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PROPERTIES OF CELLULOSE REINFORCED COMPOSITES: A REVIEW

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ABSTRACT

This paper provides a review of cellulose, sources, extraction, molecular structure, cellulose whiskers, preparations, and morphology. The mechanical and thermal properties of cellulose reinforced composites are also discussed. Detail structure of Nano whiskers is also reported. As a renewable biomaterial, the most common source of cellulose is the plant. These plants include fruit fibers (coir), seed fibers (cotton), wood, leaf fibers (sisal), bast fibers (jute, kenaf, and hemp). Other sources of cellulose are from micro-organisms such as fungi, tunicates, bacteria, and algae. Cellulose whiskers are isolated from cellulose fibers by acid hydrolysis. Cellulose micro fibril structures are made of both amorphous and crystalline regions. The amorphous regions are vulnerable to hydrolysis by acids compared to the crystalline domains. Several techniques among which are Field Emission Scanning Electron Microscopy (FESEM), Transmission electron microscopy (TEM) and Atomic Force Microscopy (AFM) have been used to study the morphology of cellulose whiskers. An interface between cellulose whisker and matrix is a transition zone between the matrix and the cellulose whiskers. It plays an important role in the overall mechanical properties of the composites. A soft interface domain will yield a greater resistance to fracture, while the composite will be low in stiffness and strength. On the other hand, a stiffer interface domain may cause the composite to be strong and stiff and less resistant to fracture. The addition of CW into polymers matrices has little or no effect on the glass transition temperature, (Tg) except on the modification of CW.

Keywords: *Cellulose, whiskers, mechanical, thermal, properties, biomaterials.*

1. INTRODUCTION

Some major advantages of Cellulose are its abundance, low density, low cost, and renewability. Some animals and bacteria can synthesize it. It can also be found in plant cell walls [1]. To replace inorganic fillers, like glass fibers and synthetic polymers, cellulose in the form of fibers has been used widely as alternative reinforcements in composite materials [2-4]. Fibers from cellulose have a large variation in their mechanical and physical properties [5]. The variations are attributed to; species, soil type, and climatic conditions. This natural fiber contains a large number of defects. These defects called kink bands and voids have a detrimental effect on their mechanical properties. The defect initiates brittle fracture when subjected to stress [6, 8]. Most of the defect in their structures is due to the processing or when isolating the fibers from plants [6, 8]. Elimination of these defects and variations in the cellulose can lead to almost defect-free, highly crystalline cellulose. According to Dufresne [9], removal of this defect can be achieved by disintegrating the fibers into nano or

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micro fibrils. Disintegrating the fibers into nanoscale sometime called whiskers has attracted considerable interest as possible reinforcements in composite materials. The interest is due to their impressive properties. These include high aspect ratio, high strength, biodegradability, low density, and renewability [2, 10-13]. Finding ways to exploit this biomaterial for a wide range of applications will lead to greater resource efficiency.

Cellulose been one of the most ubiquitous materials in nature, has been widely used in the formation of paper, wood, board, and fibers [14-16]. As raw materials, cellulose has been used to make regenerated cellulose products such as films and fibers [17-18]. Plants such as cotton, pulp, flax, sisal, and hemp fibers are the raw material sources of cellulose [18-19].

Cellulose whiskers (CWs) are produced from cellulose fibers by acid hydrolysis [20] To obtain a highly yields crystalline whiskers, selective degradation of the more accessible amorphous part of the material is done. The whiskers are rod-like in appearance with very high aspect ratio (L/D) and surface area characteristics. This property gives the advantage of better interfacial interactions between the whiskers and the matrix. Depending on the origin and the hydrolysis procedures, the aspect ratios are found to vary. Incorporating a small number of whiskers into a polymer matrix can lead to nanocomposites material. Most nanocomposites exhibit significant mechanical properties when compared to the neat polymer. Tashiro and Kobayashi [21] reported a theoretical value of Young's modulus for a perfect crystal of native cellulose along the chain axis as 167.5 GPa

Interfacial behavior between CWs and the polymer matrix strongly influence the mechanical properties of composites. One major problem that results in poor mechanical properties is the poor adhesion and dispersion between CWs-polymer matrix interactions. To solve this problem, thereby enhancing the properties, studies which include improving dispersion using surfactants [22] and surface chemical modification through partial silylation [23] have been reported. Due to the presence of hydroxyl-rich surface of CWs, they form hydrogen bonds, particularly with polar surfaces, thereby strengthening the interface. Hydrogen bonds between CWs help in the formation of a rigid three-dimensional network above their percolation threshold [24]

2. CELLULOSE

2.1 Cellulose sources

There are several sources of cellulose available for use. Been a renewable biomaterial, the most common source where the production of over 100 billion tons per year [17, 25] is the plant. The plant which can equally be called the vegetable kingdom includes fruit fibers (coir), seed fibers (cotton), wood, leaf fibers (sisal), bast fibers (jute, kenaf, and hemp), and other plant substances. Other sources of cellulose are from micro-organisms such as fungi, tunicates, bacteria, and algae. Tunicates are marine invertebrate animals from the subphylum Tunicata family. Research in this area focuses on a class of tunicates known as *sea squirts* (*Ascidiacea*). A Specie of the marine invertebrate filter feeders. There are over 2300 species of *Ascidiacea;* examples are *Halocynthia roretzi* [26], *Halocynthia papillosa*, [27], and *Metandroxarpa uedai*. [28]. The outer tissue of the tunicates is called *a tunic*. From here, a purified cellulose fraction termed *tunicin* is extracted. Tunicate cellulose is composed of almost pure cellulose of CIβ allomorph type with high crystallinity. The micro-fibrils of tunicate cellulose have a very large aspect ratio (60–70) and high specific surface area $(150-170m^2/g)$ [29-31]. Different species of algae, brown, green, gray, and red, have also been considered as sources of cellulose. For example, *Micrasterias denticulate, Valonia*, *Micrasterias rotate, Micrasterias denticulate*, *Coldophora*, *Boerogesenia* [32, 33] have been used. By acid hydrolysis and mechanical treatment, CHWs with a large aspect ratio (>40) can be extracted from an algae cell wall [16]

2.2 Extraction of Cellulose

Cellulose can also be extracted from softwoods and hardwoods, plant fibers or seeds, tunicates, and micro-organisms such as bacteria, algae, and fungi. Cellulose from plants is the key source of cellulose with a production of 1011-1012 tons per year [17]. Hemicelluloses and lignin are the two major constituents of plants. Therefore, heavy chemicals and mechanical treatments are required to separate cellulose fibrils from these constituents. Figure 1 shows the process of isolating cellulose fibrils from other constituents.

