-1} is linked to the stretching of O–H from the intramolecular and intermolecular hydrogen bonds. It can also be linked to N-H stretching. The vibrational band observed between 2992 and 2842 cm^{-1} refers to the stretching C–H from alkyl groups and the peaks between 1716–1590 cm^{-1} are due to the stretching C=O and C–O can mean formation of ester linkage between jute polymer solution and CC. The peaks for C–O–C at 1170–945 cm^{-1} and for bending vibration related to CH$_2$ groups at 1410–1316

54

cm^{-1} are also observed in the spectrum of the composite. Table 4.3 shows the peaks and their possible assignments.

Table 4-3 FTIR Peaks and possible functional group assignments.

Peaks (cm^{-1})	Possible assignments
3306	O-H stretching or N-H stretching
2921	C-H stretching
1649	C=O stretching
1585	N-H bending or C=O and C–O stretching
1421	O-H bending or bending vibration related to CH$_2$ groups or COO Symmetrical stretch
1328	C-N stretching
1057	C-O stretching or C-N stretching
828	C-H bending

The peaks were analyzed using the Sigma Aldrich IR group table (Table 4.3). The strong and broad peak near 3306 cm^{-1} can be caused by O-H stretching or N-H stretching. The peak near 2921 cm^{-1} is caused by c-H stretching. Presence of C=O functional group may be proven by the peak present near 1649 cm^{-1}. The sharp peak near 158 cm^{-1} can be caused by either N-H bending or C=O and C–O stretching. Peak at 1421 cm^{-1} could prove the presence of O-H bending or it might be due to the bending vibration related to CH$_2$ groups or it can also be evidence of the presence of COO symmetrical stretch. Peak at 1328 cm^{-1} can be caused by C-N stretching. The Peak near 1057 cm^{-1} can be due to C-O stretching or C-N stretching. Peak at 828 cm^{-1} proves the presence of C-H bending.

4.2.2 X-Ray Diffraction

To explore the crystallinity of the cellulose crystal reinforced jute polymer composite films, XRD was conducted. XRD patterns help understand the formation and change in crystal structure which is shown in the Figure 4.11 showing counts against degrees 2-theta (2θ) graph.
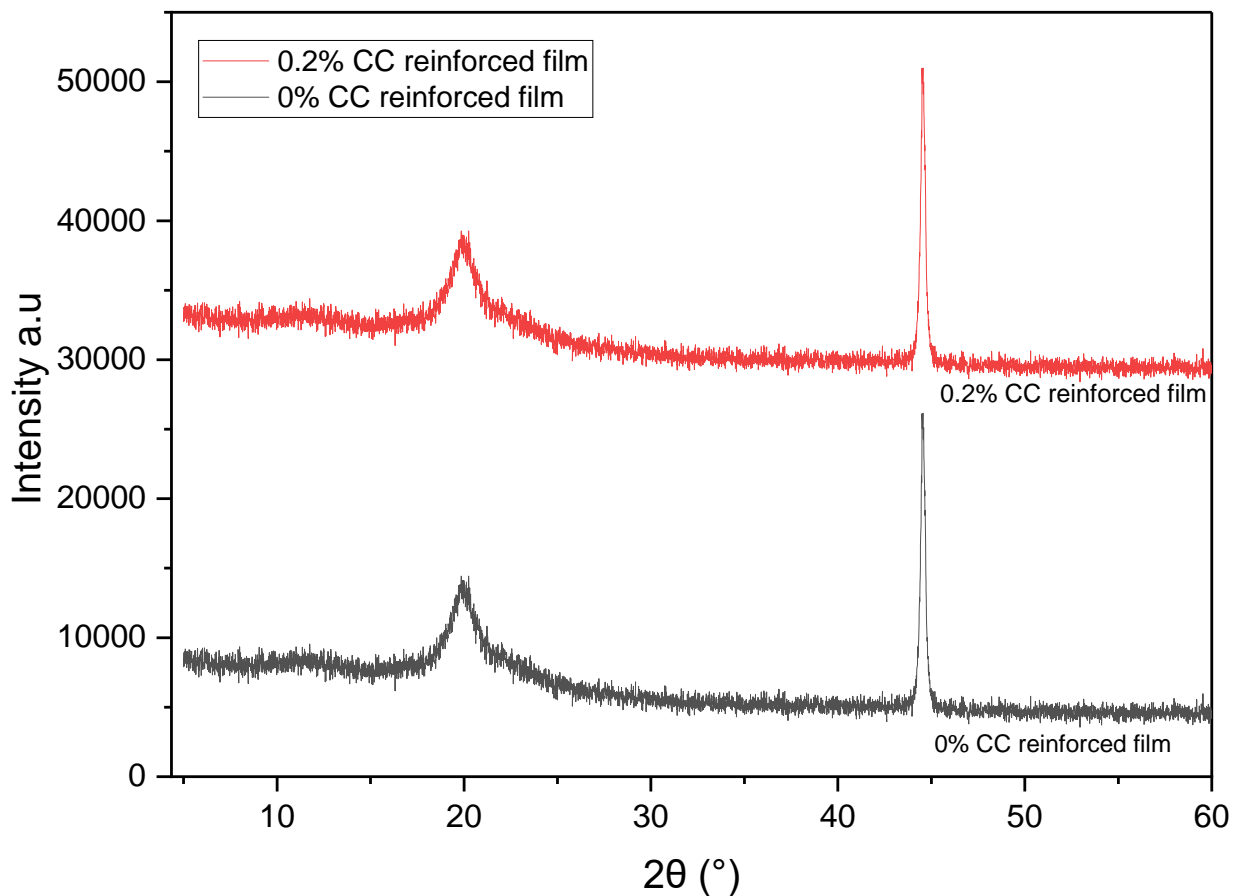
Figure 4.11 XRD graph for 0% CC reinforced and 0.2% CC reinforced jute polymer films.

The crystallinity of the films was found to be 32.97% and the crystallite size was 37.6nm. It can be seen from the graph that there is no difference between the XRD graphs for 0% CC reinforced composite and 0.2% CC reinforced composite which gives us the conclusion that incorporation of 0.2% CC has made no change in the crystalline properties of the composite films. There is a sharp peak near $2\Theta= 20°$, which can be evident of the presence of cellulose crystal even before the reinforcement was added.

