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A COMPARATIVE STUDY OF CELLULOSE NANO, MICRO AND HYBRID FIBER FILMS FABRICATED FROM SUGARCANE BAGASSE AND ITS APPLICATIONS

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ABSTRACT

Sugarcane Bagasse (SCB) is a biomass of agricultural waste produced during the processing of sugarcane. Cellulose nano and microfibers were prepared from bagasse by alkaline and acid hydrolysis followed by ultrasonication. Both the nanofiber suspensions obtained were mixed to fabricate the hybrid fibers. All the fibers obtained were homogenized and vacuum filtrated to obtain fiber films. The prepared fibers were characterized by FESEM, XRD, and FT IR. The hydro stability of the fiber films was determined by contact angle measurement and the mechanical strength of the films was obtained by measuring the tensile strength. Cellulose nanofiber film exhibited improved properties than the other two fibers. All the fibers were useful in fabricating biodegradable and hydro-stable drinking straws and food packaging containers.

KEYWORDS: Cellulose, nanofiber, microfiber, hybrid fiber, sugar cane bagasse.

INTRODUCTION

Sugarcane (Saccharum officinarum) is a major crop grown in tropical regions of the world. In 2020, about 1.9 billion metric tons of sugarcane were produced worldwide.[1] SCB is typically used to produce heat and electricity in sugar mills (cogeneration), but can also be used for paper making, as cattle feed and for manufacturing of disposable food containers.[2] The SCB, a lignocellulosic residue after extraction of sugarcane juice is composed of 40–50% cellulose and 25–35% hemicellulose. The remainder is made up of lignin, wax and other materials.[3] Cellulose has a 50 – 90 % crystalline structure depending on its source. Cellulose is a linear polymer made up by β -1, 4 -D-glucose units and hemicellulose, a heterogeneous polysaccharide composed by differentiated amounts of hexose and pentose sugars. Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents, amorphous, and hydrophobic in nature.[4] The three hydroxyl groups in cellulose in positions like C-2, C- 3 (secondary -OH) and C-6 (primary -OH) produce strong intermolecular and intramolecular hydrogen bonds.[5] The lignin works as a glue between cellulose and hemicellulose which makes the material rigid.[6] The production of nanocellulose from the cellulose fibers extracted from the SCB is a better alternative to the use of biomass.

The production of nanocellulose fibers with a diameter less than 100 nm from SCB is a good illustration of a waste-to-wealth economy.[7] The future of our civilization depends on waste reduction, sustainable development, and lowering the need for fossil fuels. It has a wide range of applications in various industries due to its physical and mechanical properties with rich surface chemistry, a high Young's modulus, high strength, great transparency, and a very low coefficient of thermal expansion and biocompatibility.[8,9] Researchers have shown great interest owing to its low cost, light weight, active surface functionalization, biodegradability, and eco-friendly nature.[10,11] Cellulose nanofibers have numerous applications as biosensors, high-strength nanocomposite, optical nanocomposite, optically transparent papers for electronic devices and filtration media.[12] Moreover, it has been used in various industries including manufacturing, cosmetics, food, biomedicine, and electronics sectors.[13]

Plastics are indispensable in daily life as they have a vast array of applications owing to their lightweight, flexibility, chemical stability etc. The use of plastic products has increased significantly in recent years, particularly with the COVID-19 pandemic leading to increased demand for single-use plastics such as masks and gloves.[14] The production of plastic waste has become a major environmental issue, with an estimated

530 million metric tons of plastic trash being produced each year.[15] This waste can have serious negative impacts on the environment, including ocean pollution, harm to wildlife, and the release of greenhouse gases. As such, there is growing concern about the need to reduce plastic consumption and develop more sustainable alternatives. Single-use plastic straws have become a major environmental concern due to their negative impacts on marine life. These straws are often sharp and can cause physical harm to sea animals, such as entanglement and ingestion, which can lead to injury or death. Furthermore, they are difficult to collect for recycling due to their small size, which often results in them being discarded and ending up in the ocean.[16] While some types of plastics, such as PLA, are biodegradable, they may not be marine-degradable. This means that while they may break down over time, they can still persist in the marine environment and cause harm to wildlife. It is therefore important to consider the environmental impacts of any material, including biodegradable plastics, and to choose materials that are sustainable and have minimal negative impacts on the environment.[17] While paper straws have been widely adopted as a replacement for plastic straws, they do have some drawbacks, such as a higher cost due to the waterproof wax layer that is often applied to them. Additionally, the wax layer can delaminate when exposed to liquids for extended periods of time, reducing the water stability of the straw and potentially affecting its performance.[18] To mitigate these issues, researchers and industry leaders are actively exploring alternative materials that can be used to produce straws that are both environmentally friendly and cost-effective. Some of the materials that are being considered include bamboo, metal, and silicone, among others. These materials offer advantages such as durability, reusability, and biodegradability, which make them more sustainable options compared to plastic or paper straws.[19] Ultimately, finding a high-performing alternative to plastic straws and the paper straws is crucial for mitigating the environmental problems brought on by these materials.

