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Nanofibers

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Abstract

Cellulose is the most available biopolymer on earth existent in wood and other lignocellulosic sources, which can be isolated as nanofibers to reinforce composites. The aim of this chapter overview was to explain cellulose nanofibers' preparation methods from different plant sources. The chemical treatment of cellulose fibers including dilute alkali swelling, acid and base hydrolysis, and bleaching was carried out followed by a mechanical method to isolate nanofibers. In this study, the effect of few plant source variations and mechanical processes used in extraction procedure on nanofibers morphology, crystallinity, and chemical composition was evaluated. Characteristics of extracted cellulose nanofibers obtained from different plant sources were presented as well.

Keywords: natural fiber, extraction, cellulose nanofibers, chemical composition, morphology, crystallinity, thermal properties

1. Introduction

Over the past few decades, the use of plants as alternative sources of fibers instead of synthetic fibers has attracted more attention of many researchers. Employing natural fibers dates back to the early 1990s when German automakers were ahead in this field [1, 2]. The main goal of using natural fibers is recycling worthless materials which are found abundantly in nature. **Table 1** shows comparison between glass and natural fibers properties [3].

Natural fiber application in construction and automotive industry is in significant progress due to low density and relatively low cost compared to glass fiber. Natural fibers are the miniature composites, which are composed of millions of microfibrils. Microfibrils are

crystalline cellulose in a matrix contains lignin, hemicellulose, and other polysaccharides [4, 5]. According to the Food and Agricultural Organization (FAO) annually more than 35 million tons of fibers from plants and animals are produced in the world. These fibers have served useful purposes in the human society as they are widely used to make such valuable commodities as fabrics, ropes, papers, and packaging [6]. Lignocellulosic natural fibers obtained from plants are regarded as green, environmentally friendly materials due to their Biodegradability and high specific strength [7]. An important aspect of these fibers is their more recent application as reinforcement in composites. Compared to their inorganic counterparts, natural fibers used in composites offer such major benefits as abundance, low cost, renewability, and biodegradability, while they enjoy additional properties including low density (1.5 g/cm³) and large surface area (50–70 m²/g) as well as such mechanical properties as high aspect ratio, modulus, and strength [8–10].

Properties	Natural fiber	Glass fiber
Density	Low	Double than natural fibers
Price	Low	Low
Renewable	Yes	No
Recycle	Yes	No
Biodegradability	Biodegradable	Nonbiodegradable

Table 1. Comparison between glass and natural fiber properties.

1.1. Sources of biofibers

Natural fibers, or lignocelluloses, are classified according to their wood and non-wood sources. Depending on the part of the plant that they are derived from, five categories of fibers are