Wood, containing 30 to 40 % of cellulose, is first reduced into chips. One of any two chemical processes can be used, that is sulphite or a sulphate process. The difference in the process been the temperature used. While sulphate is kept at $170-180^o\mathrm{C}$, sulphite process temperature is $130-140^{\circ}\mathrm{C}$. Chlorine or peroxide chemicals act as a bleaching agent. A pulp containing 90 to 95 % of cellulose is obtained after washing, drying, and packaging. The absence of lignin or hemicelluloses or other plant constituents in bacterial and tunicate cellulose made it possible for a pure form of cellulose from these sources [34], thereby reducing the purification treatments. In other words, only alkali solutions like sodium hydroxide are used to remove impurities, such as leftover cell debris coming from the bacterial cellulose synthesis. In addition to the quality been obtained due to purification, the purification process has been found to improve the physical properties of bacterial cellulose sheets. Some of the properties include thermal stability, thermo-mechanical and mechanical properties [35, 36]. Table 1 shows the percentage composition of cellulose from different sources. Depending on the type of plant, having different cellulose contents, as shown in Table 1, the separation process of cellulose from other wood constituents can be more or less harsh, time-consuming, and expensive.

2.3 Molecular structure of cellulose

Cellulose is a linear syndiotactic homopolymer. It is made of anhydroglucopyranose units of lengths 1.03 nm. This length is linked by β-(1, 4)-glycosidic bonds resulting into the formations of a molecular sequence [37, 38]. Depending on the source, method of isolation, and the molecular weight determination methods, the molecular weight of cellulose varies widely (50000-2.5 million) [39]. Each of the anhydroglucopyrose units of the cellulose has two secondary OH groups and one primary OH group (the C6-OH) at the C3and C2 positions. This OH groups can undergo esterification and etherification chemical reactions [40]. The presence of these hydroxyl groups, also favors hydrogen bonding between the cellulose polymer chains (intermolecular) hydrogen bonding and also within individual polymer chains (intra-molecular) hydrogen bonding. The stiffness of the cellulose macromolecule is imparted due to these intra and intermolecular hydrogen bonding. While intermolecular hydrogen bonding, enhance mechanical interrelation within the cellulose polymer chains, intra-molecular hydrogen bonding contributes more to the axial toughness of individual cellulose polymer chains. Intermolecular hydrogen bonding could also occur among cellulose fibrils, which might clarify the good mechanical properties of some cellulose films formed from these materials.

As shown in Figure 2, each anhydroglucose element is in the chair conformation, with the OH groups in the equatorial, and the H atom in the axial points [41]. The anhydroglucose units are positioned 180° to each other consecutively about the main axis, which results in unstrained linear conformation with the least steric limitation [41].

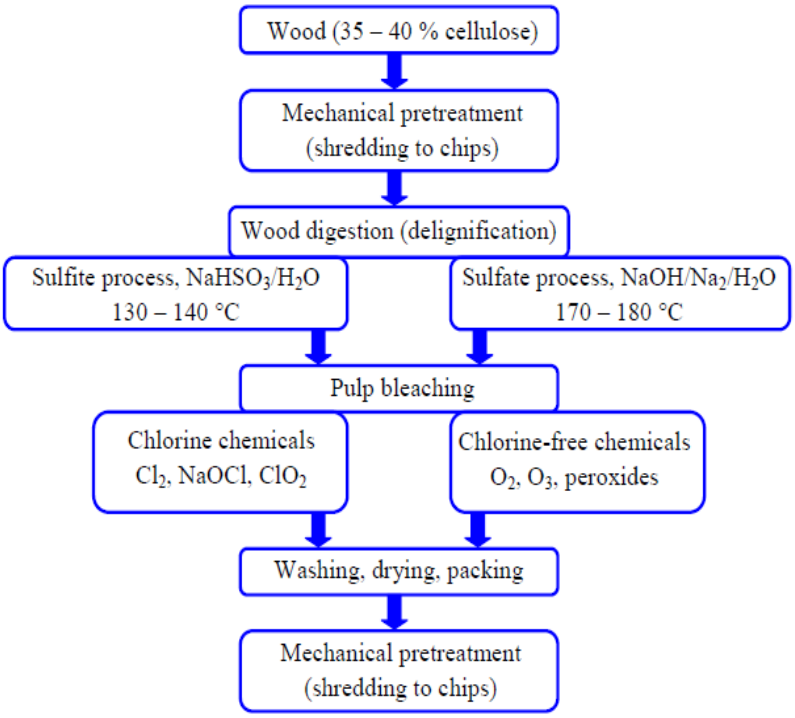

Figure 1: Isolation cellulose fibrils [17]

Table 1: Percentage composition of cellulose from different [14]