The development of high-performance polymeric materials with excellent mechanical qualities has received a lot of attention. These materials are based on natural polymers including silk, chitosan, and cellulose which can form noncovalent interlinking hydrogen bonds. The hierarchical structure makes it possible to produce cellulose fibers with diameters that range from microscale to nanoscale by using known chemical and mechanical processes.[20] Here binder-free cellulose-based drinking straws comprising of nano and microfibers were developed.

MATERIALS AND METHODS

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^{o}c for 72 hours. Then the size of the fibers was reduced into a granular form using a blender. After sieving, a granular form of 100 micrometers in size was obtained. All chemicals used are of analytical grades.

Alkaline Treatment and Bleaching

Alkaline treatment of the granular form of SCB was done with 2% (w/v) sodium hydroxide (NaOH) solution in a 1L beaker. This substantially reduced the amount of lignin and hemicellulose. The above mixture was heated in a water bath at 80°c for 5 hours 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. The process was repeated with 12 % (w/v) NaOH at 80°c for an hour further. The SCB after alkaline treatment is bleached with 200 mL of aqueous hydrogen peroxide (H_2O_2) taken in a 1:1 ratio. The sample is bleached at 75°c for 15 min. Then the bleached samples are washed and filtered three times using a vacuum pump to eliminate all the impurities.

For the preparation of microfibers from the SCB; the dry bagasse was first broken down for 4 hours at 80°C in a solution of 4% sodium hydroxide and it was bleached with hydrogen peroxide. 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. (Fig. 1 & 3).

Acid Hydrolysis

The cellulose thus obtained was acid hydrolyzed to preferentially remove the non-crystalline portions over the crystalline sections. For nanofibres, the samples were treated with 1% (v/v) H_2SO_4 solution at 80^{0}c for an hour. Then washed and filtered ten times to remove all impurities and stored in a refrigerator at 4^{o}c until further treatment. For the preparation of microfibers, the bleached fibers were refluxed with 60% (w/v) sulfuric acid for 2.5 hours at 60^{o}C, leaving a collection of evenly scattered microfibers. In order to stop the process, ice water was introduced. (Fig. 1 & 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^{o}C for further processing.

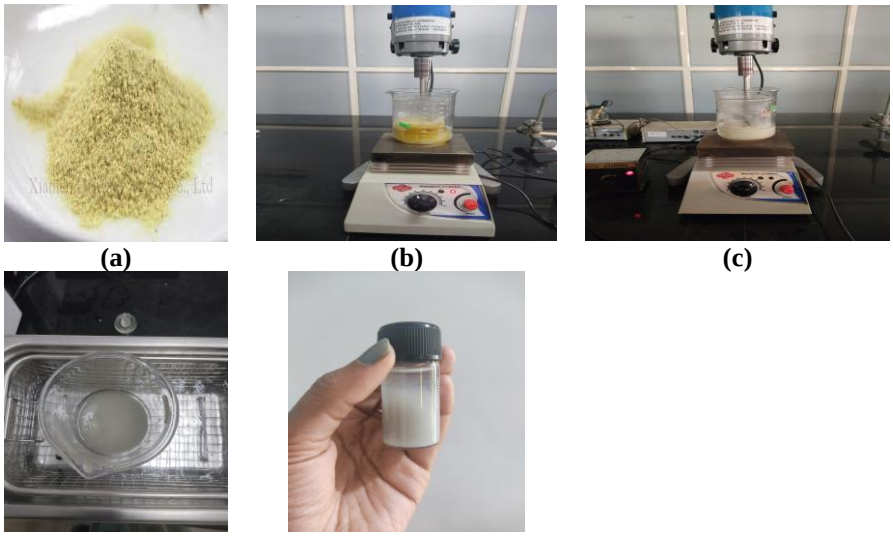
The MFs were washed with water and dispersed for 5 min with repeated cooling using an ultrasonicator. The dispersion medium was then gradually changed from water to tertiary butanol.

