

PROJECT REPORT

On

**“A COMPARATIVE STUDY OF CELLULOSE NANOFIBER
FILM AND MICROFIBER FILM FABRICATED FROM
SUGARCANE
BAGASSE AND ITS APPLICATIONS”**

Submitted by
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AM21CHE013

*In partial fulfillment for the award of the
Post graduate degree in Chemistry*



DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

**ST. TERESA'S COLLEGE (AUTONOMOUS)
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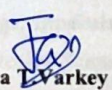


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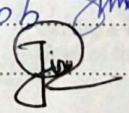
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CERTIFICATE

This is to certify that the project work entitled “**A COMPARATIVE STUDY OF CELLULOSE NANOFIBER FILM AND MICROFIBER FILM FABRICATED FROM SUGARCANE BAGASSE AND ITS APPLICATIONS**” is the work done **PRAJNA K B** under the guidance of **Dr. Jaya T.Varkey**, Professor, Department of Chemistry and Centre for Research, St. Teresa's College, Ernakulam in partial fulfilment of the award of the Degree of Master of Science in Chemistry at St. Teresa's College, Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

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CERTIFICATE

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Dr. Jaya T.Varkey
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DECLARATION

We hereby declare that the project work entitled “**A COMPARATIVE STUDY OF CELLULOSE NANOFIBER FILM AND MICROFIBER FILM FABRICATED FROM SUGARCANE BAGASSE AND ITS APPLICATIONS**” submitted to Department of Chemistry and Centre for Research, St. Teresa’s College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by us under the guidance of **Dr. JAYA T.VARKEY, PROFESSOR**, Department of Chemistry and Centre for Research, St. Teresa’s College (Autonomous), Ernakulam and this project work is submitted in the partial fulfilment of the requirements for the award of the Degree of Masters of Science in Chemistry.

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Abbreviation	
SCB	- Sugarcane bagasse
AGU	- Anhydro-D-glucopyranose units
NF	- Nanofiber
MF	- Microfiber
AFM	- Atomic Force Microscopy
SEM	- Scanning Electron Microscopy
FESEM-	Field Emission Scanning Electron Microscopy
TEM	- Transmission Electron Microscopy
FTIR	- Fourier Transform Infra-Red
XRD	- X-Ray Diffraction
IR	- Infra-Red Radiation
CNF	- Cellulose Nanofiber
CMF	- Cellulose Microfiber

Contents

CNS - Cellulose Nanofiber Suspension	
CNC - Cellulose Nanofiber Crystals	
AHP - Alkaline Hydrogen Peroxide	
LBMS - Ligno-cellulosic Biomass Materials	
FWHM - Full Width at Half Maximum	

Chapter 1

Introduction

A sustainable development is one that "meets the demands of the present without jeopardising the ability of future generations to fulfil their own requirements," according to the Brundtland Report of the International Commission on Environment and Development. According to this notion, current procedures and activities should not endanger societal norms or traditions. Due to differences in size, wealth, living standards, culture, and political and administrative systems, different countries have varying capacities for achieving sustainable development. Industrialized nation's efforts to pursue sustainable development may be facilitated by their wealth and cutting-edge technology, but this is not always the case. Using material resources wisely, reducing waste production, and disposing of it in a way that actively advances the social, environmental, and economic objectives of sustainable development are all examples of sustainable waste management. The following methods that process planning can actively address sustainable waste management are:

1. Optimum utilization of materials required for the building.
2. Reducing the amount of waste generated.
3. Management of construction and demolition wastes.
4. Materials specifications (e.g., use of reclaimed and recycled materials).
5. Provision of recycling space/facilities.

The different waste management options can be availed in an order known as the Waste Management Hierarchy that reflects the relative sustainability.[1]

1.1 CELLULOSE

The fundamental component of plant cell walls and fibers like cotton is cellulose, an insoluble material. It is a natural polymer that is utilized in place of numerous other polymers. The primary ingredient of paper, cardboard, and textiles made of cotton or other plant fibers is cellulose. Films and cellulose derivatives are also made using it. It is odourless, tasteless, biodegradable, and chiral.

Natural cellulose's shape, length, and diameter depend on where it came from and how it was extracted. Crystalline and amorphous domains both exist in natural cellulose. Its crystallinity can change depending on the extraction methods and the source. In comparison to the crystalline region, the amorphous region is less dense and more likely to interact with another chemical group. Yet, compared to the amorphous one, the crystalline domains are more resilient to mechanical, chemical, and enzymatic treatments. Several forms of cellulose, such as cellulose I, II, III, and IV, can be obtained depending on the molecule orientations, van der Waals, intra and inter molecular interactions, isolation technique, and treatment method [2].

These monosaccharide-based carbohydrate polymers range in size from a few tens to thousands of units (Glucose). Plants are primarily made of cellulose, which is also the primary component of the food chain. Plants are also the primary or first link in the food chain. A very significant compound and the most prevalent naturally occurring biopolymer is cellulose [3,4]. Cellulose is the primary component of many natural fibers, including cotton and higher plants [5,6]. Anhydro-D-glucopyranose units are found in long chains in it (AGU). Every cellulose molecule, with the exception of the terminal ends, contains three hydroxyl groups per AGU.

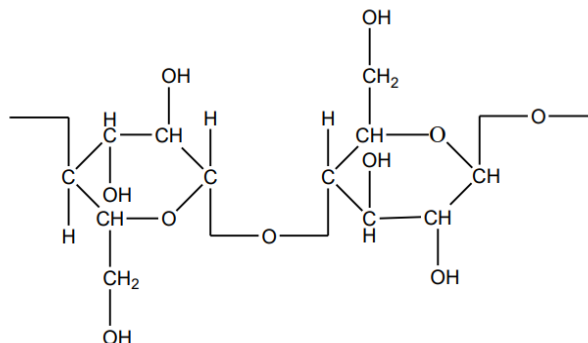


Fig 1.1. Structure of cellulose

1.2 SOURCES OF CELLULOSE AND WASTE MATERIAL SOURCE

A polymer made of polysaccharides is cellulose. The introduction of polymer in the creation and development of drug delivery systems resulted from the fusion of polymer and pharmaceutical sciences. The main goal of polymeric delivery systems is to achieve controlled or sustained drug delivery. Vascular plants are the main source of cellulose for industry. The cotton plant is the main source for textiles as well as resources for the majority of applications in the construction industry. Textile fibers are not isolated from woody fibers, whereas most paper products are made from wood pulp. Although cotton fibers are a biological source of nearly pure cellulose, these fibers are typically used for other cellulose derivatives, pharmaceuticals, or chemical engineering uses, such as chromatography, paints, and explosives rather than food grade cellulose. Additionally, bacterial sources of cellulose have been created using *Acetobacter xylinum*, which ferments corn syrup's glucose-fermenting substrates. For financial reasons, different types of cellulose are used for various applications. Wood is typically used to produce pulp

and paper. Different methods of cellulose extraction have been developed; these methods include oxidation, micro-ionization, etherification, and esterification, which turn prepared celluloses into derivatives of cellulose. The obtained derivatives are hydroxyl propyl methylcellulose (HPMC), hydroxypropyl cellulose (HPC), microcrystalline cellulose (MCC), silicified microcrystalline cellulose (SMCC), hydroxyethyl cellulose (HEC), sodium carboxymethyl cellulose (SCMC), ethyl cellulose (EC), methylcellulose (MC), oxycellulose (OC), hydroxyl ethyl cellulose (HEC) etc used in pharmaceutical application. Depending on its concentration, cellulose can serve as a binder, diluent, or disintegrant. Because of its enormous value, cellulose is frequently used in pharmaceutical applications.

1.3 DIFFERENT SOURCES FOR CELLULOSE:

1.3.1 NATURAL FIBERS

Natural fibers are made from plant, animal and mineral sources. Natural fibers can be classified according to their origin. VEGETABLE FIBER: -Vegetable fibers are generally composed mainly of cellulose. Examples include cotton, jute, flax, ramie, sisal and hemp. Cellulose fibers serve in the manufacture of paper and cloth. This fiber can be further categorized into the following [7,8].

The most used vegetable fibers are – cotton, flax, and hemp. Although sisal, jute, kenaf, bamboo is also used often.

Category	Description	Examples	% of cellulose
Seed fibers	Fibers collected from seeds or seed cases	Cotton , kapok	90
Leaf fibers	Fibers collected from leaves.	Sisal, fique, agave.	33
Bast fibers	Fibers are collected from the skin or bast surrounding the stem of their respective plants.	flax, jute, kenaf,	33
Skin		Hemp, ramie, rattan, and vine fibers.	
Fruit fibers	Fibers are collected from the fruit of the plant,	Coconut (coir) fiber.	30-50
Stalk fibers	Fibers are actually the stalks of the plant.	Rice, barley, wheat straws, bamboo ,grass, Tree wood	40-50

Table.1.3.1. Different types of fibers and its corresponding percentage of cellulose

1.3.2 SYNTHETIC FIBERS

Or synthetic materials like petrochemicals are typically the source of man-made fibers. However, some types of synthetic fibers, like rayon modal and the more recently created Lyocell, are made from natural cellulose. There are two types of cellulose-based fibers: modified cellulose, such as cellulose acetates, and regenerated or pure cellulose, such as from the cuprammonium process [9].

Fiber classification in reinforced plastics falls into two classes.

1. Short fibers are known as discontinuous fibers, with a general aspect ratio (defined as the ratio of fiber length 2 diameter) between 20-60.
2. Long fibers also known as continuous fibers, with aspect ratio is between 200-500.

CELLULOSE FIBERS- A subset of synthetic fibers made from natural cellulose are called cellulose fibers. There are numerous sources for the cellulose. Beach trees are used to make Modal, and bamboo is used to make bamboo fiber, seaweed is used to make sea cell, etc. A cellulose fiber made from sugar cane is called bagasse.