Sources	Composition (%)			
	Cellulose	Hemicellulose	Lignin	Extract
Wheat straw	30	50	15	5
Coir	32-43	10-20	43-49	4
Corn stalks	35	25	35	5
Kenaf	36	21	18	2
Bagasse	40	30	20	10
Softwood	40-44	25-29	25-31	1-5
Hardwood	43-47	25-35	16-24	2-8
Com cobs	45	35	25	5
Flax (unretted)	63	12	2	6
Hemp	70	22	6	2
Flax (retted)	71	21	2	6
Jute	71	14	13	2
Istle	73	4-8	17	2
Sisal	73	14	11	2
Rammie	76	17	1	6
Henequen	78	4-8	13	4
Sunn hemp	80	10	6	3
Cotton	95	2	1	0.4

The hydrogen bonds are formed amongst the ring oxygen atom of one glycosyl unit and the hydrogen atom of the C-3 OH group of the succeeding ring across the glucosidic linkage [42]. These hydrogen bonds encumber the free gyration of the rings on their linking glycosidic bonds, causing stiffening of the chain. The ribbon-like character observed for the cellulose macromolecule permits adjacent cellulose chains to fit together in a well-arranged crystalline region [43]. This clarifies the strength of plant material. The hydrogen bonds also contribute to the insolvability of cellulose in common solvents, except for some acids that can destroy the intermolecular bonds [44]. Figure 3 illustrates the intra- and intermolecular hydrogen bonds within the cellulose structure.

During biosynthesis, separate cellulose molecules are packed into bulky units called elementary fibrils before being bonded in the fabrication of micro fibrils. The micro fibrils are then assembled into cellulose fibers. These linear micro fibrils cellulose chains are firmly bound to each other by van der Waals, intra- and intermolecular hydrogen bonding's, which are then spiraled together in the walls of plant cells [45]. Due to the disarray of cellulose chains, there are relatively weak regions of the micro fibril having weaker internal bonding. This disordered region is called an amorphous region. Here the disintegration of the cellulose into rod-like particles under acid hydrolysis conditions can take place [46]

Interest in cellulose macromolecules is due to the crystalline and orientated organization. Tightly crowded cellulose chains bound together by a complex inter- and intra-molecular hydrogen bond network can be observed at the ordered crystalline region. The physical properties of the cellulose, among which are swelling, adsorption and accessibility for chemical modification

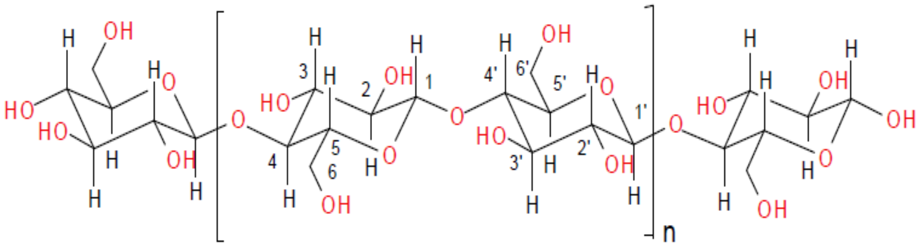

Figure 2 Chemical structure of cellulose biopolymer(Fan et al., 1987) [41].

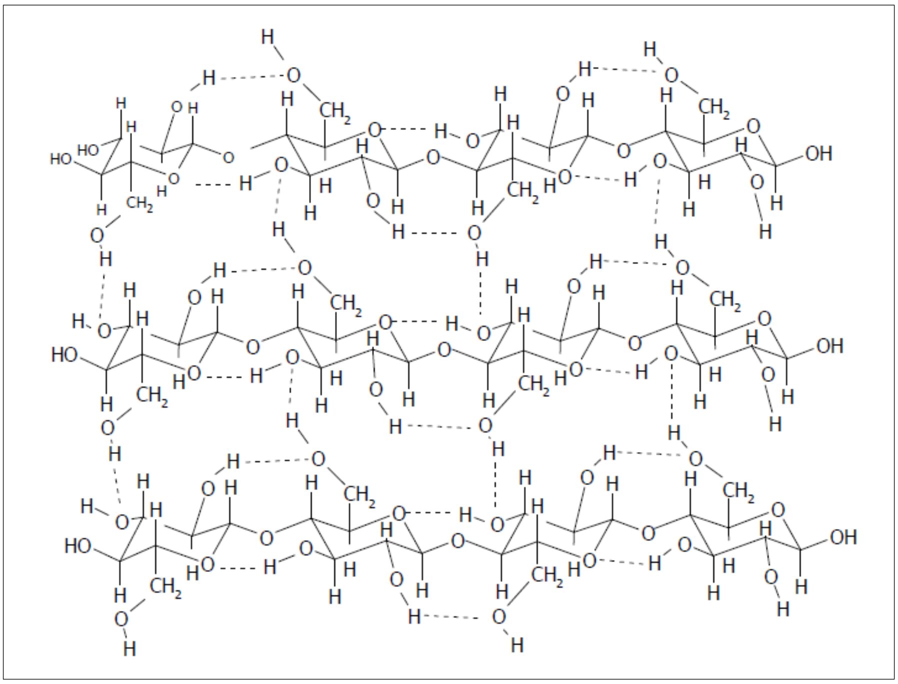

Figure 3 Intra- and intermolecular hydrogen bonds within a cellulose structure [44]

are influenced by these crystalline structures [47]. The first study work giving details of the crystalline structure, and the packing of native celluloses was reported by Meyer *et al*. [48] The report proposed that ramie cellulose has a structure with a monoclinic unit cell. The unit cell is made of two anti-parallel polysaccharide chains with dimensions a = 0.835 nm, b = 0.79 nm. Where c is the fiber axis, equal to 1.03 nm, and γ = 84° [48] A different model of the native crystalline structure of alga Valonia having a triclinic unit cell was reported by Finkenstadt and Millane [49].