There is a very sharp peak near $2\Theta= 44.52°$, which is indicative of a pure crystalline salt. Previous literature shows that such peak near $2\Theta= 44°$ can appear because of the presence of Urea which is used as both plasticizer and crosslinker [60, 61]. The presence of amides can also be evidenced by the FTIR graphs where peaks for N-H and C=O functional groups were found.

It has also been evidenced that in some cases amides can alter with the crystalline properties of cellulose which can be a reason why addition of cellulose crystal has no effect on the crystalline properties of the polymer films [56].

4.2.3 Scanning Electron Microscopy

Scanning electron Microscopy was conducted to determine the morphology of cellulose crystal reinforced jute polymer films. It is clear from the images that the films have a lot of voids or pores in them. From Figure 4.12 (a), the 0% CC reinforced films show that it is filled with pores. The pores can be caused by trapped air bubbles. The emergence of pores has been significantly reduced by 0.1% CC reinforcement (Figure 4.12 (b)) and further reduced after 0.2% CC reinforcement (Figure 4.12 (c)). This should mean that there has been good interfacial adhesion between CC and matrix polymer. FTIR has shown presence of -OH groups in polymer matrix. Cellulose crystal also has large number of -OH functional groups on its surface. As a result, hydrogen can form improving interfacial adhesion. On the other hand, Figure 4.12 (d) shows further increasing CC concentrations to 0.3%, gives re-emergence of pores and shows agglomeration. Increasing the CC concentration even more to 0.4% shows large agglomerations and pores.

The results of the SEM images can be explained by reinforcing CC up to 0.2% helps reduce pores and does not agglomerate which means the viscosity of the solution reached at an optimum level. Further increasing CC loading creates agglomeration and increases the viscosity of these films too much. This thick solution entraps air and upon drying, creates pores or voids.
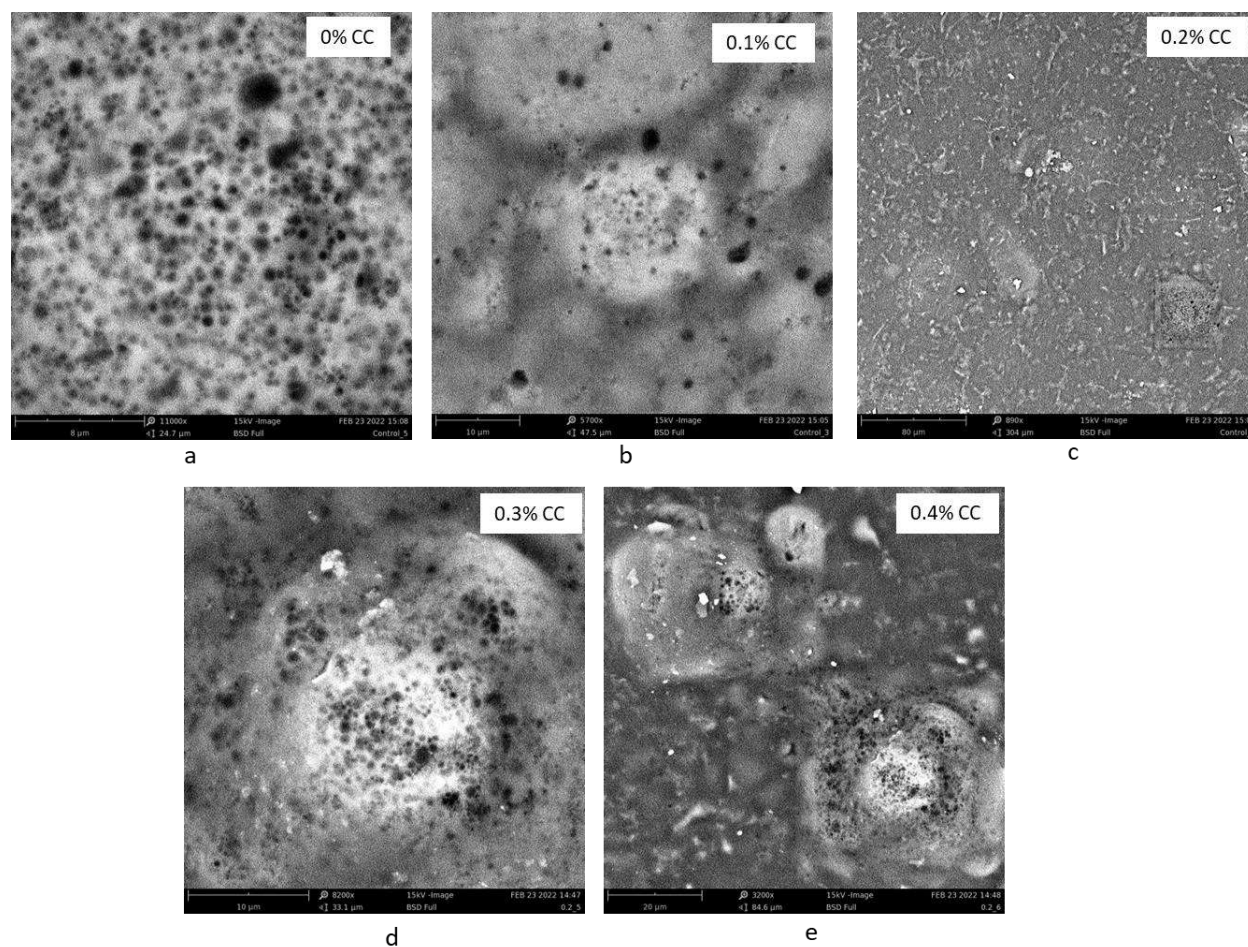
Figure 4.12 SEM image of (a) 0%CC, (b) 0.1%CC,(c) 0.2%CCs, (d) 0.3%CC and (e) 0.4%CC reinforced composite films.

4.2.4 Differential Scanning Calorimetry (DSC) for Composite Films

Differential scanning calorimetry (DSC) is a common analytical technique for studying thermal characteristics of polymers. Properties like glass transition temperature (Tg), melting temperature (Tm), crystallization temperature (Tc) can be determined using DSC. The DSC results of prepared films with different concentrations of cellulose crystal (CC) are shown in Table 4.4 and Figures 4.13-4.17.