Here we use waste from sugarcane to create cellulose.

1.4 SUGARCANE BAGASSE - A SOURCE OF CELLULOSIC FIBER

Tropical nations cultivate sugarcane (*Saccharum officinarum*) in large quantities. The world produced 1.84 billion tonnes of sugarcane in 2017 [10]. Both sugar and alcohol mills use it. However, those mills are unable to completely consume it, as about 30% of the pulpy fibrous residue they produce is left over [11,12,13]. Bagasse is the name for these byproducts [14]. Bagasse is used for a variety of purposes, such as the paper industry, as a feedstock for biofuel, etc. [15,16]. Cellulosic material is referred to as sugarcane bagasse [17]. It is typically a waste type, though it might have some specific uses. Given that it contains a sizable amount of cellulose, this cellulose can be extracted and used for a variety of purposes. The fibrous materials may also be used as fiber in the textile and civil engineering sector, too though they may need some unique treatments before being used. To create a completely new type of material, this bagasse can be used to reinforce composite materials [18]. The main

benefit of using bagasse is that it is a pure waste product. If this product can be used in any application, even after a few straightforward pre-treatments, the process still results in a very affordable end product, and it will undoubtedly be fully or partially biodegradable, which is a crucial element in today's society. Additionally, if the right technique is applied, the extracted fiber can exhibit fairly good mechanical characteristics [18]. Additionally, sustainable regenerated textile fibers can be created using the extracted cellulose [19].

1.5 APPLICATIONS

In the textile industry, fibrous materials are typically used most frequently. However, sugarcane bagasse is unable to provide the fibers with the necessary qualities, such as fineness, crimp, tensile strength, etc. [22], to make them suitable for textile applications. The aforementioned table makes clear that sugarcane bagasse fibers are considerably coarser and less strong than other fibers, such as cotton and flax, which are widely used in textile products. Only coir and sisal fiber have demonstrated some similarity, and these fibers aren't frequently used in textile applications. However, these fibers are not completely useless. In fact, natural fibers like flax and cotton that don't have better properties are frequently used as reinforcement in composites [30]. Pre-treatment of the fibers included 10% H₂SO₄ and 1% NaOH. Increased 15.5% tensile strength, 45.4% impact strength, and 32.4% flexural rigidity were achieved with the addition of 20% fiber. In a polyester composite made with bagasse fiber reinforcement, Monteiro et al. discovered that the reinforcement increased the material's flexural rigidity. [27]. Oladele also found an increase in tensile strength with bagasse fiber addition in polyester composite [30]. Moubarik et al. showed that dignified sugarcane bagasse fiber

significantly improved the mechanical properties of low-density polyethylene composite [31]. Monterio et al. reported that bagasse fiber-reinforced multi-layered epoxy composite could show similar performance to Kevlar multi-layered sheet [32]. However, synthetic polymers like epoxy, polypropylene, and polyethylene are used. Composites made of certain types of the matrix can biodegrade only partially. Natural polymers, of which starch is one of the most prevalent, have also been used to create fully biodegradable materials. Additionally, starch has been used to alter textile materials [33]. There have been some excellent examples of starch composites reinforced with sugarcane bagasse. The addition of sugarcane bagasse fiber increases the composite's crystallinity, as demonstrated by Gilfillan et al. [20]. The accumulation of sugarcane bagasse fiber increased the tensile strength and decreased the water absorbency of the starch composite, as demonstrated by Vallejos et al. in their study [23]. A disposable food container made of sugarcane bagasse reinforced starch composite was created by Jeefferie et al [26].

1.6 PHYSICAL STRUCTURE AND CHEMICAL COMPOSITION OF SUGARCANE BAGASSE FIBER

Bast fibers are plant fibers that are derived from stalks or stems [34]. The plants that produce jute, flax, ramie, and other bast fibers are classified as dicotyledons because their leaves have net veins [35]. The leaves of sugarcane have parallel veins. As opposed to bast fiber, where the fiber bundles are arranged in a specific ring pattern throughout the stem of the fiber, this type of fiber is not classified as bast fiber [35]. The outer rind and the inner pith of the sugar cane stalk can be separated. Longer and finer bundles of fibers are found in the outer part of the rind, whereas shorter fibers are found in the inner part [34, 36]. Both types of fibers are

actually present in bagasse [11]. Depending on the source, cellulose has a crystalline structure that ranges from 50 to 90%, whereas hemicellulose has an amorphous structure that contains ingredients like xylose, glucose, etc. [17]. Anhydro-glucose units in cellulose are connected by 1, 4 glycosidic bonds, making it more akin to a natural linear polymer [17,39]. It has three hydroxyl groups with varying degrees of reactivity because C-2 and C-3 have secondary -OH groups, while C-6 has a primary -OH [39, 40]. Strong intramolecular and intermolecular hydrogen bonds are created by these hydroxyl groups [40]. These cellulose polymers are dispersed in fibrils, which are encased in lignin and hemicellulose. Between cellulose and hemicellulose, lignin acts as a glue, which gives the material its rigidity [17]. It is a three-dimensional polymer containing three different phenyl-propane precursor monomer namely, p-coumaryl, coniferyl, and sinapyl alcohol, which are joined together by alkyl-aryl, aryl-aryl, and alkyl-alkyl bonds [17, 41]. The chemical composition of sugarcane bagasse is given below in Table given below [16,17, 42, 43, 44, 45, 46, 47, 48, 49, 50]. This substance is raw, unprocessed sugarcane bagasse. However, various pre-treatments can assist in reducing the contents, such as hemi-cellulose, lignin, etc., so that 55-89% cellulose can be produced from these bagasse samples [16, 47].

1.7 CELLULOSE MICROFIBERS

The native cellulose fibers are subjected to controlled acid hydrolysis, which breaks them up so that their constituent rod-shaped elementary crystalline microfibrils can be dispersed. These rods' colloidal suspensions show birefringence and organized liquid crystalline phases [51]. *Valonia* spp. [52] and tunicates [53] are examples of plant sources of cellulose that have been reported to produce whisker-like particles with

lateral dimensions that are typically in the 3–20 nm range. Despite the fact that the particles are frequently referred to as microfibers (MFs), they are actually nano particulates. The use of sugarcane bagasse as a source for creating highly crystalline MFs has received very little press. Therefore, it is essential to show that MFs can be separated from bagasse for use in the future. The morphological changes taking place during the conversion process was studied using various characterization techniques.

Table 1. Chemical composition of sugarcane bagasse.

Name of the Content	Percentage
Cellulose	26–47
Hemicellulose	19–33
Lignin	14–23
Ash	1–5

Table.1.7 Chemical composition of sugarcane bagasse

Three distinct steps are involved in the isolation of cellulose microfibers from bagasse. Initially bagasse is subjected to a conventional pulping process by which lignin and hemicellulose is eliminated. After two stages of homogenization and ultimately acid hydrolysis, the obtained cellulosic fibers are mechanically separated into their individual microfibrils (MFs). The dimensions of the resulting microfibers depend on the hydrolysis conditions. Persistent discoloration shows that sugarcane bagasse cellulose is much more resistant to hydrolysis than tunicate, bacterial, or even wood cellulose. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) reveal that the transverse size of the particles ranged from 200 nm to a few microns. These MFs can be used as reinforcing components in composites with common engineering thermoplastics or biodegradable thermoplastic co-polyesters.

1.8 CELLULOSE NANOFIBER

A potential source of nanocellulose, such as cellulose nanocrystals (CNCs) and cellulose nanofibers, is sugarcane bagasse (CNFs). The composition, size, and shape of CNCs and CNFs differ. At the same level of nanocellulose concentration, CNFs outperform CNCs in terms of strength, modulus, and aspect ratio. [54,55]. Due to their exceptional qualities, including low density, high surface area, and good mechanical strength, isolated cellulose nanofibers and their derivatives have a wide range of applications, from paper packaging, sensor, water purification, textile, and drug delivery [56–62]. Despite the substantial benefits that open the door for numerous applications, cellulose's complex structure makes it difficult to distinguish plant cells from fibers on a regular basis. Cellulose fibers are extensively bundled up in hemicellulose and lignin, which can have adverse effects on the mechanical separation [63]. To improve fibrillation the fiber source is subjected to pre-treatment method prior to mechanical process. Among the many pre-treatment methods reported for the delignification of biomass, physical, biological, chemical (Kraft soda, ionic liquids, acid and alkaline hydrolysis) and combined methods (steam and ammonia fiber explosion) are involved. [64-70]. However, every method has its merits and demerits. The physical pre-treatment like grinding and milling which requires only fewer chemicals, consumes high energy particularly on a large-scale production [71] while the biological method selectively degrades lignin and hemicellulose but the rate of hydrolysis is slow and time consuming. [70-72]. The chemical methods are extensively studied, for example, the most used method in the paper and pulp industry Kraft process produces a large number of harmful chemicals such as hydrogen sulphide [73]. Although Dilute acid pre-treatment can be used for efficient removal of hemicellulose, it is

corrosive to equipment causing environmental pollutions[74]. Alkali - based pre-treatment is more open to enzymatic hydrolysis because it selectively removes lignin and limits carbohydrates degradation compared to other chemical methods[75]. Sodium hydroxide, lime, ammonia and alkaline hydrogen peroxide (AHP) are included in this alkaline treatment[75,76]. Hydrogen peroxide is extensively used in the pulp and paper industry for bleaching and pulp brightness enhancement. The hydroperoxyl anion generated at alkaline pH (pH 11.5) from the use of hydrogen peroxide is responsible for dissolving lignin and hemicellulose [77]. The development of AHP pre-treatment for enhancing enzymatic hydrolysis of lignocellulose feedstocks have been contributed by several researchers[76,78-80]. For example, Lignin and hemicellulose from corncobs with removal ratio of 75.4% and 38.7%, respectively after 6h of treatment with AHP was fractionated by Su et al[29]. After the pre-treatment, mechanical methods like high- pressure micro fluidization, high-pressure homogenization, grinding and high intensity ultrasonication was used to prepare CNFs. Both chemical degradation and mechanical disintegration is caused by ultrasonication in a liquid medium. During the process, high temperature, pressure and shear force is generated due to acoustic cavitation and the resulting extreme environment promotes a reduction in substantial particle size [84,85]. Over the years, the ultrasonication method widely used in CNF preparations from plant biomass is emerging as a more convenient approach, referred as a green process [72,87,88]. A fine thread-like individual structure of CNFs from pre-treated SCB with a steam explosion and alkali-hydrothermal catalysis in combination with 30% H₂O₂ and ultrasonication was developed by Feng et al [63]. Similarly, Khawas et al. isolated crystalline CNFs from the banana peel, pre-treated in different chemicals such as NaOH (20%),

KOH (5%) NaClO₃ (1%) and H₂SO₄ (1%) followed by ultrasonication [89].