2.4 Whiskers from cellulose

The application of natural cellulose fibers is limited due to the wide varied properties. These variations could be attributed to the complex structure of the cell wall. This cell wall contains highly crystalline cellulose micro fibrils embedded in a nonfibrous polymer matrix. During extraction and processing from their natural sources, defections due to chemicals or reagents are used can be generated. As a result of this defect utilization as reinforcement material mostly at load bearing composites is limited. Bearing this in mind research to produce defect-free cellulose whiskers with high crystallinity and stiffness has been carried [50] Cellulose whiskers in literature have so many nomenclatures. These are nano-fibers, nano-fibrils, micro-crystallites, nano-crystals, or even nanoparticles.

2.5 Preparation of cellulose whiskers

Cellulose whiskers (CWs) are isolated from cellulose fibers using the process called acid hydrolysis. Cellulose micro-fibril structures are made of both amorphous and crystalline regions. Due to randomly arranged cellulose chains, the crystalline regions have higher density when compared to the amorphous regions [40]. Therefore, the amorphous regions are vulnerable to hydrolysis by acids. Due to the tight packing and extensive hydrogen bonding networks, the crystalline domains are not readily accessible during acid hydrolysis process. The initials reaction only occurs on the surface of the crystallites [40]

During acid hydrolysis process, the hydronium ions, from the protonation of water, diffuse mostly into the disordered regions. This movement rapidly forms an intermediary complex by protonation of the glycosidic linkage, as shown in Figure 4 [40]. The protonation of the β-1,4-glucosidic bonds results in the slowly scissioning of the bond, thereby producing fragments of rod-like CWs [48]. The slitting of the hydrolytic cleavage of the glycosidic linkage bond is the rate-determining step of the process. This dilapidation leads to a decrease in molecular weight or degree of polymerization (DP), chemical modification, and thus waning down the strength properties of the cellulose.

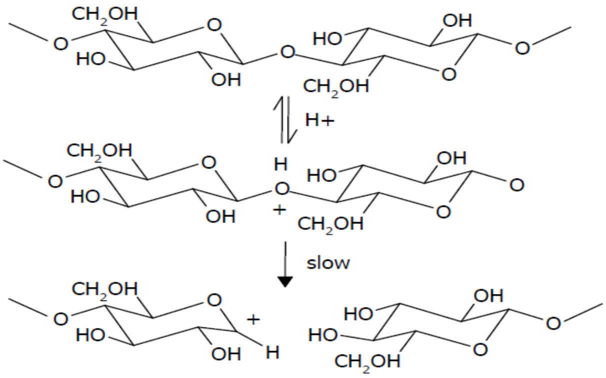

Figure 4 Mechanism of acid hydrolysis of cellulose [40]

Depending on the source, the length value of cellulose whiskers varies. For wood are about 180-200 nm, 100-120 nm for cotton, and more than 1000 nm for the Valonia and tunicates [51]. CWs or nanofibrils have been produced from a variety of sources using acid hydrolysis. Example is from tunicate [52,53] bacterial cellulose [54, 55], cotton [56, 57], and microcrystalline cellulose [58, 59]. The hydrolysis conditions that is, temperature, time, acid concentration and types of acid affect the properties of the cellulose whiskers produced. To prevent complete hydrolysis of cellulose into glucose, mild hydrolysis conditions are needed.

The effect of the preparation conditions on microcrystalline cellulose derived from filter paper powder has been reported [56]. Optimization of the acid hydrolysis conditions were carried out by varying the hydrolysis time, temperature and the intensity of ultrasonic treatments. At a hydrolysis temperature of 45 °C, an ivory-white suspension with a yield of 44 % after a 1-hour reaction was observed. An increase in surface charge of the particles and a decrease in the particle length were observed as the hydrolysis time increased. The decrease in particle size was attributed to an increase of the ultrasonic treatment time initially but remained unchanged upon further treatment. The effect of acid to pulp ratio and reaction time on cellulose whisker properties from hydrolyzed black spruce acid sulphite pulp have been reported by Beck-Candanedo *et al.* [60]. The extension of the hydrolysis time produced smaller nanoparticles with a slim size poly-disparity. Bondeson *et al.* [59] varied the acid and microcrystalline cellulose concentrations, hydrolysis time, temperature, and the ultrasonic treatment time, during optimization of the production of an aqueous steady colloid suspension of cellulose whiskers from microcrystalline cellulose. The result shows that cellulose whiskers' width of less than 10 nm and length of 200-400 nm were produced when the concentration of sulphuric acid was 63.5% (w/w) in 2 h time with a yield of 30% (base on the initial weight).

In another research, Beck-Candanedo *et al.* [60] reported the usage of sulphuric acid as the hydrolyzing agent in the preparation of CWs. Here H_2SO_4 presents the sulphate ester groups to the surface of cellulose whiskers, thereby promoting the dispersion of whiskers in aqueous solvents, leading to a highly stable suspension. In distinction to $\mathrm{H_2SO_4}$ behavior, hydrochloric acid hydrolysis produces cellulose whiskers with slight surface charge resulting in difficulties in attaining a good dispersion of the whiskers. Nonetheless, the sulphate ester group, introduced during sulphuric acid hydrolysis, has been found to denigrate the thermal stability of cellulose whiskers [55]. This sulphate ester group causes a significant decline in degradation temperature.

Araki *et al.* [58] studies have shown that the rheological behavior of the HCl and $\mathrm{H_2SO_4}$ treated suspensions are significantly different.