Table 4-4 Glass transition temperature and melting point of composite films

Sample	Glass Transition Temperature (°C)	Melting Temperature T_m (°C)
0% CC	80.50	208.69
0.1 % CC	97.56	228.31
0.2 % CC	110.61	242.46
0.3 % CC	112.94	232.70
0.4 % CC	110.44	234.70

From Table 4.4, it can be seen that the glass transition temperature (T_g) has improved slightly with the addition of cellulose crystal (CC). In 0% CC reinforced film, the glass transition temperature was found to be around 80.50°C. In 0.1% CC reinforced films, the T_g was around 97 °C, in 0.2% CC reinforced films, the T_g was around 110°C, in 0.3% CC reinforced films, the T_g was 112°C, in 0.4% CC reinforced films, the T_g was 110°C. So, it can be said that the glass transition temperature increased with gradual increase of cellulose crystal concentration. The reason behind this increase may be intermolecular hydrogen bonding between the CC and polymer matrix. Another possible reason might be covalent crosslinking network formed between CC and the matrix. Crosslinking hinders the motion of the polymer chains and thus increases glass transition temperature [9].

The table also shows that there has been a slight increase in melting temperature in polymer films. In 0% CC reinforced film, the melting temperature was found to be around 208°C. In 0.1% CC reinforced films, the T_m was around 228°C, in 0.2% CC reinforced films, the T_m was around 242°C, in 0.3% CC reinforced films, the T_m was around 232°C, in 0.4% CC reinforced films, the T_m was around 234°C. This increase in melting temperature can also be attributed to intermolecular hydrogen bonding. Tighter packing may also work as a reason behind increase in melting temperature [9]. Figure 4.13-4.17 shows the different DSC curves of samples
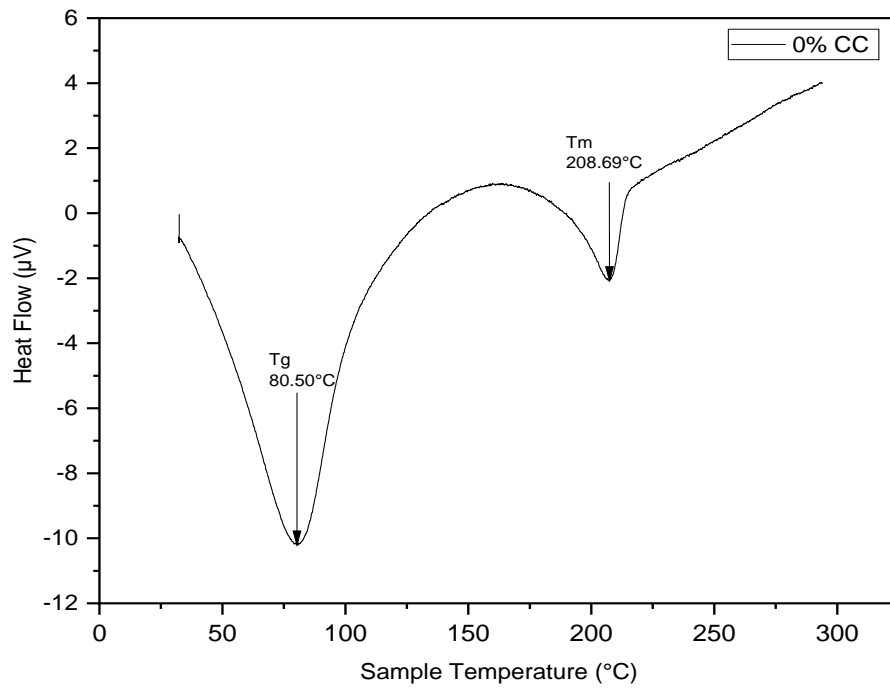
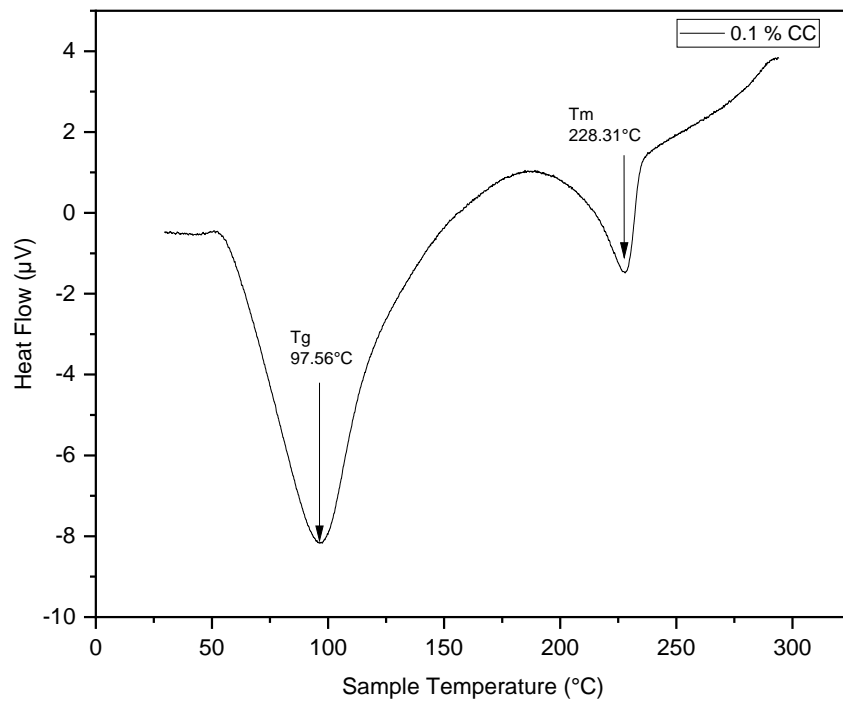*Figure 4.13 DSC curve of 0 % CC reinforced composite*