In all if the above-mentioned studies which isolated CNF, considered the environmentally friendly ultrasonication-assisted method, which involved simplification of processing steps with minimal chemical use. It is of rising interest in CNF preparation from plant biomass.

1.9 FILM FABRICATION

Film fabrication from CNF/MF/mixed fiber is an ongoing challenge due to the lack of common solvents for its dissolution and high cost of available green solvents such as ionic liquids [90]. Other solvents such as NaOH/urea, LiOH/urea and ZnCl₂ solutions are considered facile routes for cellulose dissolution but require further purification which could be harmful to public health and environment. For example, High exposure to ZnCl₂ in aquatic organisms(Zebrafish) causing potential teratogenic effects was demonstrated by Salvaggio et al [91]. On contrary compression molding in a hot press is an alternative method of developing high-strength cellulose films or sheets from wet cellulose [92,93]. By means of compression-molding in a hot press ,smooth plastic-like surface without any additive from commercial alpha cellulose with high tensile strength (22.4 MPa) was developed by Pintiaux et al [94]. Hence it is desirable to formulate environmental friendly approaches to utilize and apply cellulose and its derivatives in a wider area. We report here a straight forward, effective and environment friendly method to develop CNF/MF/mixed fiber films from agro-residue sugarcane bagasse. To make film, cellulose suspension containg 1.5g cellulose in solid (microfiber, nanofiber or mixed fiber, respectively) was blended well and vacuum filtrated into a wet film by means of suction.

OBJECTIVES

- Sustainable waste management by utilizing bagasse, a major biowaste after sucrose extraction from sugarcane.
- Fabrication of Cellulose Microfiber Film and Nanofiber Film.
- Comparison of the exceptional properties including the
 - 1) Mechanical performance
 - 2) Hydro-stability
- Characterization and morphological analysis by XRD, FESEM and FTIR.
 - Surface characterization by Contact angle measurement and Tensile strength test.

Chapter 2

Literature review

Y. R. Loh et al. 2013 from Curtin University Sarawak emphasised on the natural, biodegradable features and chemical constituents of the Sugarcane bagasse (SCB) which have been a highly potential source and versatile ingredient in composite materials. Green materials with low pollutant indices were sought after due to their low cost and eco-friendliness. Studies were carried out on the effects, performances and applications of SCB in its original conditions, and transformed forms. Treatments with appropriate chemicals and/or processes, combination with materials of distinct properties and manipulation of manufacturing methodologies resulted in better outcomes[16].

Kullasatri Saelee et al. 2014 attended the 26 th Annual Meeting of the Thai Society for Biotechnology and International Conference, Chiang Rai and investigated the extraction of cellulose from SCB using an environmentally acceptable pre-treatment based on xylanase and steam explosion. According to the results of the chemical analysis, extracted cellulose had more cellulose and less hemicellulose and lignin than raw material. The findings of FTIR and SEM analysis proved that lignin and hemicelluloses were both eliminated throughout the extraction procedure. Additionally, the xylanase treatment was successful in reducing chemical bleaching by

23%. Thus the environmentally friendly approach, steam explosion, and xylanase pretreatment revealed a tremendous potential environmentally friendly method for cellulose extraction, which can be utilised on an industrial scale [47].

Zuluaga et al. 2009 from the University of Pontificia Bolivariana did a comparative research on four distinct alkaline treatments for cellulose microfibril separation from banana rachis vascular bundles. High performance anion exchange chromatography was used to analyse the neutral sugar composition and attenuated total reflection of isolated cellulose microfibrils. The average diameter and estimated length of the peroxide alkaline, peroxide alkaline-hydrochloric acid, or 5 weight percent potassium hydroxide-treated cellulose microfibrils were 3-5 nm and several micrometers, respectively. The results of X-ray diffraction, ¹³C NMR, and ATR-FTIR revealed that the cellulose microfibrils from banana rachis may be interpreted as either cellulose IV or cellulose I, despite the fact that their low crystallinity makes it difficult to identify their structure. Although the structure of the specimens treated with a stronger (18 wt%) KOH solution was changed to cellulose II, they were still microfibrillated [65].

M Slavutsky et al. 2014 from the Universidad Nacional de Salta, Argentina produced cellulose nanocrystals (CNC) from Sugarcane bagasse. The water barrier qualities of films made of starch and starch/CNC were investigated. The reinforced starch/CNC films exhibit a lower affinity to water molecules than starch films, according to measurements of the films' solubility, contact angle, and water sorption isotherm. On each side of the

film, the driving force and the water activity (a_w) values were examined for their impacts on permeability. According to permeability, diffusivity, and solubility coefficients, the permeation process is primarily regulated by water diffusion and is consequently dependent on the winding pathway created by the integration of CNC. The similarities in the chemical composition of the two molecules facilitate the interaction between CNC and starch chain. From CF produced by alkaline hydrolysis of sugarcane bagasse, CNC was created. The water resistance and water barrier properties of the starch films matrix were enhanced by the addition of CNC. Due to hydrogen bonding, the polymer matrix and CNC's comparable chemical structures allowed for robust attachment. Water sorption isotherms and contact angle measurements showed that reinforced films have decreased attraction for water molecules [21].

Jeefferie Abd Razak et al. 2011 from the Technical University of Malaysia explored the potential use of sugar cane fibre cellulose (SCFC) as a green composite for single-use food containers. In order to ascertain the mechanical and physical properties, in addition to the fracture morphology by using the optical microscope observation, various engineering properties for SCFC composites were tested out. The reinforcement role of different fibre loading into the outcomes of generated composites is clearly indicated by the morphological view on the mechanical and physical testing cracked surfaces. Although the results indicated that composites performed well in terms of their mechanical and physical qualities, there was poor adhesion between the SCFC composite. Overall, the creation of this novel material for use in food packaging offers a tremendous prospective answer for an environmentally friendly and secure packaging medium, whether it be for food, consumers, or the environment [26].

Daehwan Kim et al. 2018 from the Laboratory of Renewable Resources Engineering, Department of Agricultural and Biological Engineering, Purdue University, USA carried out Pretreatment processes that solubilize hemicellulose and/or lignin, reduce substrate particle sizes and the crystalline content of cellulose, and increase biomass surface area all change the chemical and physical structure of lignocellulosic materials. By improving the accessibility of acids or enzymes to the surface of the cellulose, these changes improve the hydrolysis of cellulose [68].

Shady S Hassan et al. 2018 from the School of Food Science and Environmental Health, Dublin Institute of Technology, Cathal Brugha Street, Ireland employed Pretreatment techniques such as chemical, physico-chemical, and biological ones for lignocellulosic biomass. Recent developments in applied chemistry methods performed in non-classical and extreme environments gave rise to potential commercially viable solutions (such as high hydrostatic pressure, high pressure homogenizers, microwave, and ultrasound technologies). When it comes to sustainable green pretreatment options for lignocellulosic biomass utilisation in a large-scale biorefinery, these emerging industrial technologies are viable contenders [72].

Maimunah Asem et al. 2021 from the Biotechnology Engineering Department, Faculty of Engineering, International Islamic University Malaysia extracted cellulose nanofibers (CNFs) from sugarcane bagasse using a mixture of treatment methods, including alkaline treatment, moderate acid hydrolysis, and ultrasonication. Initially, The SCB fibres were defibrillated and dispersed using ultrasonication at 70% amplitude

after being treated with sodium hydroxide and aqueous hydrogen peroxide, a bleaching agent, before moderate acid hydrolysis. The cellulose fibres isolated from SCB that had been treated with moderate sulfuric acid were the main subject of the investigation on acid hydrolysis. The diameter and length of isolated CNFs in the FESEM pictures ranged from 20 to 30 nm to several micrometres, respectively. This finding indicates that the combined treatment approaches are quite successful in separating CNFs from the plant biomass. Additionally, XRD examination shows that cellulose type I with a 42% crystallinity has peaks at 2 θ of 15.2 and 22, demonstrating its presence. The FTIR spectra, however, demonstrate that each CNF was successfully isolated because non-cellulosic components were removed. This outcome confirms that all amorphous components, including lignin and hemicellulose, were eliminated. With the use of ultrasonication, the combination of alkaline treatment and mild acid hydrolysis was able to successfully remove CNFs from SCB that had lengthy entangled network fibrils. The CNFs should be strong and have a high aspect ratio, making them ideal for use as reinforcement for creating nanocomposites [96].