While $\mathrm{H_2SO_4}$ treated suspension showed no time dependence in viscosity, HCl suspension was thixotropic at concentrations >0.5% (w/v) and rheopectic at concentrations <0.3%. Cellulose whiskers can be produced using different acid suspensions. Only $\mathrm{H_2SO_4}$ hydrolyzed suspensions can form an ordered phase at a concentration above a certain critical value. $\mathrm{H_2SO_4}$ suspensions displayed birefringent characteristics and formed a chiral nematic well-ordered phase with visual appearances of a cholesteric liquid crystal [61]. The presence of negatively charged sulphate ester groups on the outward of the whiskers results into polyelectrolyte properties [56]

2.6 Morphology of cellulose whiskers

Several techniques have been used to study the morphological features of cellulose whiskers. These include Field Emission Scanning Electron Microscopy (FESEM), Transmission electron microscopy (TEM), light scattering- including small-angle neutron scattering (SANS) and atomic force microscopy (AFM) [62]. Others include polarized and depolarized dynamic light scattering (DLS, DDLS) [63] Using small-angle scattering techniques (neutron and X-ray), Terech *et al.* [62] reported that whiskers from marine animal are long and with rigid cross-sectional rectangular shape (88 x 182 Å2) fibers. With the aid of polarized and depolarized dynamic light scattering (DLS and DDLS), de Souza Lima *et al.,*[63] using the Broersma's relations reported a cross-sectional diameter of 15 mm and a length of 255 nm for cotton whiskers and a cross-sectional diameter of 16 nm and length of 1160 nm for tunicate whiskers. Field emission scanning electron microscopy (FESEM) can be used for surface morphology analysis of cellulose whiskers. FESEM is a fast and more convenient method for analyzing the dispersion and orientation of cellulose whiskers in the matrix, especially bulk cellulose nanocomposite samples. Among the information obtained include proof of the existence or non-existence of aggregates, fracture, and voids in the samples. Between FESEM and SEM, FESEM is preferred as it has higher resolution and brightness even at low voltages [64] and can easily detect agglomerates in cellulose whiskers.

Detailed information as per the dimensions and nano-sized distribution of cellulose whiskers can be obtained using TEM and AFM. Due to its superior resolution, TEM has been used to observe the features of individual whiskers. Images, as provided by TEM, revealed that aggregation whiskers particles could be due to the drying period during the sample preparation. Diffraction, mass-thickness and phase contrast are the basic contrast mechanisms, which contribute to the formation of TEM images. AFM, an alternative technique to characterize the surface morphology of cellulose whiskers, has been shown to produce artifacts initiated by the complexity of the tip dimensions with the sample dimension [65]. When compared with TEM and FE-SEM, the tip broadening effect reveals a different shape. This observation was reported by Hanley *et al.* [66]. It was reported that the cross-sections of algal cellulose micro fibrils, as observed by AFM topography, showed a rounded profile caused by the convolution with the shape of the AFM tip while TEM revealed squares profile. There have being an increase in the use of AFM to examine bulk structures of nanocomposites and cellulose whiskers [64, 66, 68]. In addition to the high resolution when compared to TEM, AFM tapping mode enables a detailed examination of soft materials by eliminating the lateral shear force. Soft materials like cellulose whiskers are difficult to image using TEM. The reasons were the sensitivity of the soft material to the electron-beam and the staining prerequisite to enhance the contrast [69]. The dimensions of hydrolyzed cellulose whiskers are dependent on, among other things, the source of the cellulose and the hydrolysis conditions used during the extraction process. The heterogeneity in dimensions could come from the variable percentage of non-crystalline regions, the packing structure of cellulose chains, and the nonselective of the hydrolysis reaction [70]. The variation in dimensions of cellulose whiskers from different sources of cellulose are shown in Table 2.2. From the table, it is observed that highly crystalline tunicate, bacterial, and algal generate cellulose whiskers with lengths of up to several microns. Wood and cotton, which have lower crystallinity compared to the rest of the sources, produce shorter whiskers. The aspect ratio value, length to width (L/W), varies from 10 to 30 for cotton and up to 70 for tunicate.

3. MECHANICAL PROPERTIES OF CELLULOSE REINFORCED COMPOSITES

3.1 Cellulose whisker-matrix interface done

An interface between cellulose whisker and matrix is the two-dimensional area between the matrix and fiber that possess intermediate properties between them [71]. It is a transition zone between the matrix and the cellulose whiskers with an undefined boundary. The interface plays an important role in the overall mechanical properties of the composites. Paul *et al.* [71] reported that a soft interface domain compared to the surrounding matrix would yield a greater resistance to fracture, while the composite will be low in stiffness and strength. In contrast, an interface region that is stiffer than the surrounding matrix may cause the composite to be strong and stiff, nevertheless less resistant to fracture. The overall characteristics of the interface are governed by the properties and structural nature of the reinforcement or fiber and the matrix. The nature of the matrix and surface energy of the cellulose whiskers affect the establishment of a network in the interface region. This network has an important impact on the mechanical properties of the resulting cellulose whisker polymer composites. Optimum mechanical properties of the composites can be achieved if whisker-whisker and whisker-matrix interactions are optimized. Good compatibility between them would result in an increase in the elastic modulus of the nano composites.

Table 2:The dimensions, Length (L) and Width (W) of cellulose whiskers from various cellulose sources using different techniques (reproduced with modification from Ref. 70)

Source	L (nm)	W (nm)	Technique	References
Bacterial	100-1000	10-50	TEM	54
Bacterial	100-1000	5-10x30-50	TEM	55
Cotton	100-150	5-10	TEM	54
Cotton	200-300	8	TEM	61
hardwood	140-150	4-5	AFM	60
Linter	25-320	6-70	TEM	26
MCC	35-265	3-48	TEM	26
Ramie	150-250	6-8	TEM	114
Ramie	50-150	5-10	TEM	75
Sisal	150-280	3.5-6.5	TEM	76
softwood	100-200	3-4	TEM	58
Tunicate		8.8x18.2	SANS	62
Tunicate	1160	16	DDLS	63
Tunicate	500-1000	10	TEM	53
Tunicate	1000-3000	15-30	TEM	28
Tunicate	100-1000	15	TEM	61
Tunicate	1073	28	TEM	26