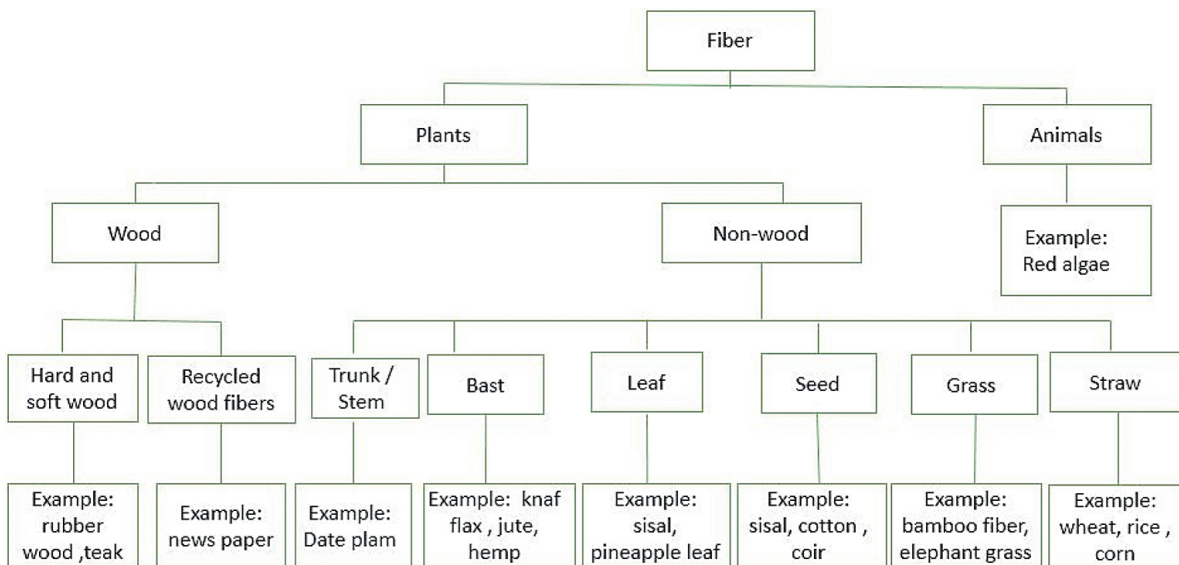


Figure 1. Classification of natural fibers.

identified: (1) bast or stem fibers; (2) leaf fibers; (3) seed-hair fibers, (4) core, pith, or straw fibers; and (5) all other plant fibers not included above. In other words, the four main categories of fibers are obtained from grain (cotton), vascular (flax, hemp, jute, rami, and wheat), grass (beet pulp, and bamboo), and algal sources (Valonica and Vettriosa).

Among the lignocellulosic sources, wood is consumed for paper production and cotton is used in the textile industry. However, only a small portion of annual plants such as hemp, wheat, soy hulls, bamboo, and other animal feed plants are used for energy production, most of which are burned as agricultural waste. **Figure 1** shows classification of natural fibers [8, 11, 12].

1.2. Structure of biofibers

Native fiber is comprised of small long thin filaments called microfibrils that consist of alternating crystalline and noncrystalline cellulose domains [13]. A single plant, typically 1–50 mm in length and around 10–50 μm in diameter, is called an elementary plant fiber. A plant fiber consist of few cells having cell walls compose of semicrystalline cellulose orientated in the direction of fiber and lying within a matrix of hemicellulose and lignin. A cell wall also surrounds a central lumen which help water uptake to the plant fiber [14, 15]. The fiber owes its high mechanical properties to 30–100 molecules of cellulose arranged in an extended chain conformation [16]. **Figure 2** presents an arrangement of cellulose fiber.

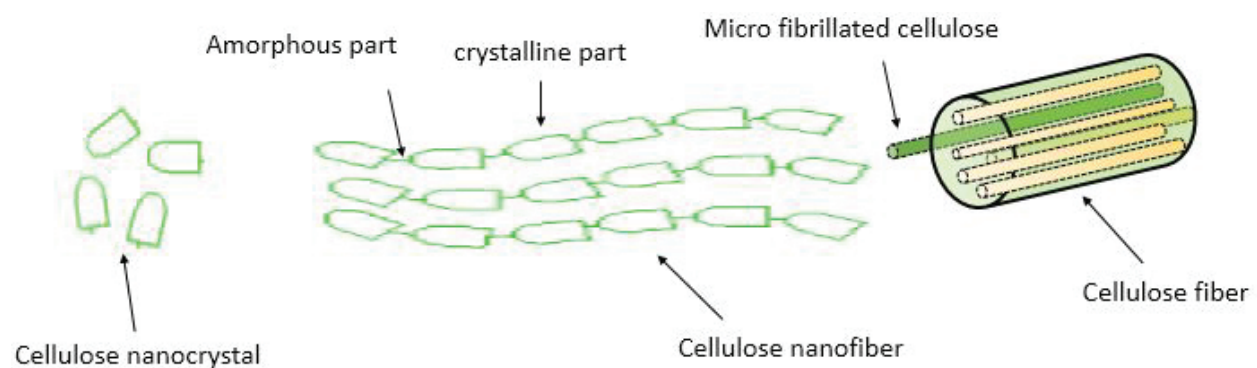


Figure 2. Scheme of cellulose fiber morphology.