Cellulose Nanofiber and Microfiber Film Fabrication

The cellulose nanofiber suspension was blended well, homogenized and vacuum filtrated into a wet film by using a funnel 14cm in diameter. The aqueous microfiber slurry was blended well and filtrated into a wet film by using a funnel 14cm in diameter. (Fig. 2 & 4).

Experimental

Preparation of Cellulose Nanofibers (CNFs) and Microfibers from Sugarcane Bagasse (SCB).

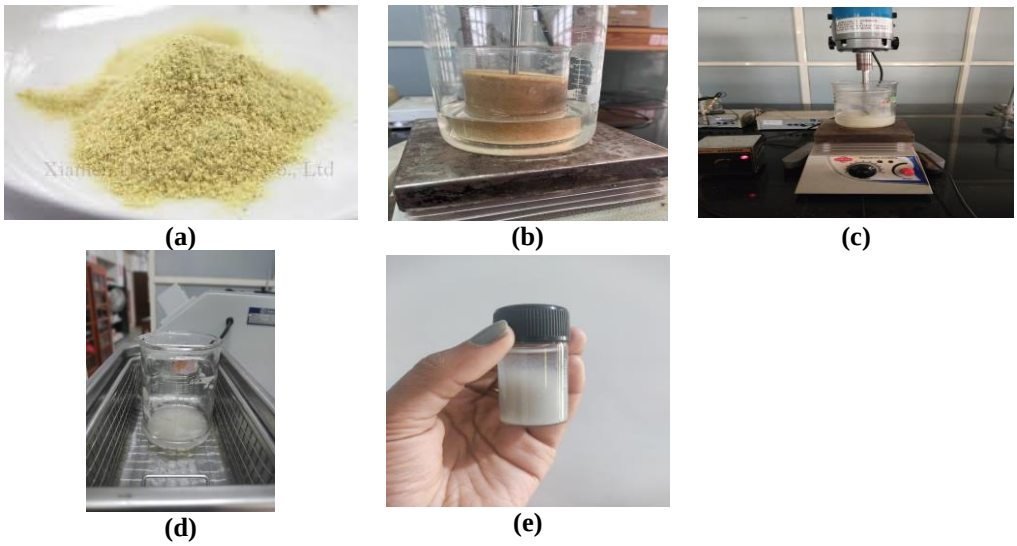


(a) (b) (c) (d) (e)

Fig. 1(a): Granular form of sugarcane bagasse (b) Alkaline treatment(c) Bleaching and acid treatment (d) Ultrasonication (e) Cellulose Nanofiber Suspension.

(a) (b) (c)

Fig. 2: (a) Homogenization (b) Vacuum filtration c) Cellulose Nanofiber film.



(a) (b) (c) (d) (e)

Fig. 3: (a) Granular form of Sugarcane bagasse (b) Alkaline treatment (c) Bleaching and acid treatment (d) Ultrasonication (e) Cellulose Microfiber Suspension.

a b c

Fig. 4 (a) Homogenization b) Vacuum filtration c) Cellulose Microfiber Film.

Cellulose hybrid film fabrication

Equal amounts of Cellulose microfiber aqueous slurries and cellulose nanofiber suspensions are mixed well and vacuum filtrated into a wet film by using a funnel 14 cm in diameter.