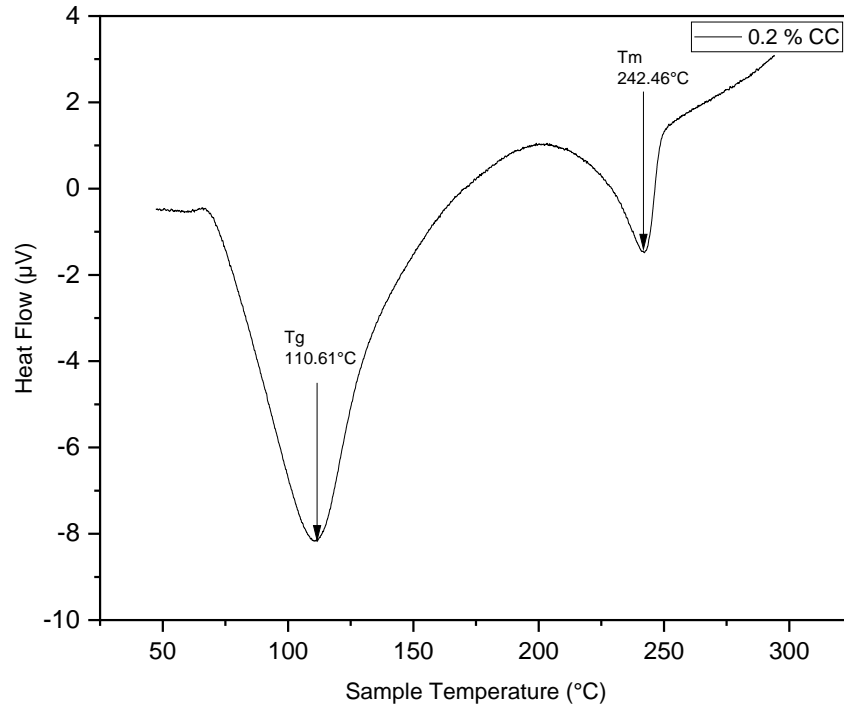*Figure 4.14 DSC curve of 0.1 % CC reinforced composite*

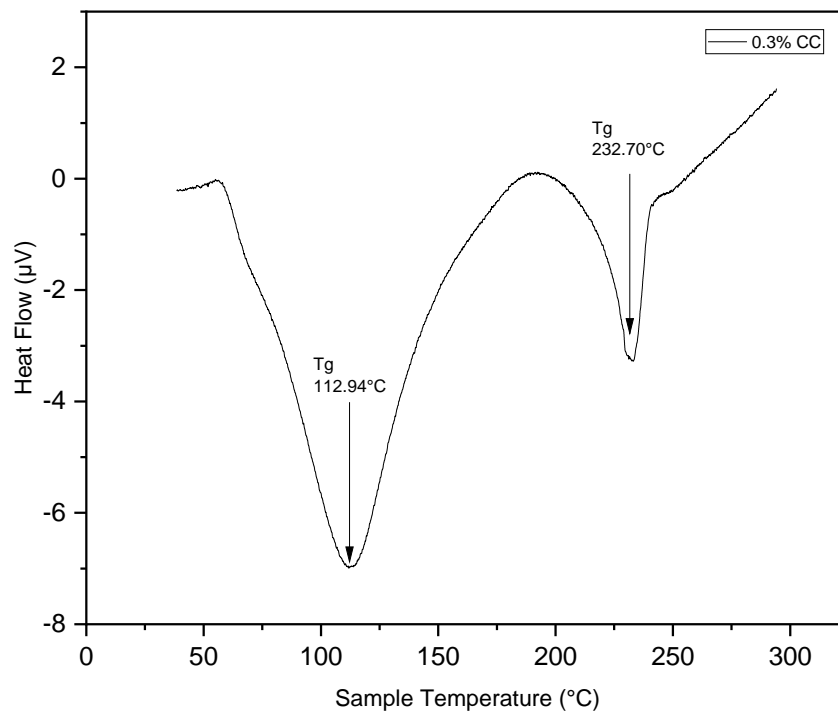*Figure 4.15 DSC curve of 0.2 % CC reinforced composite*

Figure 4.16 DSC curve of 0.3 % CC reinforced composite
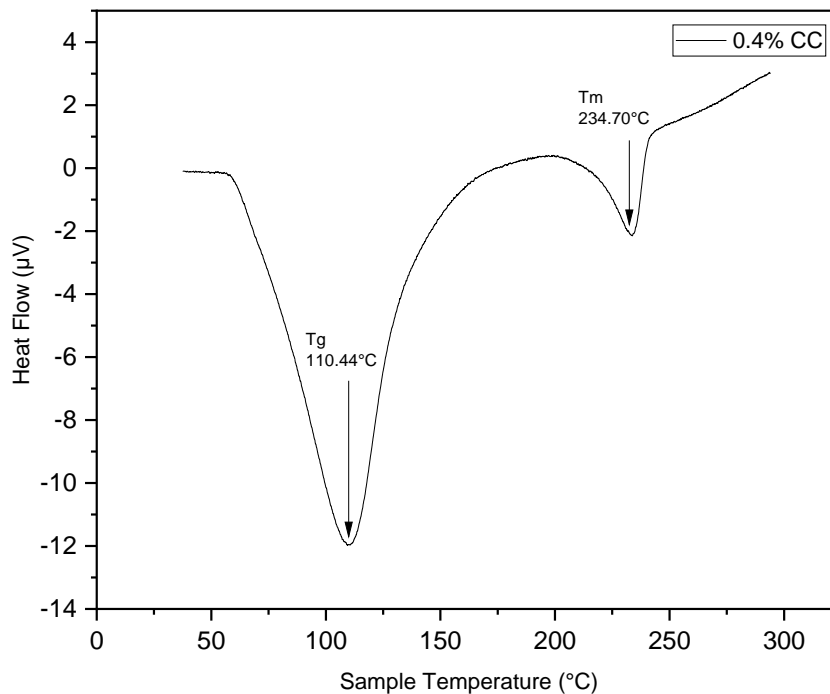
Figure 4.17 DSC curve of 0.4 % CC reinforced composite

4.2.5 Thermogravimetric Analysis

The thermal stability of prepared bio composite films was investigated by thermogravimetric analysis. The thermogravimetric analysis curves of bio-composite films using varied percentage of CC were shown in Figures 4.18-4.22. From these graphs, it can be seen that there are three parts of the TGA plots depending on temperature zones. The first zone indicates the evaporation of moisture content, impurities, vapors and high volatile components and this zone ranges from 100-200°C. The second zone shows the thermal stability of the material. It lies between onset temperatures and offset temperatures. The last and third temperature zone starts from the offset temperature, which indicates the degradation of material. In the third zone, thermally unstable materials show a flatter line than the materials that are thermally stable.

The initial degradation temperature and the final degradation temperature of biocomposite films with varied CC percentage are shown in Table 4.5. It can be seen from the data that the initial degradation temperature increased with increasing CC% up until 0.2. After that, the increase in CC decreased the degradation temperature. The final degradation temperature also showed similar

trend. Nevertheless, the use of CC increased the degradation properties of the initial film prepared with 0% CC use. The residual weight is highest for 0.2 % CC reinforced films. The residual weight increased with use of CC until 0.2% and then decreased with further increase of CC. This can be explained by factors affecting the thermal stability of composites. Intermolecular bonding between the reinforcement and the polymer matrix is a strong influencer of thermal stability. The filler and the matrix both have -OH groups and so, form hydrogen bonds which increase the thermal energy required for cleavage of the composite films. Mandal and Chakrabarty found similar results [9].