Figure 3 shows the cell wall structure of a fiber [14, 17].

The secondary cell wall consists of an outer (S1), a middle (S2), and an inner (S3) layer, each consisting of microfibrils oriented in a specific angle with respect to one another [18–20].

The main constituents of natural fibers include cellulose, hemicellulose, lignin, pectin, wax, and water-soluble compounds. Hemicellulose is contains polysaccharides (excluding pectin) which remains connected to cellulose after lignin is removed. Hemicellulose is different from cellulose in three main ways [16]: First, it comprises various units of sugars (xylose, mannose, galactose, glucose, and rhamnose) [21]; second, it has a considerably higher degree of branch-

ing; and third, its degree of polymerization is 10–100 times lower than that of cellulose. In contrast to cellulose, the constituents of hemicellulose vary from plant to plant. Consequently, hemicellulose is amorphous in structure and surrounds cellulose nanofibers [14, 16, 22].

Lignin is a perfectly amorphous and hydrophobic polymer formed by a combination of linear and cyclic hydrocarbon derivatives of phenyl propane. The structure of lignin is not yet known, but its mechanical properties are known to be inferior to those of cellulose [14, 16]. It provides the necessary hardness and firmness to plants. Lignin cannot be hydrolyzed in acid but is immediately oxidized in a warm alkaline environment and easily removed with phenol [16].

Pectin is the collective name for heteropolysaccharides mainly made of polygalacturonic acid. It is an amorphous polymer that gives flexibility to the plant [16].

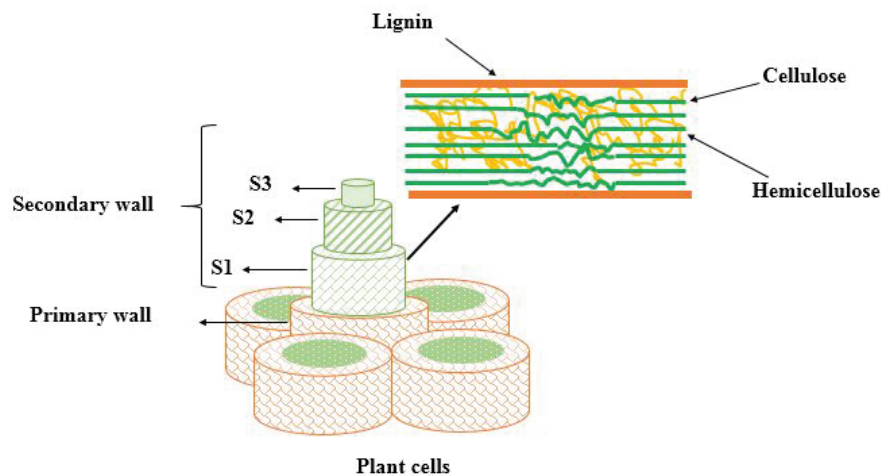


Figure 3. Scheme of plant fiber structure, S1, S2, and S3 layers.

1.3. Chemo-physical properties of cellulose

The specific structure of cellulose biopolymers defines their chemical and mechanical properties. As shown in **Figure 4**, the molecular structure of cellulose consists of β -D-anhydroglucopyranose repeating units that are bonded covalently together using acetal functional groups between the equatorial groups of C4 and C1 carbon atoms (β -1, 4-glycosidic bonds [23, 24].

Sensitivity to the hydrolytic attack of the β -1, 4-glycosidic linkages between the glucose repeating units is the factor determining the chemical stability of a cellulose molecule. It is clear from the molecular structure of cellulose that it is a linear polymeric chain having a large number of hydroxyl groups. The reason for this linear conformation is the β -glucose link at the C1–O–C4 to yield cellobiose units [23, 25, 26].

A second intramolecular hydrogen bonding may exist between the hydroxyl functional groups on the C6 and C2' carbon atoms of the neighboring glucose units. Moreover, an intermolecular hydrogen bonding exists between the hydroxyl groups on the C6 and C3" carbon atoms of cellulose molecules that are adjacently located on the same plane [23, 27–29].