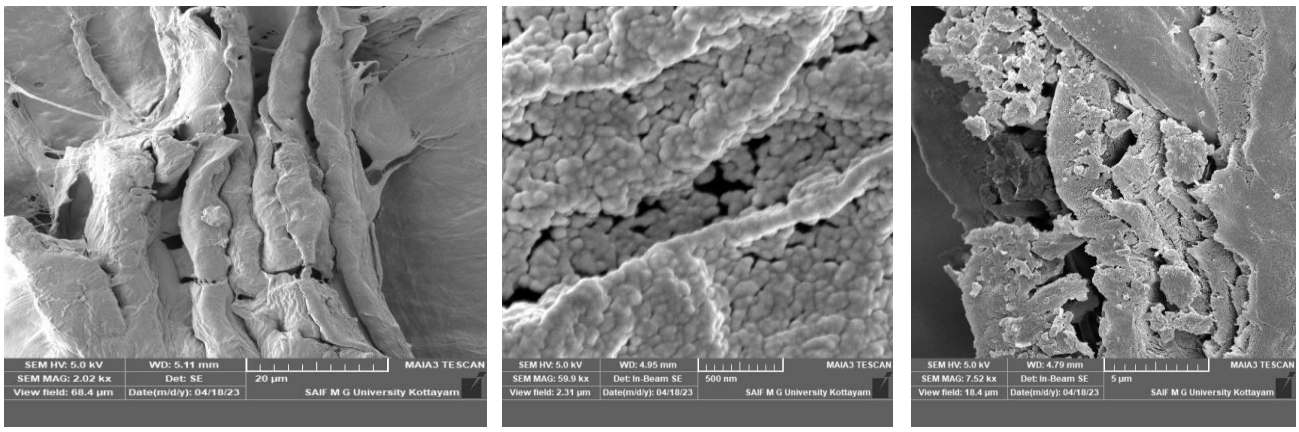
RESULTS AND DISCUSSION

Field Emission Scanning Electron Microscopy

An advanced technique called field emission scanning electron microscopy (FESEM) is utilized to visualize 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 conducted in a high vacuum. Thus, FESEM Analysis is conducted in order to examine the morphology of the prepared nanofiber film as well as microfiber film.

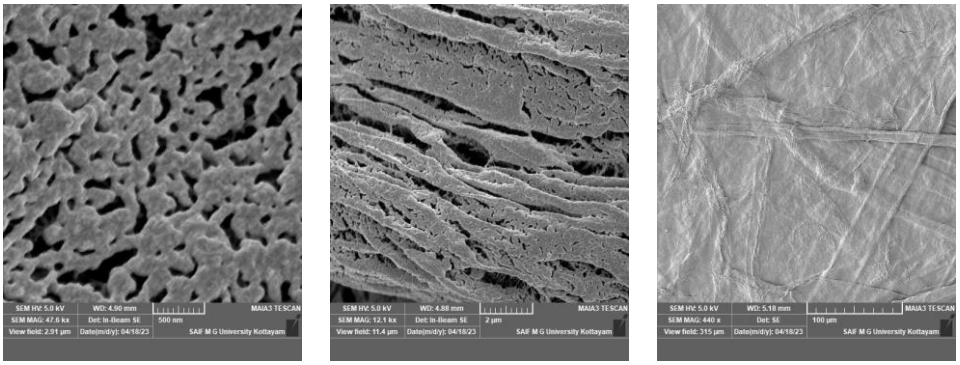
The FESEM images of a nanofiber film made from sugarcane bagasse (SCB) at various magnifications are shown in Figure 5 (a), (b) and (c). As shown in Fig. (b), the film samples that underwent an alkaline treatment, acid hydrolysis, and a lengthy ultrasonication time formed fibers with a uniformly long rod-shaped structure. According to Fig (b), 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 micrometres.

The cellulose microfiber film's FESEM micrographs (Fig. 6), 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.



a b c

Fig. 5: FESEM images of Microfiber film.



a b c

Fig. 6: FESEM images of Nanofiber film.

X-ray Diffraction (XRD) Analysis

The crystallinity of samples was characterized by X-ray diffraction (XRD) measurement (Fig. 7) on a D/max-III X-ray diffractometer equipped with nickel-filtered Cu Kα radiation (λ = 0.15418). The diffraction angle (2θ) ranged from 3° to 90° and the step size was 0.01°. The d-spacing of films were calculated with the Bragg's law;