Deepanjan Bhattacharya et al. 2007 from the Eastman Chemical Company, Global Coatings Application Development, Kingsport, USA undertook three independent steps to separate the cellulose microfibrils from the bagasse. In the beginning, bagasse underwent a traditional pulping procedure to remove lignin and hemicellulose. The resulting whole cellulose fibres were then mechanically split into their constituent parts by a two-stage homogenization procedure, and then acid hydrolyzed. The hydrolysis conditions had an impact on the size of the resultant micro fibrils. The cellulose made from bagasse, a by-product of sugarcane, was

much more resistant to hydrolysis than tunicate, bacterial, or even wood celluloses, as seen by persistent discolouration. The entire cellulose fibres was separated via mechanical shearing and controlled hydrolysis into micron-sized components. It was discovered that hydrolysis of the cellulose fibres with 60% (w/v) sulfuric acid for 2.5 hours at 60 C was ideal since it removed the majority of the amorphous domains with little to no harm to the crystal structure. The size of the MFs was distributed, and it ranged from a few hundred nanometers to a few microns. Under the aforementioned hydrolysis dispersion circumstances, complete release of each individual MF from the microfibrillar bundles was not feasible. More extreme circumstances did reduce the aggregation phenomena between the individual MF, but they also caused significant crystal degradation. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) results showed that the particles' transverse sizes ranged from 200 nm to a few microns. Additionally, solid-state NMR was utilised to investigate the morphological alterations occurring in cellulose. Solid-state NMR spectroscopy did demonstrate that all of the lignin had been removed throughout the pulping procedure. The MFs' ¹³C NMR spectra also demonstrated that the amorphous regions that were initially present in the unhydrolyzed cellulose fibres were significantly reduced as a result of hydrolysis and mechanical shearing [97].

S. Panthapulakkal et al. 2012 from the Centre for Biocomposites and Biomaterials Processing, Faculty of Forestry, University of Toronto, Canada fabricated compression-molded cellulose-nanofibril-film reinforced polycarbonate composites. Mechanical defibrillation was used to create nanofibers from wood pulp fibres, and the generated fibres had a

diameter distribution of 1-100 nm. The nanofibre suspensions were used to create nanofibre films, which were then examined for strength, crystallinity, and thermal characteristics. The produced nanofiber sheets have a strength and modulus of 240 MPa and 11 GPa, respectively. The sheets' thermal characteristics proved that manufacturing fibre sheets at high temperatures was appropriate. The thermal stability of the fibre films during the compression moulding process was shown by the tensile characteristics of the films subjected to composite processing conditions. By pressing-molding nanofiber sheets of varying thickness between polycarbonate sheets at 205°C under pressure, various nanocomposites with variable fibre loading were created. The addition of the fibres enhanced the polycarbonate's tensile modulus and strength. With 10% of the fibres, the thermoplastic's strength increased by 24%, and with 18% of the fibres, it increased by up to 30%. The polycarbonate's tensile modulus showed a substantial improvement (about 100%) [93].

Xuezhu Xu et al. 2013 from the Department of Mechanical Engineering, North Dakota State University, Fargo, North Dakota, United States carefully compared the morphologies, crystalline structures, dispersion characteristics in polyethylene oxide (PEO) matrix, interactions with matrix, and resultant reinforcing effects on the matrix polymer. Solution casting was used to create transparent PEO/CNC and PEO/CNF nanocomposites with up to 10 wt% nanofibers. The above-mentioned properties of nanocellulose fibres and composites were examined using scanning electron microscopy (SEM), wide-angle X-ray diffraction (WXR), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analyzer (DMA), and tensile testing. Due to their larger aspect ratio and fibre entanglement,

CNFs produced materials with better strength and modulus than CNCs at the same nanocellulose concentration, but with lower strain-at-failure due to their comparatively large fibre agglomerates. There were good matches between the anticipated and experimental values when the modulus of the composites was simulated using the Kardos and Ouali models. The criteria for choosing the best nanocellulose as a biobased nano-reinforcement material in polymer nanocomposites can be developed with the use of systematic comparative studies of this kind [55].

Amine Moubarik et al. 2013 from the University of Sultan Moulay Slimane utilised three different steps to separate the cellulose fibres from the bagasse of Moroccan sugar cane. Bagasse was first treated with hot water (70°C) to remove hemicellulose, followed by an alkaline aqueous solution (15% sodium hydroxide (NaOH), 98°C) to remove lignin, and then a bleaching step. Different complimentary analyses (FT-IR, ¹³C NMR, and TG) examined the cellulose fibres in sugar cane bagasse. Using low density polyethylene as a matrix, the reinforcing ability of cellulose fibres derived from sugar cane bagasse was studied. There was no bound lignin present in the cellulosic preparations. The intrinsic viscosity, the average viscosity, and the molecular weight were 511ml/g, 1769, and 286578g/mol, respectively. A good interface adhesion between cellulose fibres and matrix was shown to improve the mechanical characteristics of composites, resulting in gains of 85% in flexural modulus and 72% in Young's modulus at a 25 weight percent fibre loading [31].

Sirlene M Costa et al. 2013 from the University of São Paulo isolated textile fibres using both commercial and sugar cane straw cellulose. After alkaline pulping with soda and anthraquinone (AQ), sugar cane straw pulps were produced. Pulps were subjected to chemical bleaching with hydrogen peroxide to remove any remaining lignin. To create fibres using N-methylmorpholine-N-oxide (NMMO), bleached pulps were employed. Chemical characteristics of straw and pulps (cellulose, polyoses, and lignin) were identified. The maximum water uptake, swelling, weight loss, and mechanical characteristics of the fibres were examined. Utilising a scanning electron microscope (SEM), microstructure was examined. The pulping yield was 30%, and the water absorption capacity of the fibres was between 60 and 73%. In 30 days, the mass loss profile was in the range of 25–26%. Straw and commercial cellulose fibres both displayed tenacity values between 4.1 and 4.3 cN/tex, which are comparable to commercial lyocell made from cellulose from wood pulp [19].

Chapter 3

Materials and Methods

3.1 INTRODUCTION

This chapter includes the characterization techniques, materials and methods used for the synthesis and characterization of cellulose microfiber and cellulose nanofiber films.

3.2 CHARACTERISATION TECHNIQUES

3.2.1 FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM)

Advanced technique called field emission scanning electron microscopy (FESEM) is utilised to visualise the microstructure of the materials. Because gas molecules have a tendency to affect the electron beam and the produced secondary and backscattered electrons utilised for imaging, FESEM is normally conducted in a high vacuum [96]. A field emission source releases electrons, and they are then accelerated in a strong electrical field gradient. These so-called primary electrons are focused and refracted by electronic lenses within the high vacuum column to create a narrow scan beam that bombards the target. As a result, each area on the item emits secondary electrons. The surface structure of the item is related to the angle and speed of these secondary electrons. The secondary electrons are captured by a detector, which then generates an electrical signal. A video scan image that can be viewed on a monitor or a digital image that can be recorded and processed further are created from this signal once it has been amplified.

3.2.2 X-RAY DIFFRACTION (XRD)

The crystallinity of samples was characterized by X-ray diffraction (XRD) measurement on a D/max-III X-ray diffractometer, equipped with nickel-filtered Cu K α radiation ($\lambda = 0.15418$). The diffraction angle (2θ) ranged from 3° to 90° and the step size was 0.01° . The d-spacings (d) of films were calculated with the Bragg equation,

$$D = \lambda / 2 \sin \theta$$

where λ is the wavelength of the X-ray source (0.15418 nm) and θ is the Bragg angle corresponding to the plane.

The apparent crystallite size (D) of the reflection plane was obtained using the Scherrer equation

$$L = K \lambda / \beta \cos \theta$$

where K is the Scherrer constant of 0.94 and β is the half-height width of the diffraction band.

3.2.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

This technique was used to manipulate structural changes on samples as a result of chemical modification by the identification of the functional groups. The changes in functional groups of the materials CNF and CMF films were investigated using FTIR spectroscopy using Nicolet, iS50, FTIR spectrophotometer. The FTIR spectra of the samples were recorded in the transmittance mode in the range of 4000 cm^{-1} to 500 cm^{-1} .

3.2.4 TENSILE STRENGTH

Tensile strength is indicative of the strength derived from factors such as fiber strength, fiber length, and bonding. Ultimate tensile strength, breaking strength, maximum elongation, and reduction in area are characteristics that can be accurately assessed by a tensile test. Young's modulus, Poisson's ratio, yield strength, and strain-hardening characteristics can all be calculated from these observations.

3.2.5 CONTACT ANGLE

Wetting, or the interaction of water with a surface, is essential to daily life as well as numerous biological and industrial processes. The contact angle measures how likely it is that the surface will become wet with water. It is the angle at the interface where water, air, and solids meet. High contact-angle values represent the surface's propensity to repel water, whilst low contact-angle values show the tendency of the water to spread and cling to the surface. Sessile-drop goniometry is the most used technique for characterising surface-wetting since it is straightforward. The technique, which derives the contact angle from the droplet's shape, can be used with a wide range of materials, including biological surfaces, polymers, metals, ceramics, and more.

The ultimate objective was to develop new areas to adapt the wetting characteristics of cellulose fibers. Cellulose-based surfaces interact with water as well as other liquids rely on the morphology of the surface and the intrinsic characteristics of the material.[95]

3.3 LIGNOCELLULOSIC BIOMASS MATERIALS (LBMS)

First, the SCB fibers which were locally collected from waste heaps in markets and along roadside were cleaned with distilled water in order to remove dirt and was dried in an oven at 55°C for 72h. Then the size of the fibers was reduced into a granular form of 100µm size by subjecting it to a size-reduction process via a grinding process by using a blender. All chemicals are of analytical grades.