Table 4-5 Degradation temperature and residue for composite films

Biocomposite	Degradation Temperature (°C)		Residue
	Initial	Final	In wt. %
Control	201	339	35.07
0.1% CC Reinforced	229	353	35.09
0.2% CC Reinforced	248	371	44.29
0.3% CC Reinforced	245	356	39.99
0.4% CC Reinforced	233	347	38

With increased CC loading, the decomposition temperature decreased. Agglomeration of CC particles caused reduction in degradation temperatures. At 0.2% CC, the hydrogen bonds reached to an optimum or saturated level. Further increase in CC particles did not form any bond with the matrix. Rather they acted as individual particles with sulfated surface. Sulfuric acid hydrolysis in higher concentrations, lower the thermal properties of cellulose crystals [9].

Figure 4.18 TGA curve of 0%CC reinforced composite.

Figure 4.19 TGA curve of 0.1 %CC reinforced composite.

Figure 4.20 TGA curve of 02 %CC reinforced composite.

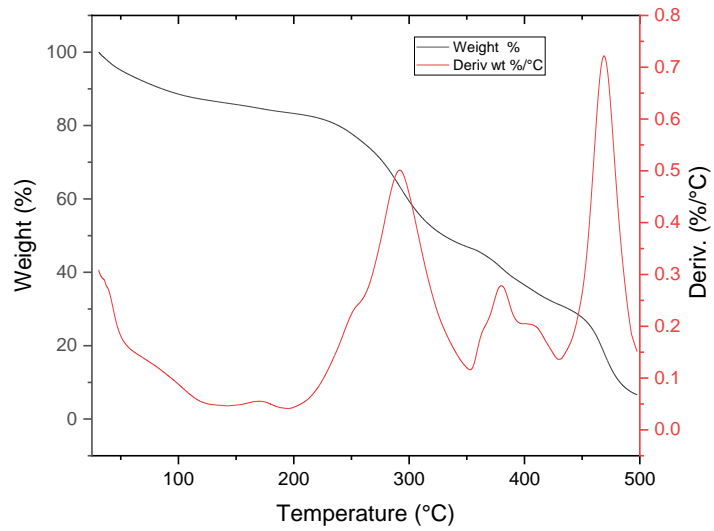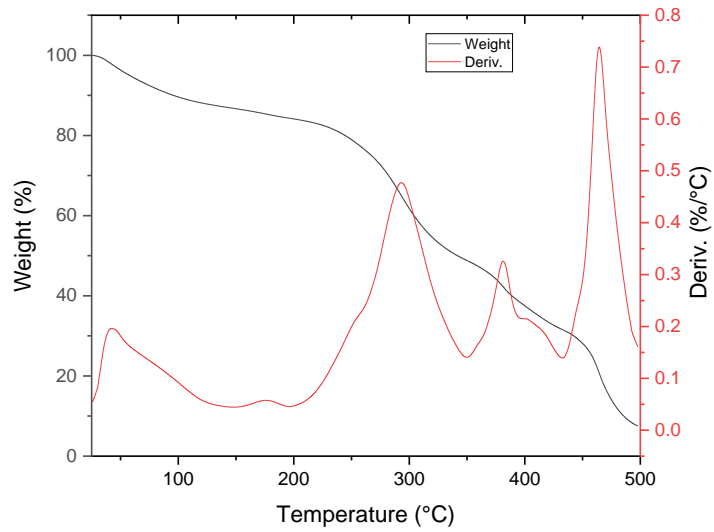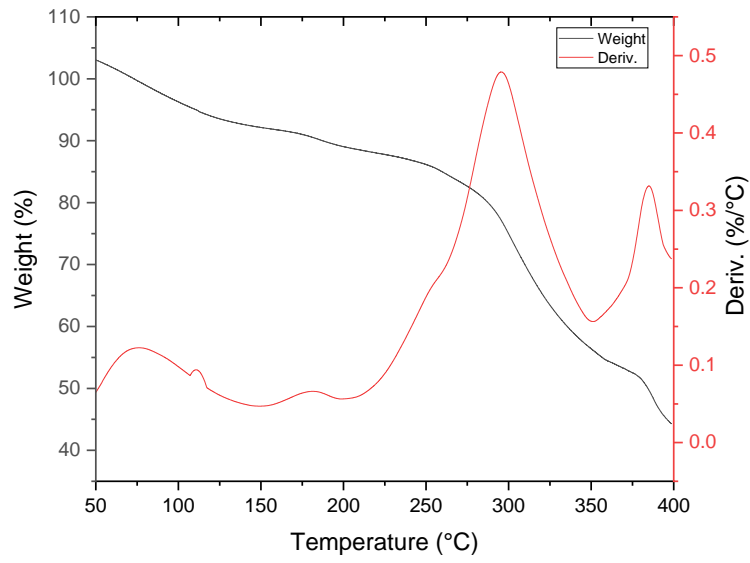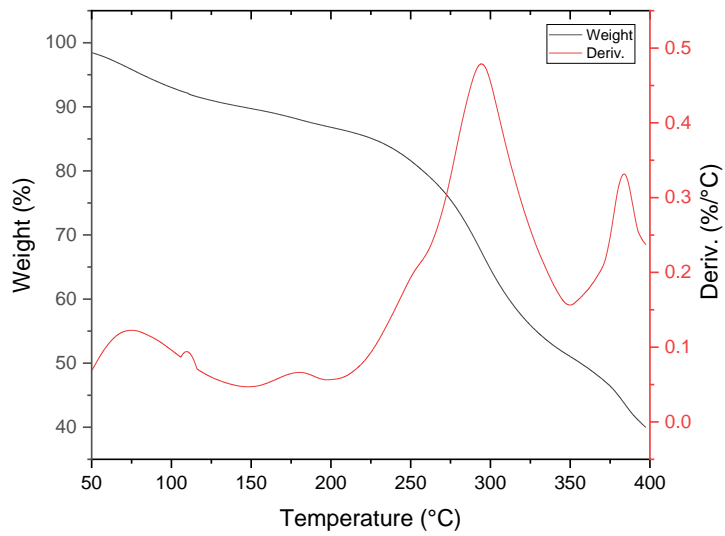*Figure 4.21 TGA curve of 0.3%CC reinforced composite.*