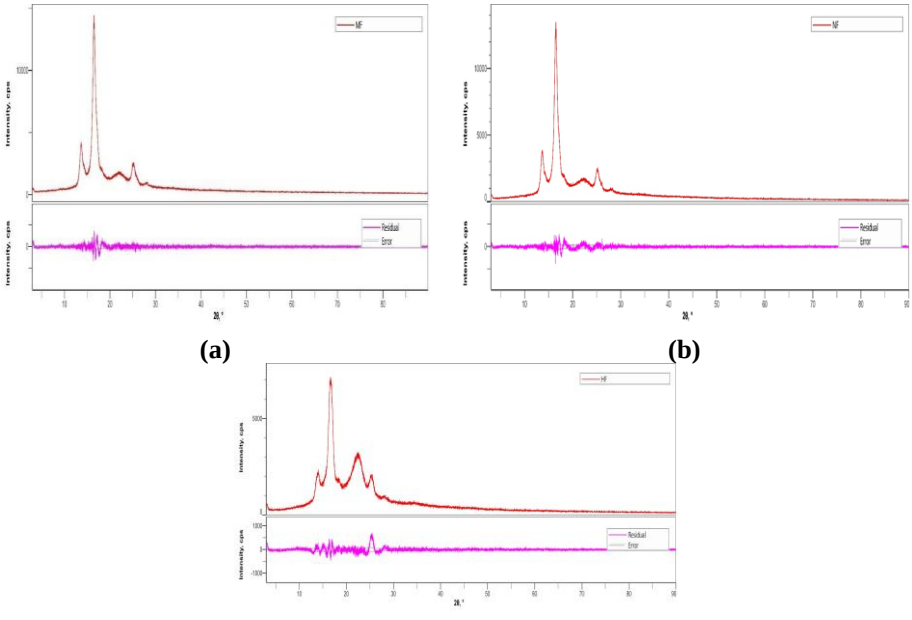
D= nλ2sinθ; where λ is the wavelength of the X-ray source (0.15418 nm) and θ is the Bragg angle corresponding to the plane. The apparent crystallite size (D) of the reflection plane was obtained using the Scherrer equation

L=Kλ/βcosθ;

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

The average crystal size was determined using Debye Scherrer equation, D=0.9 λ/B cos θ.

In the XRD spectrum of the cellulose nanofiber film, three clear peaks were obtained at 2 θ values of 13.641°, 16.465° and a major peak at 25.183° which shows the corresponding average size of 10.65nm for nanofiber film. In the XRD spectrum of cellulose microfiber film, three clear peaks were observed at 2 θ values 13.635°, 16.437° and 25.077° which gives the corresponding average size of 9.50nm for the microfiber film. The hybrid fiber film shows three clear peaks at 2θ values 13.944, 16.624 and 22.478 which gives the corresponding average size of 5.78nm.



(a) **(b)**

(c)

Fig. 7: XRD spectrum of a) Nanofiber film b) Microfiber film c) Hybrid fiber film.

Fourier transforms infrared (FTIR) Analysis

The presence of functional groups in SCB was identified using FTIR analysis. 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}. (Fig 8)

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}.

The spectrum demonstrated in the figure exhibits identical patterns but varies in the terms of peak sharpness. The FTIR bands at the range of 3200 and 3400 cm^{-1} show 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} show C=O broadening.

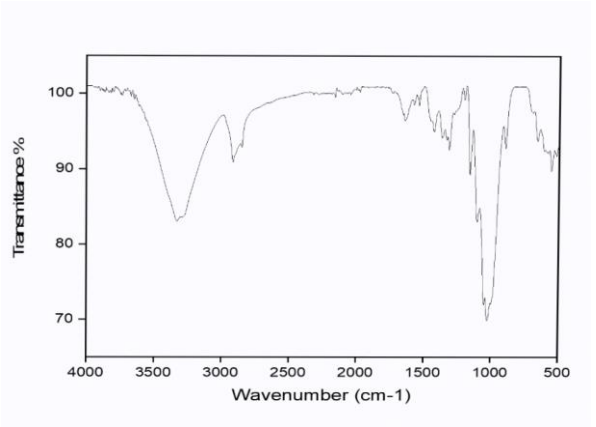


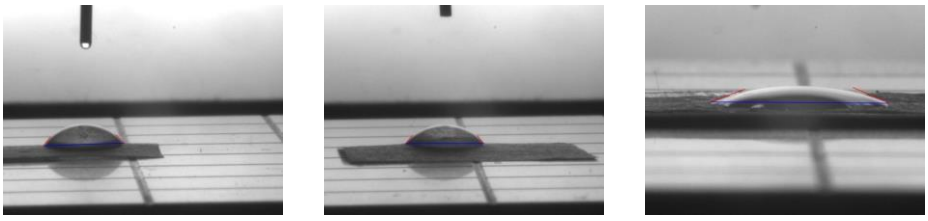
Fig. 8: FTIR of Cellulose nanofiber.

Contact angle measurements

Contact angle is one of the common ways to measure the wetting stability of a surface or materials. Wetting is determined by measuring contact angle which the liquid forms in contact with the solids/liquids. Calculating the contact angle of the three films, not only tells whether the sample film is hydrophobic or hydrophilic, it also indicates the stability of the film in water. Hydrostability is determined by the 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.