Using cotton seed linter cellulose crystallites as the filler Lu *et al.* [72] reported the mechanical properties of glycerol plasticized starch composites. The result shows that as the cellulose crystallite increases from 0 to 30 wt. %, Young's modulus of the composite increased from 36 MPa for the neat polymer to 301 MPa for the bio-composite, while the tensile strength increased from 2.5 for the neat polymer to 7.8 MPa for the bio-composite. This improvement was believed to be due to the hydrogen bond interactions between whisker-matrix and whisker-whisker. The interfacial interface between the matrix and cellulose whiskers could be enhanced by chemically modifying the cellulose whiskers with long-chain molecules such as polymer chains, [73] surfactants, [74] organic acid chloride, [75] and isocyanates [76]. Stress transfer from matrix to reinforcement dependent largely on the degree of adhesion between matrix and reinforcement. Strong adhesion is needed for an effective stress transfer and distribution of load throughout the interface. Researches on the information of the interfacial behavior between matrix and cellulose whiskers have been carried out. Different techniques have being used to characterize the interface of lignocellulosic fiber-reinforced composites. These include microscopic, spectroscopic, micro-mechanical, and thermodynamic. Micro bond test and single-fibers pull-out test are the well known micro mechanical techniques. In a pull-out test, the end of the fiber is embedded in a polymer matrix before pulling it out, while restraining the matrix. In a micro bond test, a small droplet of the matrix deposited on the fibers is sheared off as the fibers are pulled while restraining the droplet [77]. These two methods are known to be among the most effective and convenient methods in estimating the interface between the matrix and fiber. They are not easily applied to nanostructured materials. With the use of AFM and SEM Hang and Barber [78] reported the determination of nano mechanical properties of individual mineralized collagen fibrils (CF) from bone tissue. The result shows a linear deformation on the start, followed by an inhomogeneous deformation above applied strains of 2-3.7% [78]. The isolation of a single fragment of cellulose whiskers without damaging them has made it difficult for the application of model nano composite. Dispersing whiskers within a composite structure has been difficult [79]. This has led to the use of Raman spectroscopy to investigate the factors affecting the interfacial behavior between nano-sized reinforcing components and polymer matrices and determine molecular deformation of cellulose nano composites.

3.2 Elastic modulus of cellulose whiskers

The elastic modulus of cellulose whiskers is significant in order to exploit their full potentials as reinforcements in composites materials. Several attempts, either theoretically or experimentally, have been made to determine the modulus of cellulose [80-85]. Meyer and Lotmar [80] obtained a value of around 120 GPa when modeling of the mechanical properties of cellulose was carried out. This value was later corrected by Lyons [81] due to the incorrect cellulose structure used by Meyer and Lotmar. The calculation as presented by Lyons was modified by Treloar in 1960 [82]. Using highly oriented bleached ramie, and an X-ray diffraction on deformed fiber bundles Sakurada *et al.* [83] reported a modulus of 138 GPa for cellulose I. Using the same methods as Sakurada *et al.*, Mann and Roldan-Gonzalez [84] reported an elastic moduli range of 70-90 GPa for cellulose I and II. In contrast, the experimental estimates of 136 ± 6 GPa was reported by Kroon-Battenburg *et al.*, [85] and 120-135 GPa calculated by Matsuo *et al.,* [86] for cellulose I. A higher theoretical Young's modulus of 167.5 GPa for cellulose I was reported by Tashiro and Kobayashi [21]. This higher value when compared to earlier reported values was thought to be due to the thermal restriction movement of the chains at low temperatures when the calculations were being carried out.

The difference between the crystal moduli of cellulose I and II as measured by X-ray diffraction and the theoretical modulus reported by previous studies was analyzed by Matsuo *et al.* [86]. They observe that the values of the experimental and theoretical crystal moduli were comparable when a series of coupling between crystalline and amorphous phases was dominant. Conversely, when a parallel coupling was present, the result is different. An increasing degree of molecular alignment and crystallinity will decrease morphological dependence. Hence, films and fibers with high crystallinity and a high degree of molecular orientation were recommended for the determination of crystal lattice moduli using X-ray diffraction. Using inelastic X-ray scattering (IXS) a much higher value of 220 GPa elastic modulus of native cellulose crystals was reported by Diddens *et al.*, [87] The high value observed here could be attributed to the sensitivity of the IXS technique crystal properties which segregate the disordered material

A new technique the Raman spectroscopic has been used to determine the elastic modulus of tunicate cellulose [30]. A shift in the Raman band located at $1095\ \mathrm{cm}^{-1}$ was used as an indication of the stress in the material. The strain sensitivity of the shift for the Raman band located at $1095\ \mathrm{cm}^{-1}$ for the tunicate cellulose was shown to be –2.4 ± $0.2\ \mathrm{cm}^{-1}\ \%^{-1}$ while the modulus obtained was around 143 GPa. A modulus of 145 GPa was obtained when a molecular mechanic approach was also used.

3.3 Preparation of cellulose nano composites

Composites usually consist of a strong and stiff component embedded in a softer polymer matrix. Cellulose polymer nano composites are composites having two-phase materials, one of these phases having dimension on the nano meter scale (10-9 m) [51, 88]. The objective of adding nano-sized cellulose particles in a polymer matrix is to advance the properties devoid of sacrificing the mechanical matrix properties. Several polymer matrices have been used for cellulose whisker based nano composites, among these are poly(oxyethylene) (POE) [89], polylactic acid (PLA)[90], poly(vinyl chloride) [91], isotactic polypropylene poly(vinyl acetate) [74, 92] and glycerol-plasticized soy protein isolate (SPI) [93]. Nano composites tend to have superior mechanical and physical properties when compared with typical composite [5, 12]. Many processing methods for the preparation of nano composites have been reported. These include a solution or solvent casting, Melt compounding [16, 95], and Partial dissolution [96-99]

In solution or solvent casting, cellulose nano fibers are dispersed in a medium such as water or organic solvents the suspension is mixed with a polymer solution and vigorously shaken. The suspension is cast on a plane that will define the shape of the film needed. Cellulose nano composite films are formed by evaporation of water or solvents. Thermoplastic polymers such as poly(lactic acid), poly(vinyl alcohol), polyethylene, polypropylene, are used as a matrix in melt compounding technique.