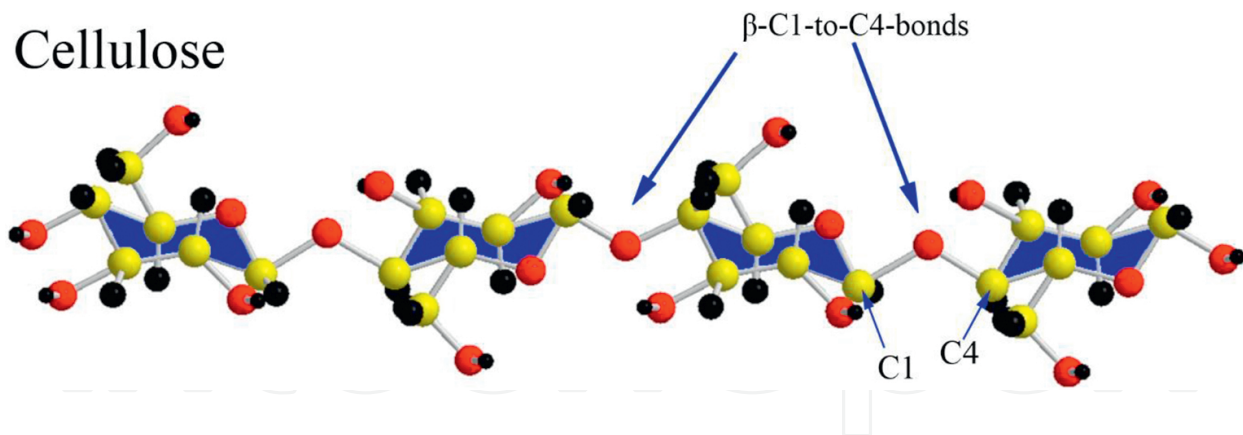


Figure 4. Show cellulose structure.

It is known from Infrared spectroscopy and X-ray diffraction (XRD) investigations of cellulose organization in plants that crystallites and low degree of scattered amorphous regions are the main constituents of cellulose [30, 31]. Native cellulose, namely cellulose I, is the crystalline cellulose while that precipitated out of alkali solutions is generally known as regenerated cellulose or cellulose II [30, 32]. Cellulose II is the most thermodynamically stable form due to the presence of an additional hydrogen bond per glucose residue [30, 33, 34].

It should be noted that cellulose gains its unique properties (Table 2) mentioned earlier after it reaches to its nanoscale [35].

Component	Young's modulus (MPa)
Biomass	20
Single fiber network	40
Microfibril	70
Cellulose nanocrystal	50–143
Cellulose nanofiber	145–150

Table 2. Young's modulus of cellulose after it reaches its nano-size [35].

Table 3 presents a comparison mechanical properties of glass, jute fibers and cellulose nanofibers [31, 36].

Specific fiber	Young's modulus (GPa)	Tensile strength (GPa)	Density (g/cm ³)
Glass fiber	~72.4 at 21°C	~3.4 at 21°C	2.54–2.62
Jute fiber	13–26	0.39–0.77	1.3–1.45
Cellulose nanofibers	~150	~10	1.5

Table 3. Comparison between mechanical properties of nanofibers and other fiber [31, 36].

1.4. Cellulose nanofibers (CNF) extraction methods

A variety of methods may be used for the extraction of cellulose nanofibers, each of which yields a unique type of nanofiber. Some of the extraction methods used are outlined below:

1.4.1. Biological method (hydrolytic enzyme)

This method is based on the use of micro-organisms, bacteria, or fungi. In this method, fibers are produced with diameters in the order of 100 nm form a bunch of nanofibers including those approximately 2 nm in diameter. These fibers have excellent intrinsic properties that yield crystallinity percentage values of around 89–84% [16].

1.4.2. Mechanical method

Mechanical or physical methods of extraction include cryocrushing, grinding, high-pressure homogenization, ultrasound, and steam explosion methods. The fibers obtained by these methods have a low strength and a small length-to-diameter ratio because of applying high tension on fibers. Another disadvantage of this method is its failure to easily manufacture fibers of nanosize diameters. [14, 16].