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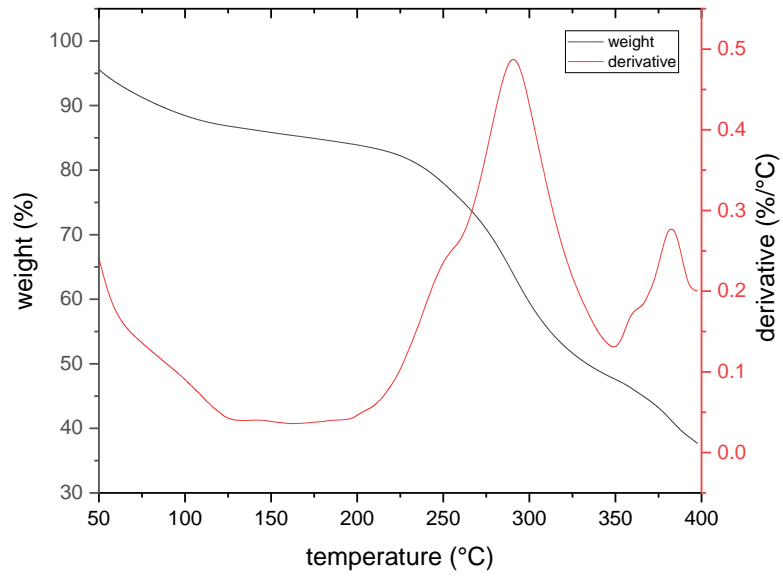
Figure 4.22 TGA curve of 0.4 %CC reinforced composite.

4.2.6 Biodegradability (Soil Burial) Test Results

Soil burial method has been used as a mode of testing biodegradability for several years. The results of the soil burial test of prepared films are shown in the Table 4.6.

Table 4-6 The results of the soil burial test of prepared films

Interval	% Degradation of samples prepared at				
	0% CC	0.1% CC	0.2% CC	0.3% CC	0.4% CC
After 15 days	13.34%	14.11%	15.56%	17.19%	21.01%
After 30 days	25.89%	30.90%	33.78%	36.59%	38.00%
After 45 days	41.22%	48.03%	55.98%	62.02%	70.87%
After 60 days	67.15%	70.19%	75.92%	82.08%	87.95%
After 75 days	78.99%	80.29%	85.63%	89.33%	91.66%
After 90 days	89.76 %	91.30 %	93.12%	96.34%	98.09%

It can be clearly seen that with increase in CC concentrations the percent weight loss of the buried composite films increased. Cellulose crystals are hydrophilic and so they attract water molecules from the soil, which in turn attract degrading enzymes. Another probable cause can be explained as, the adsorption of water causes the cellulosic materials to swell which crack the films. This causes the microbes and degrading enzymes present in the soil to enter the film more easily accelerating the degradation [60] . Pictures of various stages of soil burial tested of 0.2% CC films are shown in Figure 4.23.

Figure 4.23 Images for various stages of film with 0.2% CC in soil burial method.

Cellulosic fibers stand out as a promising candidate to provide access for moisture and microbial enzymes within bioplastic composites. Several researchers have proposed that cellulosic materials play a related role when they are present in bioplastic composites. Opening of channels within composites, allowing access for enzymatic biodegradation. Various researchers have suggested that faster degradation can be achieved if something is added to the mixture to allow diffusion within the bioplastic material [62].

4.2.7 Tensile properties

Tensile properties of the composite with 0%, 0.1%, 0.2% ,0.3% and 0.4% cellulose crystal loading were measured, and the results are shown in Figures 4.24 and 4.25 and Table 4.7. It can be seen that the tensile strength of the composite films increased with increasing cellulose crystal (CC) concentrations up to 0.2% and then decreased. The reasons behind this can be attributed to the interfacial adhesion between CC and matrix polymer. This trend has previously been shown in literature [61]. Because of the presence of large number of -OH groups in both cellulose and polymer matrix and generated hydrogen bonds motivates localized stability and as a result can give better mechanical properties.
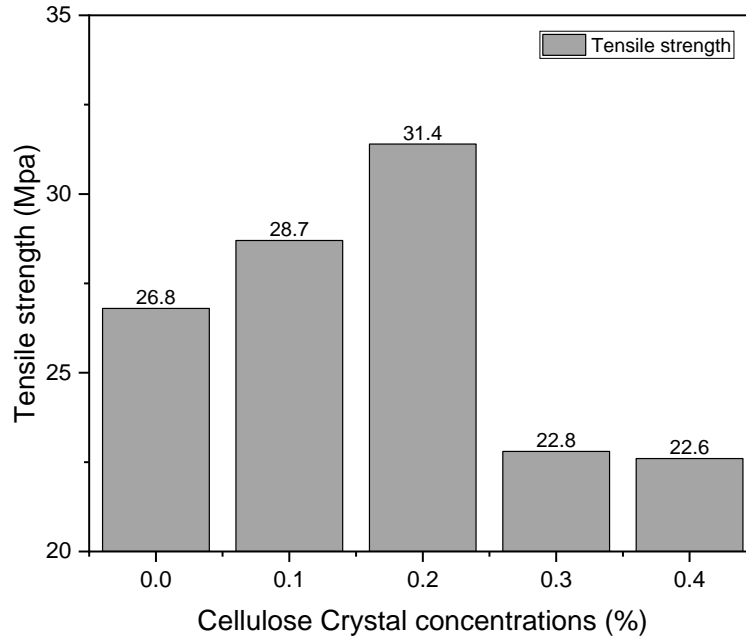
Figure 4.24 : Tensile strength for different concentrations of cellulose crystal loading in composite films.
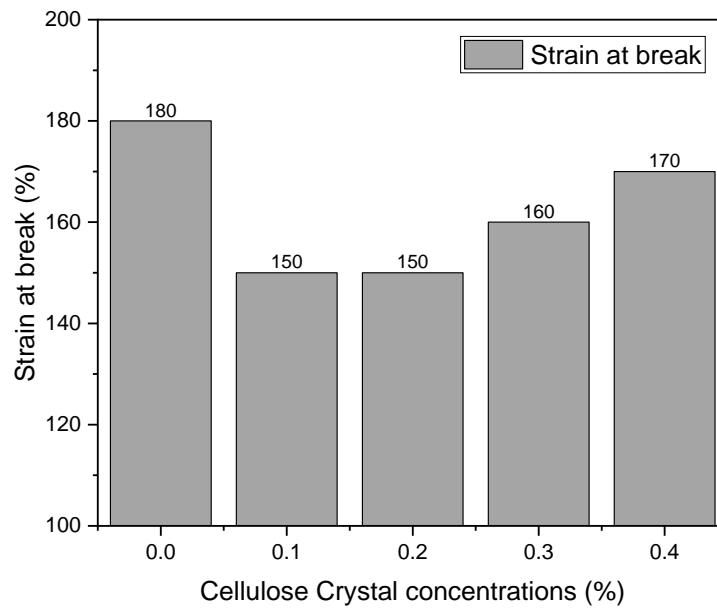
Figure 4.25 Strain at break for different concentrations of cellulose crystal loading in composite films.