The thermoplastic polymer, as listed above, is mixed with cellulose nano fibers using compounding mixing and then extrusion. Compression molding or injection molding are then used to prepare specimens. In partial dissolution method of nanocomposite preparation, cellulose fibers, microcrystalline cellulose, or bacterial cellulose are dispersed in a mixture solution of, N-dimethylacetamide (DMAc) and lithium chloride (LiCl) for a specific period of time. During this period, the surface of cellulose to be used as a matrix phase reinforced by the remaining on dissolved cellulose component will be dissolved [96-99]. These composite materials show outstanding interfacial compatibility because both matrix and reinforcing phases are cellulose [97-99]

Three different treatments were given to CWs; CWs treated with maleic anhydride (MA) grafted PP (MAPP), CWs treated with surfactant and CWs without surface modification. Nano composites films were produced using atactic polypropylene (PP) polymer as matrix [100]. It was reported that all the CW films investigated had improved mechanical properties for both tensile and dynamic mechanical analysis (DMA) testing when compared with neat PP. In another report, Ljungberg *et al.* [74] used isotactic PP polymer matrix as against atactic polypropylene (PP) polymer with the same treatment applied to CWs. Here the mechanical properties at large deformation depended strongly on the dispersion quality of the whiskers.

The mechanical properties of $\mathrm{LiClO_4}$-doped ethylene oxide-epichlorohydrin reinforced CWs at different loading of 1-15 wt. % were reported to have better properties with a small reduction in the electrical conductivities [101]. With a small amount of acrylic acid and copolymerization of styrene and butyl acrylate Favier *et al.* [51] mixed CWs to form polymer lattices. The effect of cellulose whiskers loading from 1 to 14 wt. % on the mechanical properties of the polymer matrix was investigated. Films heated above the glass transition temperature of the polymer were found to have improved on their mechanical properties. Nano whiskers from drumstick fruit fibers of Moringa oleifera were prepared by acid hydrolysis [102]. Epoxy matrix was used as resin at different weight fractions (0.06, 0.12 or 0.18 wt. %) of CWs. In comparison with the neat cured epoxy resin, the tensile and bending moduli of the epoxy composites increased by 31.4 % and 38.2 %, respectively, at 0.18 wt. % while the tensile and bending strength significantly decreased by 48.7 % and 41.6 % respectively at the same 0.18 wt. % nano whiskers. Polypropylene (PP), a polar polymer, and cellulose nano whiskers, a polar material, were used to produce nano polymer composites by Elif *et al.* [103]. Improvement of the compatibility was made by using maleic anhydride grafted PP which serve as a coupling agent. The polymer matrix dissolved in toluene to enhance the uniform distribution of CWs. The tensile strength of the composite compared with neat PP improves by 70–80 % with the addition of CWs. The crystallinity was observed to have improved by about 50 % in the CWs.

3.4 Micro-fibrillated Cellulose Nano composites

Nano cellulose can be separated into three main categories: namely cellulose nano whiskers (CNWs), bacterial cellulose (BC) and micro fibrillated cellulose (MFC) [13, 15]. Cellulose nano whiskers (CNWs), sometimes called nano crystalline cellulose (NCC), are generated by acid hydrolysis to remove the amorphous regions from cellulose sources. This is followed by the ultrasonic treatment [13, 15]. 90 % crystallinity of rod-like shaped cellulose nano fibers are obtained after treatment [3, 15]. The dimensions (width and length) depend on the source of raw materials. The flexibility of the material is limited due to fewer amorphous regions [13].

Bacterial cellulose (BC), also known as bacterial nano cellulose (BNC), can be produced from different species of bacteria, among which are *Agrobacterium*, *Rhizobium, Acetobacter*, and *Sarcina*. Bacteria are fermented in the low molecular weight carbon sources such as glucose [10, 15, 99, 104]. Nano fibers with diameter ranging from 20 nm to 100 nm are obtained. Bacterial cellulose materials are found to have high crystallinity, molecular weight, and good mechanical properties [12, 15, 104].

Microfibrilalted cellulose (MFC), also called nano fibrillated cellulose (NFC), is a network of interconnected nano fibrils and micro-fibrils with diameters in the range of 5 - 100 nm. These fibrils have a higher aspect ratio and are more flexible than cellulose whiskers [12, 15]. Due to the superior properties of MFC to other natural fibers, MFC has been used to prepare composite materials with a large number of polymers.

Table 3 Mechanical properties of PLA composites reinforced by MFC prepared by different techniques. Mechanical properties of neat PLA are provided in the brackets.

Manufacturing process	MFC Content (wt. %)	ε (%)	σ (MPa)	E (GPa)	Reference
Premixing, kneading and compression molding	10	2.2(4.2)	75(56.2)	4.7(3.4)	[111]
	20	1.7(3.1)	69.4(60.9)	5.7(4.0)	[112]
	10	2(3.1)	66.2(60.9)	4.7(4)	

These include acrylic resin [19, 106], polyurethane [123], poly(vinyl alcohol) [2,107,108], and phenol-formaldehyde resin [109] among others.

The effect of MFC on the mechanical properties of MFC reinforced polyurethane thermoplastic composite has been reported [123]. At 16.5 wt. % of MFC, the stiffness and strength of the composite were found to increase by 3,000 % and ~500 %, respectively, when compared with the pure polyurethane resin. MFC reinforced poly(vinyl alcohol) composites exhibited outstanding mechanical properties and biodegradability [2]. Compared to the pure resin MFC reinforced phenol formaldehyde composites were found to increase by ~50 % [109]. Due to environmental waste problems, poly(lactic acid) (PLA), a biodegradable polymer, has attracted extensive attention. Similarities of the mechanical properties and processing routes of PLA have given it an advantage over conventional oil-based polymers such as polyolefins [5, 110]. This advantage has led to the production of green composites with MFC [10, 12, 111]. Table 3.3 is examples of MFC reinforced PLA composites prepared using different techniques and their mechanical properties.