1.4.3. Chemo-mechanical method

These comprise the most common methods used for producing nanofibers with diameters less and length-to-diameter ratios higher than those produced by the mechanical method [16]. In these methods, the non-cellulosic content is removed by acid hydrolysis and alkali treatment [37]. Comparison of the advantages and disadvantages of conventional nanofiber extraction methods indicates that the chemical-mechanical ones are the safest for nanofiber isolation. **Figure 5** schematically present a chemo-mechanical method for production of cellulose nanofibers

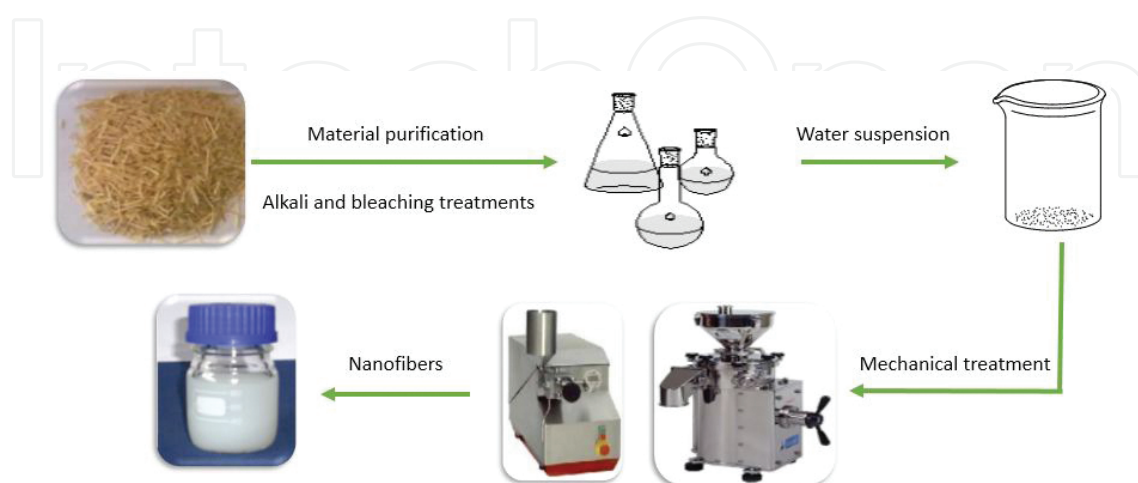


Figure 5. Scheme of chemo-mechanical method for production of cellulose nanofibers.

2. Experimental

2.1. Chemical treatment for CNF isolation

Some researchers have used an alkaline-acid pretreatment prior to mechanical isolation of CNF in order to solubilize lignin, hemicellulose, and pectins [2, 38]. The chemical treatment is accomplished in the following four steps:

- (1) Soaking fibers in the 17.5 wt.% sodium hydroxide (NaOH) solution for 2 h; thus, the exposed surface area of the cellulosic fibers is enhanced and they become more susceptible to hydrolysis [16];
- (2) Hydrolyzing the fibers in the hydrochloric acid (HCL) solution (2 M) at 80°C to solubilize hemicellulose [39];
- (3) Treating the fibers with 2 wt.% NaOH solution for 2 h at 80°C in order to disrupt the lignin structure and to break down the carbohydrate and lignin linkages [16, 40]; and
- (4) Bleaching the fibers with sodium hypochlorite, sodium chlorite, and hydrogen peroxide performed in an acidic environment at 50°C for 1 h [41].

2.2. Mechanical treatment

Cellulose nanofibers are extracted from the secondary cell walls by mechanical treatment without any damages to the cellulose. The degree of polymerization of cellulose, morphology, and aspect ratio of the CNFs depend on the defibrillation technique employed. Refining, grinding, and ultrasonication processes are performed for the mechanical isolation of CNF from wood and non-wood fibers [10, 42].