MATERIALS

- Sugarcane bagasse
- Sodium hydroxide (NaOH)
- Hydrogen peroxide (H₂O₂)
- Sulphuric acid (H₂SO₄)
- Distilled water

METHODS

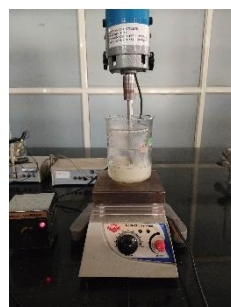
3.4 PREPARATION OF CELLULOSE NANOFIBERS (CNFs) FROM SUGARCANE BAGASSE(SCB)



(a)



(b)



(c)



(d)



(e)

Fig.3.4. (a) Granular form of sugarcane bagasse (b) Alkaline treatment (c) Bleaching and acid treatment (d) Ultrasonication (e) Cellulose Nanofiber Suspension.

3.4.1 ALKALINE TREATMENT

Alkaline treatment involved the transfer of ground SCB to a 1L beaker filled with a 2% (w/v) sodium hydroxide (NaOH) solution. Followed by heating the mixture in a water bath at 80 °c for 5h to produce white solid residues. Then the solid residues were filtered and washed with deionized water about three times during the filtration process using a vacuum pump to separate the white precipitate from the solution mixture. Repeated the process with 12 % (w/v) NaOH at 80⁰c for an hour.

3.4.2 BLEACHING AND HYDROLYSIS PROCESSES

200 mL of aqueous hydrogen peroxide (H₂O₂), a bleaching agent taken in a 1:1 ratio was used to dissolve the alkaline treated SCB at 75⁰c for 15 min. Then washed and filtered the bleached samples about three times using a vacuum pump to eliminate all impurities. With 1% (v/v) H₂SO₄ solution, the treated SCB fibers were further treated at 80⁰c for an hour.

Then the treated samples were washed and filtered ten times to remove all impurities and stored in a refrigerator at 4°C until further treatment.

3.4.3 ULTRASONICATION

The treated samples went through a 2-hour procedure of ultrasonication with a predetermined amplitude of 70%. The treated samples' flasks were kept in an ice bath throughout the procedure to prevent overheating issues. The cellulose suspension samples were then separated from the pellets (solid structure) using a centrifuge at a rotational speed of 10,000 rpm for 15 min. They were then kept in a refrigerator at 4°C pending further processing [97].

3.4.4 CELLULOSE NANOFIBER FILM FABRICATION

The cellulose nanofiber suspension was blended well, homogenized and vacuum filtrated into a wet film by using a funnel with 14cm in diameter.



Fig.3.4.4. Cellulose Nanofiber film.

3.5 PREPARATION OF CELLULOSE MICROFIBERS (CMFs) FROM SUGARCANE BAGASSE(SCB)

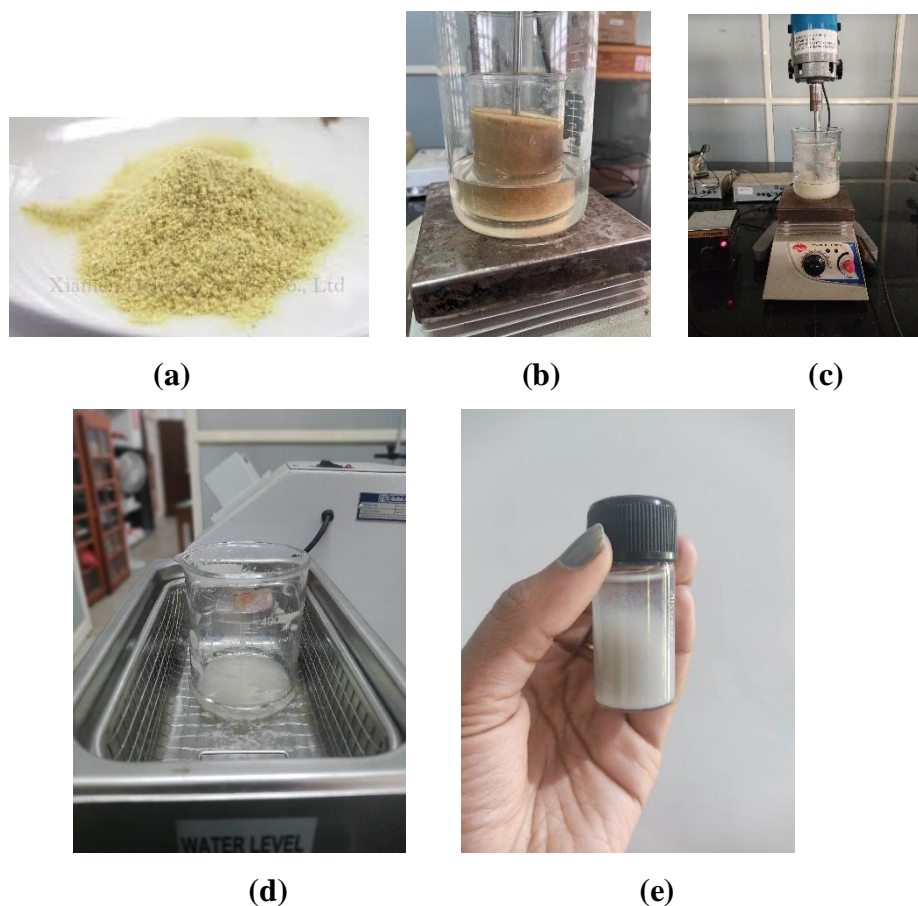


Fig.3.5. (a) Granular form of sugarcane bagasse (b) Alkaline treatment (c) Bleaching and acid treatment (d) Ultrasonication (e) Cellulose Microfiber suspension.

3.5.1ALKALINE TREATMENT AND BLEACHING

The dry bagasse was first broken down for 4 hours at 80°C in a solution of 4% sodium hydroxide. This substantially reduced the amount of lignin

and hemicellulose. The product was afterwards bleached with hydrogen peroxide due to persistent discolouration in order to get rid of any lingering lignin and hemicellulose that might have been there. The bleached cellulose fibres were repeatedly rinsed, initially with a 5% aqueous sodium hydroxide solution and then with deionized water, to achieve a neutral pH.

3.5.2 HOMOGENIZATION

It was homogenised to reduce the fibers into smaller particles. This propels the suspension of the MFs at extremely high speeds through two small orifices. By adjusting the pressure, the degree of mechanical breakdown of the fibers can be managed.

3.5.3 ACID HYDROLYSIS

The cellulose thus obtained was acid hydrolyzed to preferentially remove the non-crystalline portions over the crystalline sections by refluxing with 60% (w/v) sulfuric acid for 2.5 hours at 60°C, leaving a collection of evenly scattered microfibers. In order to stop the process, ice water was introduced.

3.5.4 ULTRASONICATION

The MFs were washed with water and dispersed for 5 min with repeated cooling using an ultrasonicator. The dispersion medium was then gradually changed from water to tertiary butanol [98].

3.5.5 CELLULOSE MICROFIBER FILM FABRICATION

The aqueous microfiber slurry was blended well and filtrated into a wet film by using a funnel with 14cm in diameter.



Fig.3.5.5. Cellulose Microfiber film.

Chapter 4

Results and discussion

4.1 X-RAY DIFFRACTION (XRD) ANALYSIS

The X-ray diffraction spectrum of the nanofiber suspension and the two films are shown below in the figures.

4.1.1 XRD ANALYSIS OF NANOFIBER SUSPENSION

In the XRD spectrum of the cellulose nanofiber suspension two clear peaks were observed. The average crystal size was determined using Debye Scherrer equation,

$$D=0.9 \lambda/B\cos\theta$$

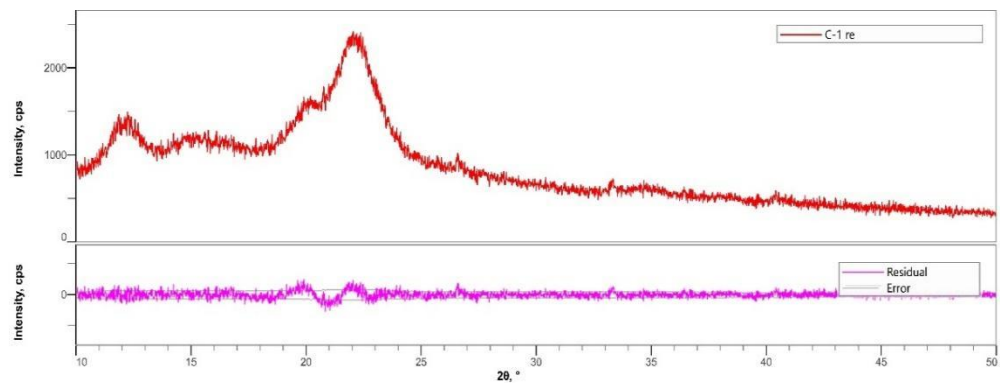


Fig.4.1.1. XRD spectrum of Nanofiber Suspension.

Analysis of peaks

Peak-1

$$2\theta = 12.07^\circ = 0.1056 \text{ radian}$$

$$\theta = 6.035^\circ = 0.02502 \text{ radian}$$

$$B = 1.43 = 0.02502 \text{ radian}$$

$$\lambda = 1.54060 \times 10^{-10}$$

From Debye Scherrer equation

$$\begin{aligned} D &= 0.9 \lambda / B \cos\theta \\ &= (0.9 \times 1.54060 \times 10^{-10}) / 0.02502 \times \cos(0.1056) \\ &= 5.9 \text{ nm} \end{aligned}$$

Peak-2

$$2\theta = 22.30^\circ = 0.1951 \text{ radian}$$

$$\theta = 11.15^\circ = 0.05005 \text{ radian}$$

$$B = 2.86$$

$$\lambda = 1.5 \times 10^{-10}$$

From Debye Scherrer equation,

$$\begin{aligned} D &= 0.9 \lambda / B \cos \theta \\ &= (0.9 \times 1.54060 \times 10^{-10}) / 0.05005 \times \cos(0.1951) \\ &= 2.96 \text{ nm} \end{aligned}$$

2θ of the intense peak(deg)	FWHM of the intense peak	Size of the particle, D(nm)	Average particle size(nm)
12.07	1.43	5.9	4.43
22.30	2.86	2.96	

Table.4 .1.1. Average particle size of Nanofiber suspension

A peak was observed at 12.07° and major peak 22.30° which shows the corresponding average particle size is 4.43 nm that confirms the nanometer range of the particles.