Table 4-7 Tensile properties of various prepared films.

CC Concentrations	Tensile strength MPa	Strain at break %
control	26.8	180
0.10%	28.7	150
0.20%	31.4	150
0.30%	22.8	160
0.40%	22.6	170

In this study, the Scanning electron micrographs clearly shows presence of pores in initial jute-polymer solution without any CC loading. Introducing CC up to 0.2%, helped reduce these pores, possibly by optimizing the viscosity of the solutions. But increasing the CC loading further did not result in pore reduction. Rather, increased CC loading introduced agglomeration of CC. These agglomeration sites work as stress concentration sites and decrease tensile strength. Another possible reason might be that the viscosity of the polymer matrix increased with increased CC loading which makes "degassing" of the polymer solution difficult and entraps small air bubbles. These air bubbles become pores upon drying and weaken the tensile strength of prepared films [63].

4.2.8 Water Absorption Test Results

Water absorption properties were measured by immersing the samples into water for 2 minutes, 5 minutes, 10 minutes, 20 minutes and then 24 hours and 3 days. Results are shown in Table 4.8 and Figures 4.26 and 4.27. It can be noticed that most of the water was absorbed within the first 20 minutes and then it came to a constant and remained the same after 24 hours. The reason behind high water absorbency can be attributed to the presence of -OH groups in both jute polymer and cellulose. The appearance of hydroxyl groups in cellulose fiber interrelates with the water molecules which encourage the intake of water. Presence of pores in the composite films were also evident in the SEM micrographs which is also a contributor of water absorption.

Table 4-8 Table for water absorption rate of various prepared composite films.

Sample name	Time Interval					
	2 minutes	5 minutes	10 minutes	20 minutes	24 hours	3 days
0% CC reinforced films	70%	73%	75%	75%	76%	81%
0.1% CC reinforced films	71%	76%	81%	78%	78%	88%
0.2% CC reinforced films	77%	77%	78%	79%	79.90%	95%
0.3% CC reinforced films	79%	81%	82%	83%	83%	99%
0.4% CC reinforced films	79%	80%	85%	89%	91%	110%
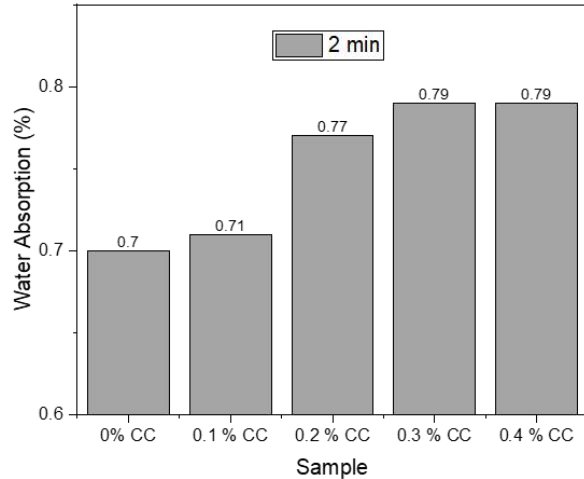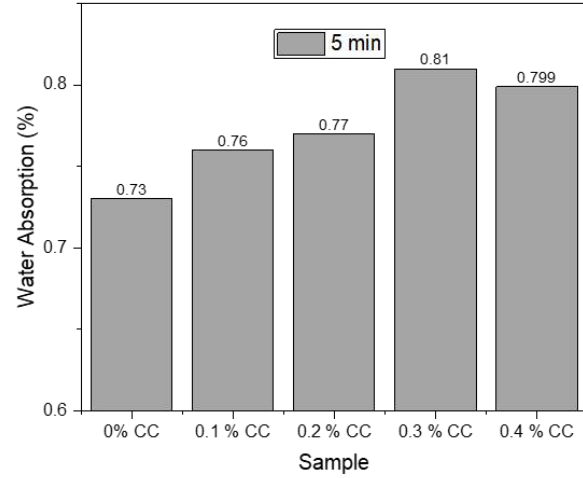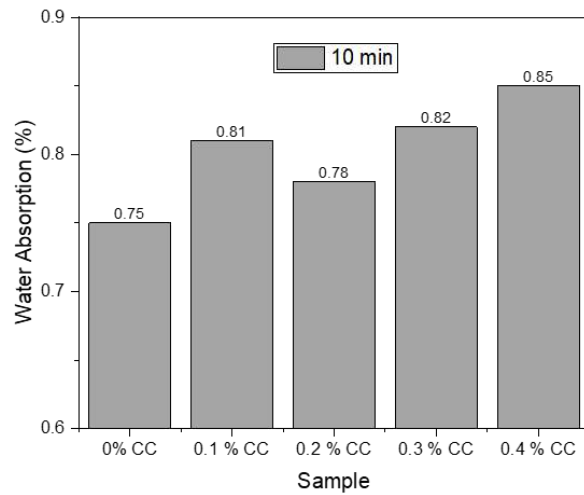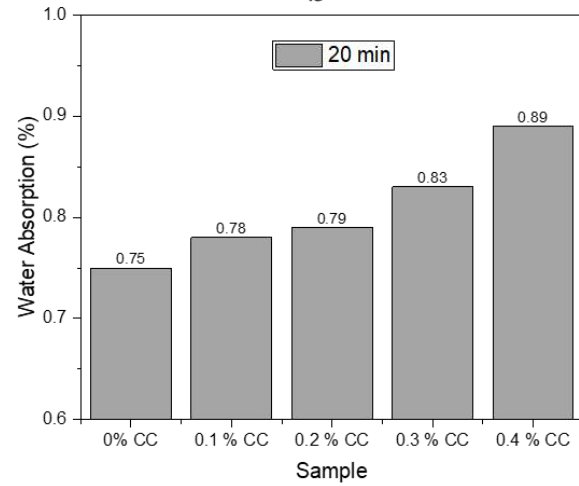
Figure 4.26 Water absorption of prepared composites at (a) 2 minutes, (b) 5 minutes, (c) 10 minutes and (d) 20 minutes time interval.
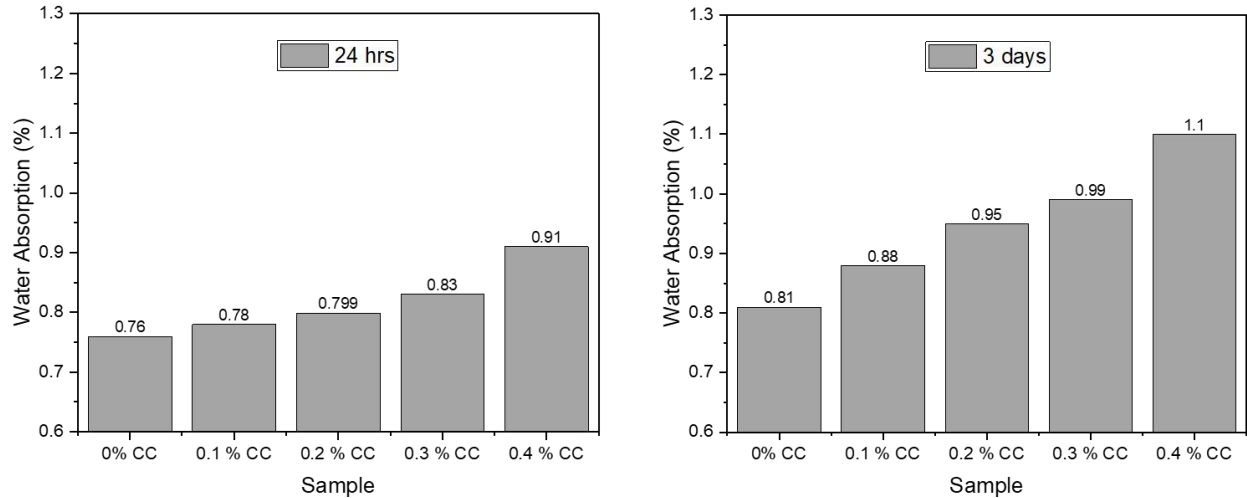
Figure 4.27 Water absorption of prepared composites after (a) 24 hours and (b) 3 days.