Due to the hydrophilic nature of cellulose, the contact angle of the nanofiber film is 78.705086^0, showing an apparent wettability. 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 (Fig. 9).

A well-defined wettability is indicated by the microfiber film's contact angle of 63.165039^0, which is caused by the integral fiber network created by hydrogen bonds along the length of the cellulose microfibers. 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. As the nanofibers are packed closely together and there are carboxyl groups, the cellulose nanofiber film exhibits a significantly slower wetting and greater hydro stability than the microfiber film.



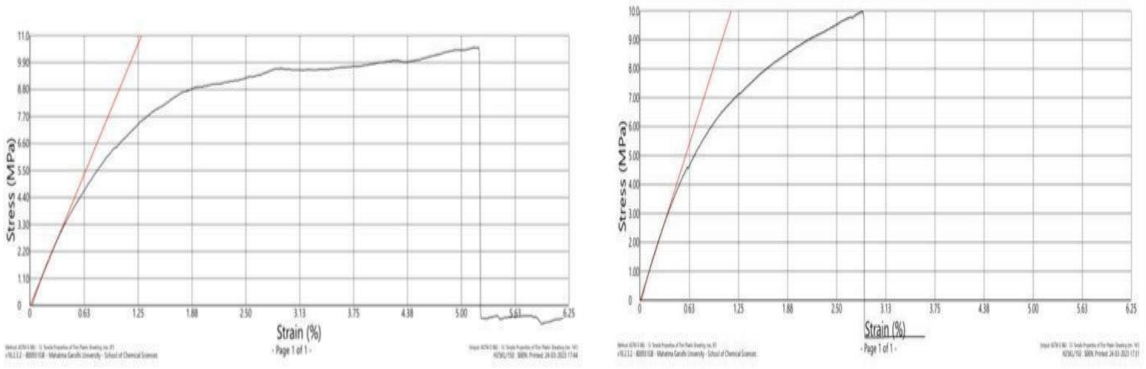
a **b** **c**

Fig. 9: Contact angle of a) Nanofiber film b) Microfiber film c) Hybrid fiber film.

Tensile strength

By calculating the tensile strength of the two films, mechanical strength of the respective films is determined which is calculated directly from the graph by taking the highest point in the curve which is the ultimate stress. Tensile tests of the two films prepared were performed and the stress-strain graphs obtained are plotted below (Fig. 10 a & b). The Tensile strength of nanofiber film is found to be 10.5 MPa obtained from the figure by finding out the ultimate stress from the stress-strain graph. The tensile strength of microfiber film is found to be 9.97 MPa. Cellulose nanofiber film is stiff, with a stiffness of 10.5 MPa 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 that

cellulose nanofiber film has a much higher fracture energy of 4,27,715 MJ/mm^3 (thus much tougher) than the cellulose microfiber film with a fracture energy of 1,92,611MJ/mm^3.



a b

Fig. 10: Stress strain graph of a) Nanofiber film b) Microfiber film.

CONCLUSION

The aim of this research is to create films made entirely of natural cellulose by using cellulose micro and nanofibers from sugarcane bagasse. The films will then be characterised using various analytical and imaging techniques, and their mechanical strength and hydrostability will be compared. Cellulose nanofibers (CNFs) are extracted from sugarcane bagasse using a combination of treatment techniques, including mild acid hydrolysis and alkaline treatment, supported by ultrasonication. The analysis of FTIR, FESEM, and XRD provided support for the synthesis of cellulose nanofiber film. Tensile strength provided insight into the two films' mechanical properties. Of the two, the cellulose nanofiber film has the highest hydrostability and the lowest wetting.

Furthermore, the earth's resources for the raw materials used to create the films are abundant and sustainable, allowing for their mass production at a low cost. Another long-needed feature that shows promise in reducing the increasingly harmful environmental effects of barely biodegradable plastic is the films' inherent degradability. Cellulose films are a great alternative to petroleum-derived plastics in straws, packaging, and other applications like drug delivery, water filtering, and sensors because of their remarkable mechanical strength, hydrostability, and low cost of raw materials.

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Contributions

Sophiya & Prajana: Methodology, data preparation and writing the original draft. Priya K.: Resources and editing the manuscript. Jaya T Varkey: Conceptualization, manuscript editing and review, supervision and project administration.

Declarations

Authors declare that there is no Competing Interest here.

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