4.1.2 XRD ANALYSIS OF NANOFIBER FILM

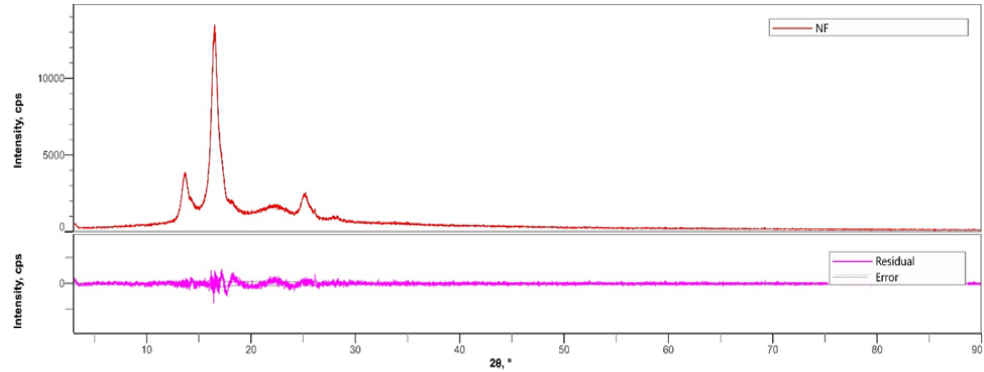


Fig.4.1.2. XRD spectrum of Nanofiber film

In the XRD spectrum of the cellulose nanofiber film three clear peaks were obtained. The average crystal size was determined using Debye Scherrer equation,

$$D=0.9 \lambda/B \cos \theta$$

Analysis of peaks

Peak-1

$$2\theta=13.641^\circ$$

$$\theta=0.818^\circ =0.1193 \text{ radian}$$

$$B=0.818=0.01431 \text{ radian}$$

$$\lambda=1.54060 \times 10^{-10}$$

From Debye Scherrer equation,

$$D = (0.9 \times 1.54060 \times 10^{-10})/0.01431 \times \cos (0.1193) \\ =10.22\text{nm}$$

Peak-2

$$2\theta=16.465^\circ$$

$$\theta=8.3225^\circ =0.1440\text{radian}$$

$$B=0.773 =0.01352 \text{ radian}$$

$$\lambda=1.54060 \times 10^{-10}$$

From Debye Scherrer equation,

$$\begin{aligned}
 D &= 0.9 \lambda / B \cos \theta \\
 &= (0.9 \times 1.54060 \times 10^{-10}) / 0.01352 \times \cos (0.1440) \\
 &= 10.85 \text{ nm}
 \end{aligned}$$

Peak-3

$$\begin{aligned}
 2\theta &= 25.183^\circ \\
 \theta &= 12.5915^\circ = 0.2203 \text{ radian} \\
 B &= 0.78 = 0.01365 \text{ radian} \\
 \lambda &= 1.54060 \times 10^{-10}
 \end{aligned}$$

From Debye Scherrer equation,

$$\begin{aligned}
 D &= 0.9 \lambda / B \cos \theta \\
 &= (0.9 \times 1.54060 \times 10^{-10}) / 0.01365 \times \cos (0.2203) \\
 &= 10.9 \text{ nm}
 \end{aligned}$$

2θ of the intense peak (deg)	FWHM of intense peak	Size of particle, D (nm)	Average particle size (nm)
13.641	0.818	10.22	10.65
16.465	0.773	10.85	
25.183	0.78	10.9	

Table.4.1.2. Average particle size of Nanofiber film.

The peaks were observed at 13.641°, 16.465° and major peak at 25.183° which shows the corresponding average size of 10.65 nm for nanofiber film.

4.1.3 XRD ANALYSIS OF MICROBER FILM

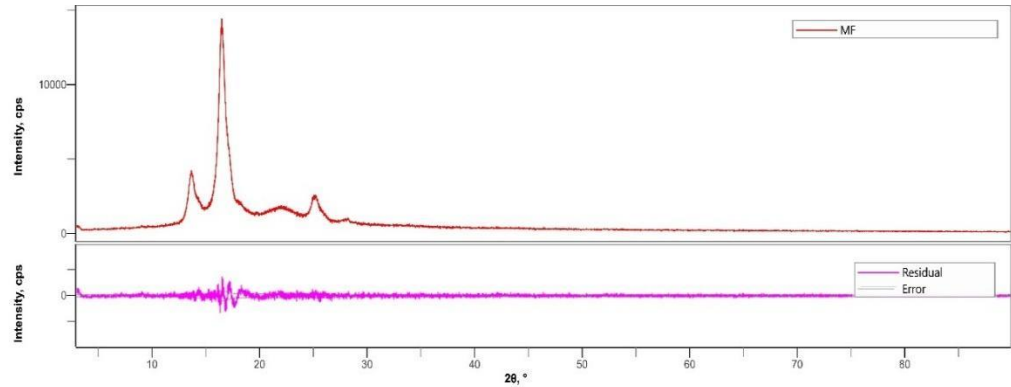


Fig. 4.1.3. XRD spectrum of Microfiber Film.

In the XRD spectrum of cellulose microfiber film, three clear peaks were observed. The average crystal size was determined using Debye Scherrer equation,

$$D=0.9 \lambda/B \cos \theta$$

Analysis of peaks

Peak-1

$$2\theta=13.635^\circ$$

$$\theta=6.8175^\circ =0.11930 \text{ radian}$$

$$B=0.817=0.01429 \text{ radian}$$

$$\lambda=1.54060 \times 10^{-10}$$

From Debye Scherrer equation,

$$D=0.9 \lambda/B \cos \theta$$

$$= (0.9 \times 1.54060 \times 10^{-10})/0.01429 \times \cos (0.11930)$$

$$=10.2\text{nm}$$

Peak-2

$$2\theta=16.437^\circ$$

$$\theta = 8.2185^\circ = 0.1438 \text{ radian}$$

$$B = 0.806 = 0.01410 \text{ radian}$$

$$\lambda = 1.54060 \times 10^{-10}$$

From Debye Scherrer equation,

$$D = 0.9 \lambda / B \cos \theta$$

$$= (0.9 \times 1.54060 \times 10^{-10}) / 0.01410 \times \cos (0.1438)$$

$$= 10.41 \text{ nm}$$

Peak-3

$$2\theta = 25.5385^\circ$$

$$\theta = 12.5385^\circ = 0.2194 \text{ radian}$$

$$B = 1.08 = 0.0189 \text{ radian}$$

$$\lambda = 1.54060 \times 10^{-10}$$

From Debye Scherrer equation,

$$D = 0.9 \lambda / B \cos \theta$$

$$= (0.9 \times 1.54060 \times 10^{-10}) / 0.0189 \times \cos (0.2194)$$

$$= 7.9 \text{ nm}$$

2θ of the intense peak (deg)	FWHM of intense peak	Size of particle, D (nm)	Average particle size (nm)
13.635	0.817	10.2	9.50
16.437	0.806	10.41	
25.077	1.08	7.9	

Table 4.1.3. Average particle size of Microfiber film

The peaks were observed at 13.635°, 16.437° and a major peak at 25.077° which shows a corresponding size of 9.50 nm for the Microfiber film.

4.2 TENSILE STRENGTH

By calculating the tensile strength of the two films, we can study the mechanical strength of the respective films which is calculated directly from the graph by taking the highest point in the curve which is the ultimate stress. We performed tensile tests of the two films prepared with their stress-strain graph plotted below (Fig.4.2.1. and Fig.4.2.2)

4.2.1 TENSILE STRENGTH OF NANOFIBER FILM

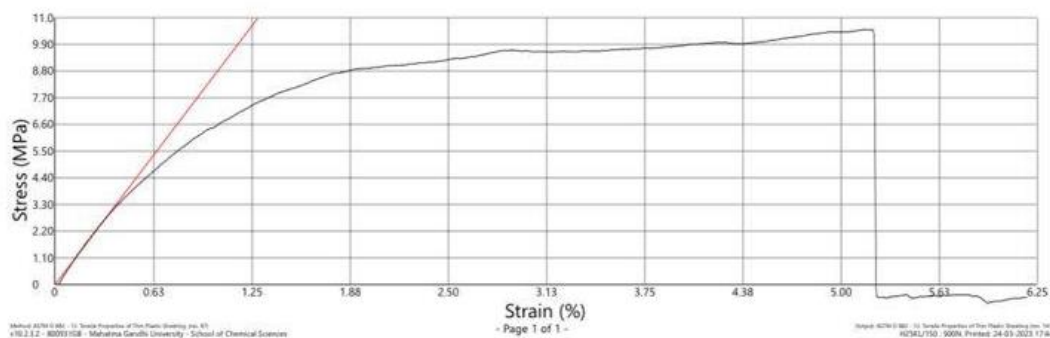


Fig. 4.2.1. Tensile Strength of Nanofiber Film.

The Tensile strength of nanofiber film is found to be 10.5MPa as obtained from the above figure (Fig. 4.2.1.). It was obtained by finding out the ultimate stress from the stress-strain graph.