2.2.1. Grinding

Grinding is used to break up cellulose microfiber into nanosized fibers. The grinding machine consists of one rotating and one static grind stone where the pulp slurry passes through. In the fibrillation mechanism using a grinder, the hydrogen bonds are disintegrated under shear forces and the pulp is transformed into nanoscale fibers [42].

2.2.2. Ultrasonication

The mechanical process in which cellulose fibers are isolated using oscillating power by means of hydrodynamic forces of an ultrasound device is called “high intensity ultra sonication” (HIUS) [43]. When the ultrasonic energy is absorbed by the molecules, the cavitation evolving during the process give rises to a strong oscillating power, which generates high-intensity waves that lead to the formation, expansion, and explosion of microscopic gas bubbles [44]. Many efforts have been directed improving the HIUS resulting oscillating power to isolate nanofibers from cellulosic sources [42]. **Table 4** reports some of the plant sources of nanoscale cellulose fibers produced by a supergrinder and the ultrasonic system.

Process	Sources
Grinding and ultrasonic	Bagasse
Grinding and ultrasonic	
Ultrasonic	Rice straw
Grinding	Rice husk
Grinding and ultrasonic	Maize
Grinding and ultrasonic	Sawdust

Table 4. Different mechanical methods for isolating cellulosic nanofibers.

3. Results and discussions

3.1. Chemical composition characterization

An important factor affecting the application of natural fibers as biodegradable materials is their chemical composition. It is, therefore, essential to determine their chemical and mechanical properties of fibers used for manufacturing different products such as composites or newspaper. The three major chemical constituents of fibers extracted from lignocellulosic products are α -cellulose, lignin, and hemicellulose [45]. The factors affecting the properties of CNFs such as yield, dimensions, and mechanical properties of nanocellulose include chemical composition, the structure of the base material, and the processing method used for their extraction. Efficient isolation of cellulosic nanomaterials strongly depends on the removal of hemicellulose and lignin [1, 7]. Lignocellulosic fibers may be transformed into individual fibers during the extraction process by employing chemical purification via acid hydrolysis, alkali treatment, and bleaching. Applying the dilute alkali treatment to the lignocellulosic fibers breaks up the structural bonds between lignin and saccharides to remove the lignin content. Acid hydrolysis is used to destroy and solubilize the hemicellulose and pectin. Bleaching separates the Klason (insoluble) lignin by oxidizers such as sodium chlorite, sodium hypochlorite, and hydrogen peroxide [2, 40, 46]. **Table 5** presents the chemical compositions of fibers extracted from different sources in the three raw, pre-, and post-bleaching stages. As it can be noticed the cellulose content from different sources after purification is in the range of 85 to 95 %; while the residual lignin content is obtained to be between 0.8 to 11%.

Figure 6 presents wheat-straw fibers before and after bleaching. Clearly, the brown color is present in the sample before the removal of insoluble lignin, indicating that lignin is an amorphous phase that keeps reducing with increasing removal efficiency. Comparison of the colors in this **Figure 5** shows that almost all the residual lignin (insoluble lignin) in the sample was eliminated and the sample becomes pure white after bleaching.

Sources	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Bagasse			
Raw fiber	42.2	21.8	23.5
Before bleaching	88.23	8.82	2.95
After bleaching	91.8	7.37	0.82
Rice straw (stem)			
Raw fiber	46.5	22.5	29.1
Before bleaching	79.3	4.8	15.9
After bleaching	-	-	-
Rice husk			
Raw fiber	34.67	27.3	25.7
Before bleaching	67.36	14.83	11.74
After bleaching	94.3	1.8	1.42
Wheat straw			
Raw fiber	50.01	25.32	24.46
Before bleaching	86.2	3.7	10.1
After bleaching	93.7	2.95	3.35
Wheat straw (stem)			
Raw fiber	49.8	27.2	23.1
Before bleaching	85.5	3.8	10.8
After bleaching	-	-	-
Sawdust			
Raw fiber	33.38	28.71	37.08
Before bleaching	57.84	18.71	23.2
After bleaching	86.24	7.76	5.98

Table 5. Chemical compositions of fibers from different sources after selective chemical treatments.