Similar results were obtained by Asem et. al. with poly-vinyl alcohol, starch and cellulose nanocomposite films. One of the key parameters in achieving better performance of nanocomposites film is by having an evenly distributed dispersion of the materials. Solutioned jute polymer and cellulose crystal work as materials with different scale dimension, which depends on many different interacting factors including the strong adhesion/bonding strength of the filler with the matrix, type of material used, and geometry and orientation of the cellulose crystals. The microstructure and the interface between the matrix and filler have an impact on the barrier properties of nanocomposites. The ultimate behavior of the barrier performance of the composites is determined by interactions between the organic and inorganic phases at the interface. The presence of void or pores in the films increases the diffusion of water through these empty. In contrast to oxygen molecules, water molecules interact not only with one another, but also with the polymer matrices where hydrogen bonds can be formed [64, 65].

CHAPTER 5

CONCLUSION AND FUTURE WORK

5. Conclusion and Future Work

5.1 Conclusion

In present research, cellulose crystal has been extracted from jute using two steps of pretreatment and then acid hydrolyzed to create pure crystalline cellulose. This synthesized cellulose was then used as reinforcement in making a composite using jute based biodegradable packaging material as matrix. The summarized findings of the present research are listed below-

- The use of alkali treatment majorly removed the hemicellulose content and partially removed the lignin. The use of bleaching treatment removed the lignin content and gave amorphous cellulose.

- Using acid hydrolysis removed the amorphous regions from the cellulose and gave pure crystalline cellulose with 70% crystallinity index and it transformed all the other polymorphs present in the raw cellulose into cellulose II. Also, the acid hydrolysis with sulfuric acid made the cellulose particles torn and showed sheared surface.

- The drying process might have affected the agglomeration properties of the powdered cellulose.

- Dissolving store-bought jute polymer packaging material into pH balanced water reduced its tensile properties (35%.). The store-bought jute polymer is not thermoplastic. Upon adding heat, it incinerates.

- The use of cellulose crystal as fillers in the jute polymer dissolved solution improved the tensile strength of the films. Loading cellulose crystal up to 0.2% increased the tensile strength to 19%. Further loading CC reduced tensile strength.

- Thermal properties of the prepared composites were slightly affected by CC reinforcement. Slight increase in thermal degradation temperature, glass transition temperature was noticed up to 0.2% CC loading.

- The morphological properties could be analyzed from the results from SEM micrographs which have shown that he films have pores. CC loading up to 0.2% showed that the pore formation decreased significantly. Increasing CC content to 0.3 and 0.4% showed significant agglomeration and pores.

- The Water absorption of the films were found to be extremely high. The films absorbed 70-80% of its weight percent of water almost instantly immersion. But the absorption slowed down after 20 minutes and remained somewhat unchanged after 3 days. The CC loading only increased the water absorption properties.
- The biodegradability of the films was tested using soil burial method. All the films were completely biodegraded after 100 days. Increased CC loading increased degradation rate of the films.

5.2   Future Work

Development of new composite products from the easily renewable natural materials has a strong potential to deliver novel biodegradable materials suitable for the packaging industry and all other applications. Recommendations for further work in this field of research involves the following-

- The process of synthesizing cellulose crystal gives black liquor (residue after bleaching). Adding sulfuric Acid to black liquor could give pure lignin and glauber salt. Lignin has a market value which will make this process very economic.
- Use of reagent can be a solution for improving water absorption properties, for example, glycerol and citric acid has shown promising results in this purpose previously with starch PVA films.
- Different drying methods of cellulose crystals can be used to see if it can reduce the agglomeration of the powdered cellulose.
- Compatibilizing agent like maleic anhydride (MAH), maleic anhydride grafted polypropylene (MA-g-PP), polyethylene-grafted-maleic anhydride (MAPE) can be studied to stop agglomeration.

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