4.2.2 TENSILE STRENGTH OF MICROFIBER FILM

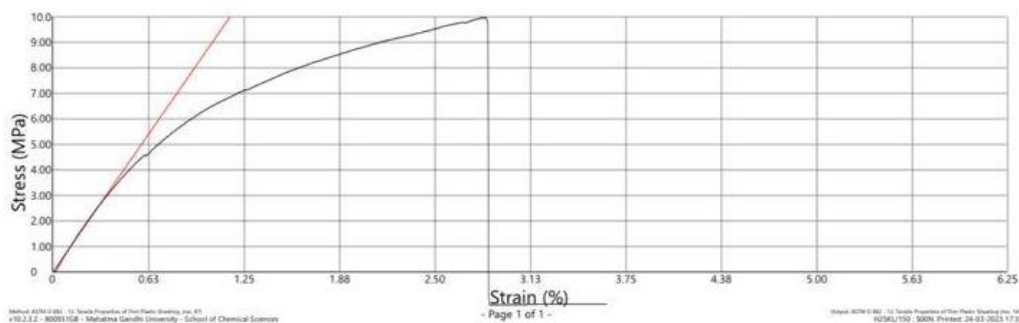


Fig. 4.2.2. Tensile strength of Microfiber Film.

The tensile strength of microfiber film is found to be 9.97MPa as obtained from the above figure (Fig.4.2.2.). It was obtained by finding out the highest point in the stress-strain graph which is the ultimate stress.

4.3 CONTACT ANGLE

Contact angle is one of the common ways to measure the wetting stability of a surface or materials. Wetting refers to the study of how a liquid deposited on a solid (or liquid) substrate spreads out. Wetting is determined by measuring contact angle which the liquid forms in contact with the solids/liquids. By calculating contact angle of the two films it not only tells us whether the sample film is hydrophobic or hydrophilic, it also tells us the stability of the film in water. And the hydrostability is found from wetting tendency of the film which is inversely proportional to the contact angle. Hence larger the contact angle or surface tension lower will be the wetting tendency and higher the hydrostability.

4.3.1 CONTACT ANGLE OF NANOFIBER FILM

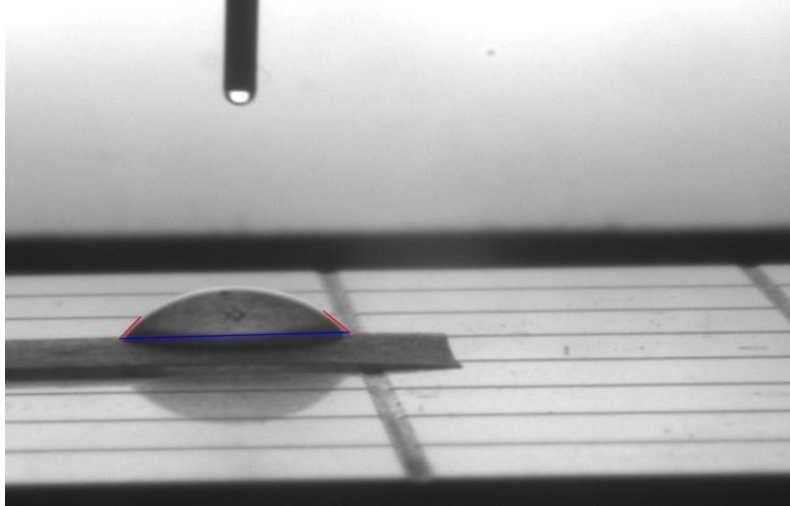


Fig. 4.3.1. Contact angle of Nanofiber Film.

The contact angle of nanofiber film is 78.705086° which is calculated by finding out the angle between the surface of the film and the drop of water used.

4.3.2 CONTACT ANGLE OF MICROFIBER FILM

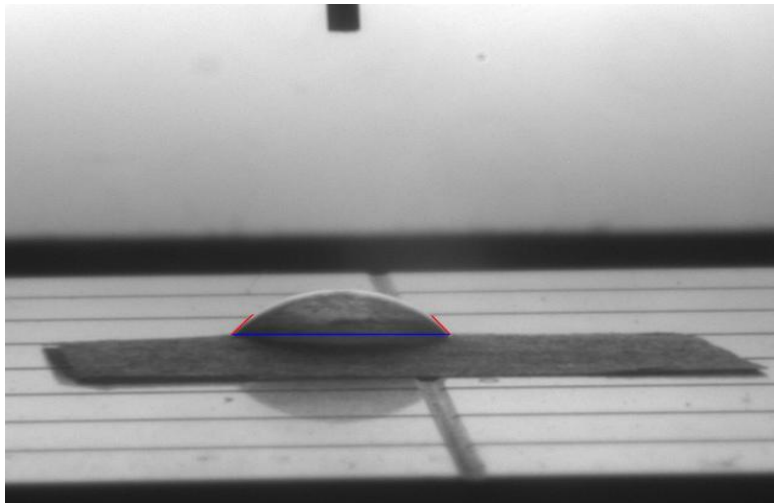


Fig. 4.3.2. Contact angle of Microfiber Film.

The contact angle of microfiber film is 63.165039° which is calculated by finding out the angle between the surface of the film and the drop of the water used.

4.4 COMPARATIVE STUDY OF TENSILE STRENGTH

CELLULOSE FILM	TENSILE STRENGTH (MPa)	FRACTIONAL ENERGY (MJ/mm ³)
NANOFIBER FILM	10.5	4,27,715
MICROFIBER FILM	9.97	1,92,611

Table.3.4. Comparative study of Tensile strength

For better understanding of the mechanical performance of the two films, we performed tensile test of the two films. Cellulose nanofiber film is stiff, with a stiffness of 10.5MPa but brittle with a fracture strain of 5.21%.

Cellulose microfiber film is compliant with a stiffness of 9.97MPa but rather ductile with a fracture strain of 2.85%. Hence nanofiber film is sufficiently stiff leading to a desirable combination of both mechanical strength and deformability.

The area underneath the stress-strain curve measures the energy needed to fracture a material (fracture energy). It is evident from fig.3.4 that cellulose nanofiber film has a much higher fracture energy of 4,27,715MJ/mm³ (thus much tougher) than the cellulose microfiber film with a fracture energy of 1,92,611MJ/mm³

4.5 COMPARATIVE STUDY OF CONTACT ANGLE

NAME OF THE FILM	CONTACT ANGLE (deg)
Nanofiber film	78.705086
Microfiber film	63.165039

Table.4.5. Comparative study of Contact angle

For better understanding of Hydrostabilities of the two films, we performed contact angle test of the two films. By measuring the contact angles of water on the film surface, we evaluated the hydrostability of the two different types of films. Due to the hydrophilic nature of cellulose, the contact angle of the nanofiber film is 78.705086° , showing an apparent wettability. A well-defined wettability is indicated by the microfiber film's contact angle of 63.165039° , which is caused by the integral fiber network created by hydrogen bonds along the length of the cellulose microfibrils. As a result, it is discovered that the Nanofiber film has a lower wetting tendency and greater hydrostability than the Microfiber film.

As the nanofibers are packed closely together and there are carboxyl groups, the cellulose nanofiber film exhibits a significantly slower wetting and greater hydrostability. The cellulose nanofiber film, however, experiences delamination at its outside edge, which causes partial disintegration. This might be explained by the dissociation effects caused by water on the hydrogen bonds formed between the short cellulose nanofibers. Due to the strong capillary effect brought on by the high porosity and low density of the cellulose microfiber film, the film exhibits substantially stronger wetting and lower hydrostability.

4.6 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY ANALYSIS OF CELLULOSE

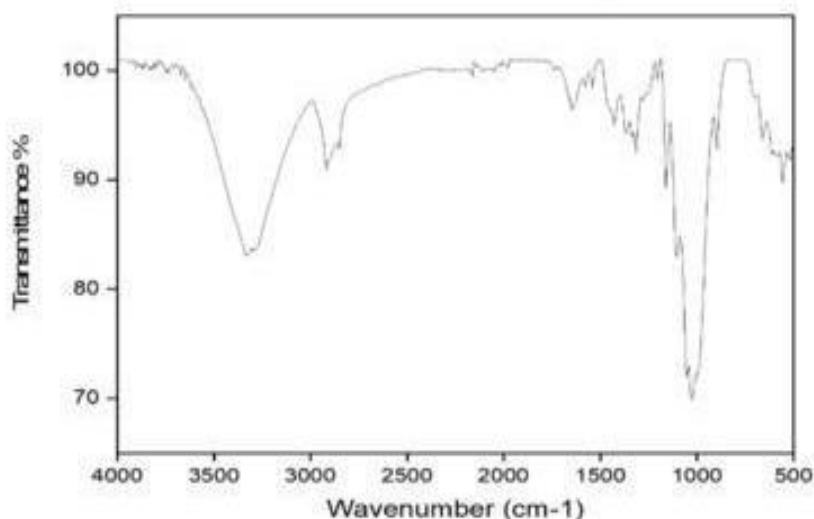


Fig4.5. FTIR spectrum of Cellulose

The presence of functional groups in SCB was identified using FTIR analysis. The spectrum demonstrated in figure exhibits identical patterns but varied in the terms of peak sharpness. The FTIR bands at the range of 3200 and 3400 cm^{-1} shows the existence of OH stretching vibrations on the hydrogen bonding of the cellulose structure. The extending peak of OH bonds at 3300 cm^{-1} is less sharp, which indicates the elimination of non-cellulosic components from the SCB fiber. When it underwent alkaline and acid treatments, due to the rapid increase in the OH concentration, the FTIR peak became sharper. The peaks at the range 1500 and 1700 cm^{-1} shows C=O broadening.

4.7 FIELD EMISSION SCANNING ELECTRON MICROSCOPE ANALYSIS

FESEM Analysis were conducted in order to examine the morphology of the prepared nanofiber film as well as microfiber film.