Figure 6. Image of raw wheat straw fiber, and its pulp before and after bleaching.

3.2. Morphology description

Cellulosic fibers are made of cell walls that collectively form its structure. It is commonly established that chemical and mechanical treatments bring about changes in fiber morphology [10, 47]. Microscopic examinations indicate that raw fiber bundles consist of individual microfibrils that are bonded together by lignin (**Figure 6**). Hence, chemical treatments are used to reduce the surface roughness and the size of the bundles. It has been reported that fiber diameter is reduced to the nanoscale as a result of chemical and mechanical treatments. This can be related to the removal of such non-cellulose constituents as lignin, hemicellulose, and waxes.

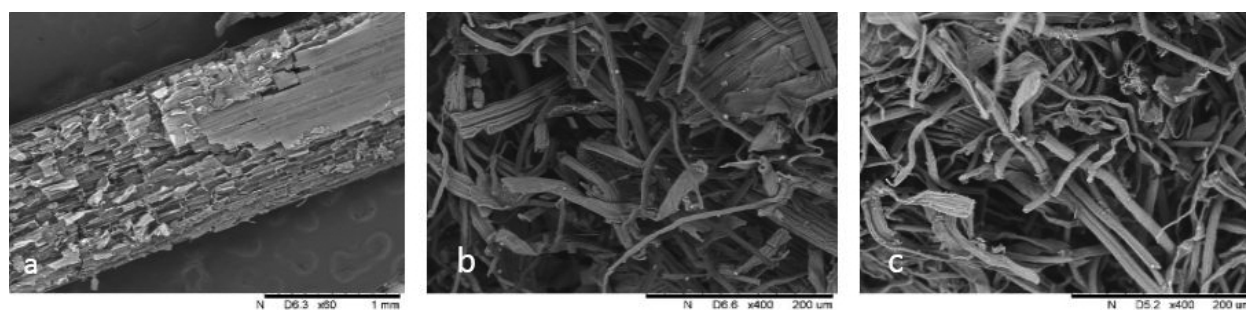


Figure 7. SEM images of a) raw fiber, b) pre-treated fiber, and c) bleached fiber.

Scanning electron microscopy (SEM), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) techniques are used to characterize the morphology of the nanocellulose fibers produced. As can be seen, in **Figure 6**, the microfibril diameter is reduced as a result of chemical operations due to removal of the non-cellulosic material. It is clear from the the FE-SEM and TEM images that the extracted nanofibers have a network structure and are in the form of entangled fibrils. **Table 6** presents the variations in the diameter of the nanocellulose fibers isolated from different plant sources. The CNFs can have diameters varying from 15–200 nm depending on their source and the mechanical method used to disintegrate them. The average diameters of individual CNFs vary from 18 to 45 nm.

Sources	Process	Diameter Average (nm)
Bagasse	Ultrasonic 700 W	44
Rice straw	Grinding	19
Wheat straw	Grinding	27.89
Wheat straw	Ultrasonic 400 W	45
Sawdust	Grinding	21.74
Sawdust	Ultrasonic 400 W	1–15 μm

Table 6. Diameters and aspect ratios of cellulosic nanofibers extracted from different sources.

Comparing the two mechanical methods used to convert microfibers to nanofibers, the grinder method was found to have a higher mechanical efficiency. This is due to its higher power compared to that of the ultrasonic device. It was found (**Table 6**) the fiber extracted from sawdust disintegrated by ultrasonic 400 have diameter between 1-15 μm . The reasons for this could be: First, the low shear stress of the ultrasound to separate the fibrils; and second, the stronger fiber structure of sawdust compared to the other sources of lignocellulose listed in **Table 6**.

Figure 8 shows the FE-SEM and TEM of CNFs as a network of intertwined long nanofibers with a cellulosic appearance.