A mixture of acetone and water was vigorously mixed in MFC and PLA. On complete dissolution of PLA, the suspension was evaporated at 70 °C. The leftover of MFC and PLA was subsequently blended by a twin rotary roller mixer. Composite sheets of PLA/MFC were made after cutting the blend into pieces and applying compression molding. PLA composites reinforced 10 wt. % MFC was observed to show the peak mechanical properties. The strength and Young's modulus of the composite were found to increase by 33 and 38 %, respectively, when compared with the pure PLA.

Increase in wt. % of MFC after 10 wt. % shows a decrease in mechanical properties. The drop in mechanical properties was attributed to the agglomeration of MFC [111]. Using a similar procedure to prepare MFC reinforced PLA composites, Suryanegara *et al*. [112] first stirred MFC in a mixture of water and acetone. The liquid segment was successively separated from a mixture of water and acetone to acetone. The acetone was removed and was replaced with dichloromethane. PLA was gradually added to the suspension and stirred for 2 hours until the PLA was completely dissolved. On evaporation of the solvent, the mixture of PLA and MFC was blended using a twin rotary roller mixer. Composite sheets of PLA/MFC were made after cutting the blend into pieces and applying compression molding. Samples were annealed at 100 °C for 60 min to obtain highly crystallized composites. At 20 wt. % reinforced MFC, the tensile strength and Young's modulus were enhanced by 20 % and 57 %, respectively, when compared with annealed PLA. Due to the high crystallinity of PLC, the strain at break decreased from 7 % to 2 %. The improvement in Young's modulus and tensile strength of the composites was attributed to the stress transfer from the polymer matrix to the stiff fibrous reinforcement of MFC, in addition to the high degree of crystallinity of the composite materials.

4. THERMAL PROPERTIES

Most literature reports that the addition CWs into polymers matrices seems not to change the glass transition temperature *T*g, irrespective of the nature of the polymer, the source of the CWs, or the processing conditions [9, 24]. Bearing in mind the high specific area of CWs, these observations seem to be in conflict with it. Cases where the T_g was affected, on the addition of CWs as filler, was attributed to the plasticization effect of water and the strong interaction between CWs and the matrix. It has been reported that for polycaprolactone-reinforced polymers [73, 113] plasticized starch [114, 115], cellulose acetate butyrate [116, 117], and poly(ethylene oxide)[87] semi crystalline polymers, the addition of CWs has no influence on the melting temperature (T_m) of the nano composites. A change in T_m was observed when chemically modified CWs were used in the nano composites, an indication that the modified CWs have strong interactions with the matrix. It can be said that the change in T_g and T_m is primarily governed by the CWs-matrix compatibility, which, to a large extent, depends on the surface chemical modification.

A cross-linked cellulose nano composites of poly(methyl vinyl ether-co-maleic acid) and poly(ethylene glycol) were produced by Goetz *et al.* [118] at different loading of 0, 25, 50, 75, and 100 wt. % of CWs. It was observed that at equilibrium, the 25 wt. % CWs film absorbed a higher amount of water when compared with 50 wt. % and 75 wt. % CWs of film. The absorption of water led to the swelling of the film-forming a stable gel. Using chloroform as a solvent and with a solution casting technique, a nano composite of poly(lactic acid) (PLA) as a polymer matrix and CWs as a nano reinforcement filler was produced by Petersson *et al.* [119]. They reported that there was no degradation in composites within the temperature range of $25 - 220\ ^oC$, where PLA was processed. Dufresne *et al.* [120] used poly(hydroxy alkanoates) latex as a polymer matrix and CWs as reinforcing filler. The effect of CWs on the glass transition temperature T_g of the polymer composites was not strong. Nevertheless, above T_g, a larger increase in composite modulus was observed as CWs increases.

A stable suspension of CWs in N, N-dimethylformamide (DMF) was used to form a nano composite [121]. CWs did not affect the thermal properties of the matrix. The wettability linked with the high dielectric constant of DMF was sufficient to disperse CWs in DMF. The tan δ peak of polyurethane reinforced CWs shifted toward a higher temperature, indicating an increase in T_g by $\sim 7 - 8\ ^oC$ [122]. Polypropylene (PP) and a polar polymer and cellulose nano whiskers a polar material was used to produce nano polymer composites [103]. Improvement of the compatibility was made by using maleic anhydride grafted PP, which serves as a coupling agent. The polymer matrix dissolved in toluene to enhance the uniform distribution of CW. As the content of CNW increases, the composite exhibits higher thermal degradation temperature, higher hydrophilicity, and higher thermal conductivity.

5. CONCLUSION

The scope, multiplicity, and productivity of research that has been stirred over the past few years by cellulose nano materials has been amazing, but not completely surprising in the current biomass and bioenergy mindful climate. Cellulose is one of the most abundant and cheap biomaterials. The availability of this biomaterial made research interesting both to the industry and academic researchers. The abundance of the material has made it possible for researchers to generate products and materials that can add value to humanity, especially when processed at the whisker level. This article is aimed at reviewing the sources of cellulose, its extraction, preparation of cellulose whiskers and its morphology, mechanical and thermal properties of CW reinforced composites. This review has endeavored to present a wide view of the interesting logical and engineering findings and progresses that have been accomplished. It has been presented that cellulose nano crystals have thrilling potential as reinforcements in nano composites. Due to their nano-size and the capability to chemically modify their surface, cellulose nano crystals will have great potential for a wide variety of applications. Different methods of extraction from either plants or animals have been presented. The mechanical properties of cellulose nano crystals, especially when properly disperse will compete well with other engineering materials.

6. REFERENCES

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