4.7.1 FESEM OF NANOFIBER FILM

The FESEM images of a nanofiber film made from sugarcane bagasse (SCB) at various magnifications are shown in figure (a), (b) and (c). As shown in Fig. (c), the film samples that underwent an alkaline treatment, acid hydrolysis, and a lengthy ultrasonication time formed fibers with a uniformly long rod-shaped structure. According to Fig (c), the generated fibers are uniformly dispersed and have dimensions that fall within the range of nanometers. This outcome shows that mild acid hydrolysis, alkaline treatment, and bleaching, followed by a prolonged ultrasonication process, separated the microfibrils from the fiber bundles and produced a homogeneous distribution of fibers. The SCB's typical diameter ranges from 10 to 20 nm.

The CNFs' random entanglement makes it impossible to quantify the fiber lengths exactly, and because the ends are hidden, the length of the fibers can reach several micrometers.

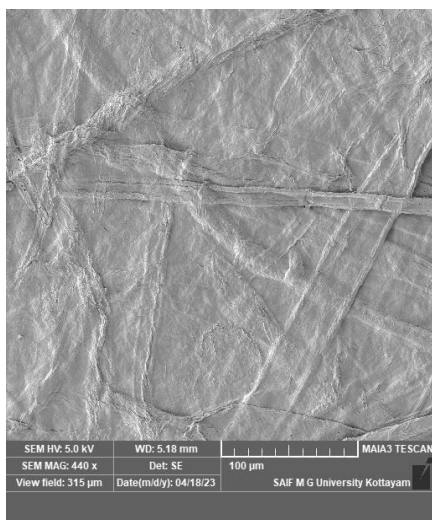
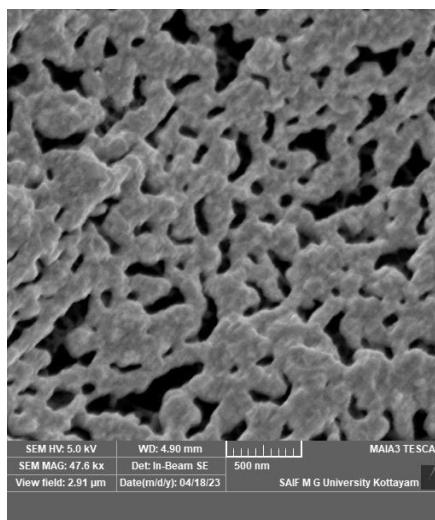


Fig (a)



Fig(b)

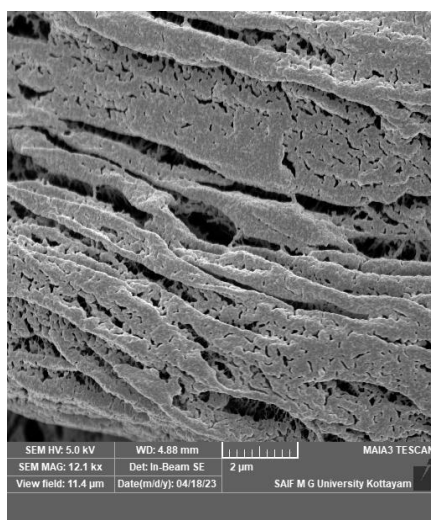


Fig (c)

Fig.3.7.1. FESEM images of Nanofiber film

4.7.2 FESEM OF MICROFIBER FILM

The cellulose microfiber film's FESEM micrographs, however, showed that the bulk of the microfibrils were in the sub-micron range and had high, or 50–120, aspect ratios. Fig.(b) depicts the bigger bundles from which the microfibers were liberated following hydrolysis, ultrasonication, and homogenization. Due to the fact that some of the microfibrillar bundles were partially dispersed and/or reaggregated during sample preparation, a wide dispersion of fiber lateral dimensions is visible. Depending on their origin, cellulose microfibrils may have transverse diameters that range from 20 to 200 nm. However, these particles are frequently aggregated, and the individual microfibrils are typically in the range of 3-20 nm.

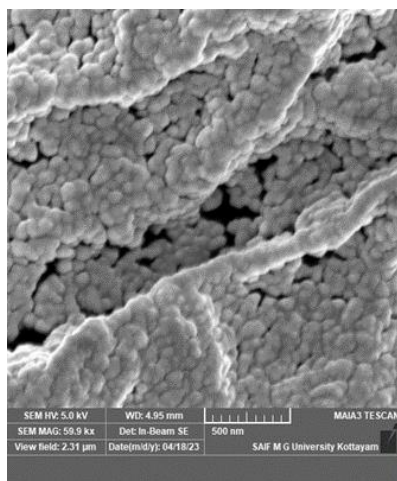


Fig (a)



Fig (b)

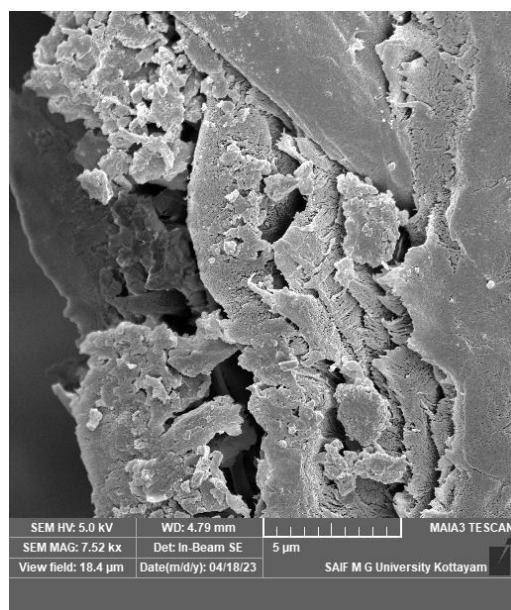


Fig (c)

Fig.4.7.2. FESEM images of Microfiber film

Chapter 5

Conclusion

The purpose of this study is to fabricate all- natural cellulose-based films composed of cellulose micro and nano fibers from Sugarcane bagasse, characterize the prepared films using a wide range of analytical and imaging techniques and compare their mechanical strength and hydrostability.

Combination treatment methods which include alkaline treatment and mild acid hydrolysis assisted with ultrasonication is used to extract cellulose nanofibers (CNFs) from sugarcane bagasse. The SCB fibers were first bleached with sodium hydroxide and aqueous hydrogen peroxide, then mild acid hydrolyzed, and last defibrillated and dispersed using ultrasonication at 70% amplitude. The alkaline treated cellulose fibers isolated from SCB is treated with mild sulfuric acid on acid hydrolysis. The production of Cellulose nanofiber film was supported by the XRD, FTIR, and FESEM studies. The CNF film's FESEM images shows diameters in the 20–30 nm range and lengths of up to several micrometers. This finding implies that the combined treatment approaches are quite successful in separating CNFs from the plant biomass. The existence of peaks at 2θ of 16.465° and 25.183° , indicating cellulose type I structure, is revealed by XRD analysis. The elimination of non-cellulosic components, however, allowed for the successful isolation of each particular CNF, as

shown by the FTIR spectra. This outcome confirms that all amorphous components, including lignin and hemicellulose, were eliminated. Thus, using a combination of alkaline treatment and mild acid hydrolysis assisted by ultrasonication, CNFs with long entangled network fibrils were successfully recovered from SCB. The CNFs should be strong and have a high aspect ratio, making them ideal for use as reinforcement for creating nanocomposites.

Three independent steps were taken to separate the cellulose microfibrils from the bagasse. In the beginning, bagasse underwent a traditional pulping procedure to remove lignin and hemicellulose. After being mechanically separated into their component microfibrils (MFs) by a two-stage homogenization procedure, the whole cellulosic fibers so produced were acid hydrolyzed. The hydrolysis conditions had an impact on the size of the resultant micro fibers. The cellulose made from bagasse, a byproduct of sugarcane, was much more resistant to hydrolysis than tunicate, bacterial, or even wood cellulose, according to persistent discolouration. The size of the MFs was distributed, and it ranged from a few hundred nanometers to a few microns. Under the above mentioned hydrolysis dispersion conditions, complete release of each individual MF from the microfibrillar bundles was not feasible. More extreme circumstances did reduce the aggregation phenomena between the individual MF, but they also caused significant crystal degradation. According to field emission scanning electron microscopy (FESEM), the particles' transverse sizes ranged from 200 nm to a few microns. The utilisation of these MFs as

reinforcing components in composites with biodegradable thermoplastic co-polyesters or other typical engineering thermoplastics is a future objective.

Tensile clarifies the mechanistic understanding of the mechanical characteristics of the two films. The stiffness of cellulose nanofiber film is 10.5 MPa, however it is also brittle, with a fracture strain of 5.21%. The cellulose microfiber film is ductile with a fracture strain of 2.85% and compliant with a stiffness of 9.97MPa. As a result, the nanofiber film has a desired mix of mechanical strength and deformability because it is sufficiently stiffer than the microfiber film.

Hydrostability is another important performance metric of the films in addition to mechanical qualities. The two films' contact angles, which are inversely correlated with their hydrostability, were measured. The contact angle of the nanofiber sheet is 78.705086° , indicating an apparent wettability, which is caused by the hydrophilic nature of cellulose. The microfiber film's contact angle of 63.165039° , which is brought on by the integral fiber network formed by hydrogen bonding along the length of the cellulose microfibrils, indicates a well defined wettability. The cellulose nanofiber film itself has a lower wetting and the highest hydrostability of the two.

Furthermore, the raw materials required for the developed films are abundant on Earth and sustainable, offering the possibility of their mass production at minimal cost. Another long-needed property that holds promise to address the growing negative environmental impact of barely

biodegradable plastic is the intrinsic degradability of the films. Therefore, cellulose films are a good contender to replace petroleum-derived plastics in packaging materials, straws, etc. along with different applications spanning from sensor, water filtration to drug delivery due to excellent mechanical strength, hydrostability and low-cost raw materials.

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