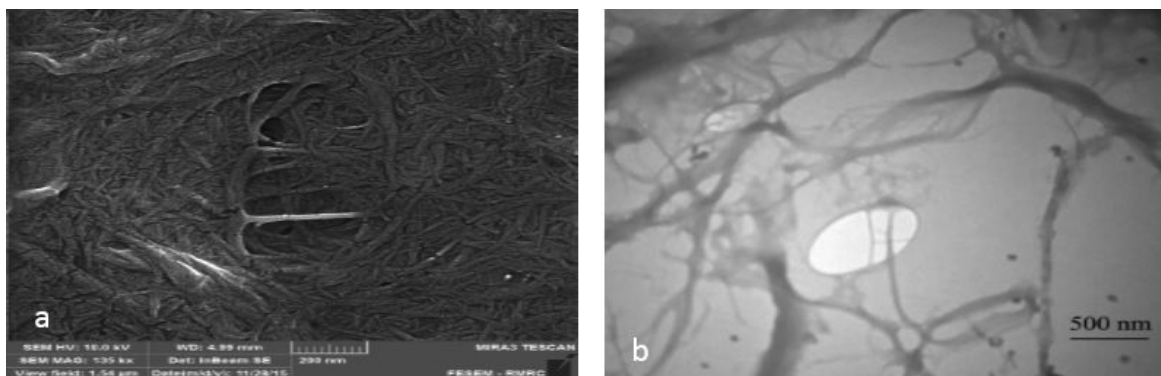


Figure 8. (a) FE-SEM and (b) TEM of cellulose nanofibers.

3.3. Crystallinity and thermal properties

The amount of crystallinity in the cellulosic nanofibers is expressed as total crystallinity index (TCI). Represented by Equation (1) in this equation, A_{1372} is absorption in 1372 cm^{-1} and A_{2900} is absorption in 2900 cm^{-1} in ATR spectrum. Generally, the peak in the infrared spectrum at 1372 cm^{-1} represents the modified C-H standardization of crystalline regions, and reveals any change in crystallinity, and that at 2900 cm^{-1} represents C-H stretching, which is a measure of amorphous regions. The absorption band at these two points represents the total crystallinity index, which is representative of the degree of crystallinity. The TCI values are reported in **Table 7**.

$$TCI = \frac{A_{1372}}{A_{2900}} \quad (1)$$

One well-known characteristic of cellulosic materials is that they experience fast thermal degradation at low to moderate temperatures, particularly at temperatures below 400°C . The thermal decomposition of lignocellulosic materials begins with the disintegration of hemicellulose followed by pyrolysis of lignin, depolymerization of cellulose, active flaming combustion, and char oxidation. The thermal stability of cellulosic fibers is an important parameter

for using them in the manufacture of composites. The structure and chemical composition of cellulosic fibers drastically influence their thermal Degradation. The first stage takes place at temperatures ranging from room temperature up to 120°C, at which a little weight loss is observed in the TGA thermogram of CNFs; Which is related to the evaporation of water. The second stage Occurres at temperatures in the range of 220 to 390°C, where the destruction of the crystalline regions are started and polymer decomposition is simultaneously triggered, which led to enhance the amorphous structure and ultimately to reduction in the degree of polymerization. The third stage from 390 to 600°C involves the complete destruction of the crystalline region and the formation of D-glucopyranosemonomers by the decomposition of cellulose, which could be further converted into free radicals [48–50].

Sources	TCI
Bagasse	1.26
Rice straw	1.4
Rice husk	1.56
Wheat straw	1.32
Wheat straw	1.232
Maize	1.564
Sawdust	2.507

Table 7. TCI values of nanofibers from different sources.

4. Conclusions

Today, cellulose nanofibers because of their unique reinforcing effect are widely used in Nanocomposite. The effect of type of plant source and mechanical process used for production of nanofibers, on its properties, including the specific surface area and aspect ratio is impressive. Among the mechanical methods used to produce nanofibers, super grinder has the maximum efficiency. Due to creating higher tension. Different sources, produce nanofibers with cellulose content ranging between 85–95% and diameter changing between 18–45 nm depend on the employed mechanical method.

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