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Cellulose based biocomposites and nanocomposites – a review

Susheel Kalia,*[1] Alain Dufresne,[2] Bibin Mathew Cherian,[3] B.S. Kaith,[4] Luc Avérous,[5] James Njuguna[6] and Elias Nassiopoulos[6]

[1]Department of Chemistry, Bahra University, Waknaghat (Shimla Hills) -173 234, Dist. Solan (Himachal Pradesh), India. E-mail: susheel_kalia@yahoo.com, susheel.kalia@gmail.com

[2]Grenoble Institute of Technology, The International School of Paper, Print Media and Biomaterials (Pagora), Saint Martin d'Hères, France. E-mail: alain.dufresne@pagora.grenoble-inp.fr

[3]Department of Natural Science, College of Agricultural Sciences, Sao Paulo State University (UNESP), Botucatu 18610-307, Sao Paulo, Brazil. E-mail: bibin@fca.unesp.br, bmcherian@gmail.com

[4]Department of Chemistry, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar – 144011 (Punjab) India. E-mail: bskaith@yahoo.co.in

[5]LIPHT-ECPM, EAC (CNRS) 4375, University Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg, Cedex 2, France. E-mail: luc.averous@unistra.fr

[6]School of Applied Sciences, Cranfield University, Bedfordshire MK43 0AL, UK. E-mail: j.njuguna@cranfield.ac.uk

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Abstract

Cellulose macro- and nano- fibers have gained increasing attention due to the high strength and stiffness, biodegradability and renewability and their production and application in development of composites. Application of cellulose nanofibers for the development of composites is a relatively new research area. Cellulose macro- and nano- fibers can be used as reinforcement in composite materials because of enhanced mechanical, thermal and biodegradation properties of composites. Cellulose fibers are hydrophilic in nature, so it becomes necessary to increase their surface roughness for the development of composites with enhanced properties. In the present article, we have reviewed the surface modification of cellulose fibers by various methods. Processing methods, properties and various applications of nanocellulose and cellulosic composites are also discussed in this article.

Key words: Cellulose, fibers, nanocellulose, biocomposites, nanocomposites

1. Introduction

Cellulose fiber reinforced polymer composites have received much attention because of their lightweight, nonabrasive, combustible, nontoxic, low cost and biodegradable properties. A lot of research work has been performed all over the world on the use of cellulose fibers as a reinforcing material for the preparation of various types of composites. However, lack of good interfacial adhesion, low melting point, and poor resistance towards moisture make the use of cellulose fiber reinforced composites less attractive. Pre-treatments of the cellulose fibers can clean the fiber surface, chemically modify the surface, stop the moisture absorption process, and increase the surface roughness [1].

The production of nano-scale cellulose fibers and their application in composite materials has gained increasing attention due to their high strength and stiffness combined with low weight, biodegradability and renewability. Application of cellulose nanofibers in polymer reinforcement is a relatively new research field [2]. The main reason to utilize cellulose nanofibers in composite materials is because one can potentially exploit the high stiffness of the cellulose crystal for reinforcement. This can be done by breaking down the hierarchical structure of the plant into individualized nanofibers of high crystallinity, therefore reducing the amount of amorphous material present [3].

In this review we describe various approaches to the synthesis of nanofibers from plant sources. Potential use of macro- and nano- fibers as reinforcing material for the development of polymers composites with enhanced properties and application of these composites in various fields are also discussed.

2. Cellulose Fibers

Cellulose fibers are being used as potential reinforcing materials because of so many advantages such as abundantly available, low weight, biodegradable, cheaper, renewable, low abrasive nature, interesting specific properties, since these are waste biomass and exhibit good mechanical properties [4-6]. Cellulose fibers also have some disadvantages such as moisture absorption, quality variations, low thermal stability and poor compatibility with the hydrophobic polymer matrix [7-8].

2.1 Chemistry of Cellulose

Cellulose is the most abundant form of living terrestrial biomass [9] and finds applications in many spheres of modern industry. Existence of cellulose as the common material of plant cell walls was first recognized by Anselm Payen in 1838 [10]. Cellulose has been shown to be a long chain polymer with repeating units of D-glucose, a simple sugar. It occurs in almost pure form in cotton fiber. However, in wood, plant leaves and stalks, it is found in combination with other materials, such as lignin and hemicelluloses. Although, generally considered a plant material but some bacteria are also found to produce cellulose.

Cellulose is a natural polymer, a long chain made by the linking of smaller molecules. The links in the cellulose chain consist of sugar, ß-D-glucose [11]. The sugar units are linked when water is eliminated by combining the H and –OH group. Linking just two of these sugars produces a disaccharide called cellobiose [12]. In the cellulose chain, the glucose units are in 6-membered rings, called pyranoses. They are joined by single oxygen atoms (acetal linkages) between

the C-1 of one pyranose ring and the C-4 of the next ring. Since a molecule of water is lost due to the reaction of an alcohol and a hemiacetal to form an acetal, the glucose units in the cellulose polymer are referred to as anhydroglucose units.

The spatial arrangement or stereochemistry of these acetal linkages is very important. The pyranose rings of the cellulose molecule have all the groups larger than hydrogen sticking-out from the periphery of the rings (equitorial positions). The stereochemistry at carbons 2, 3, 4 and 5 of the glucose molecule are fixed, but in pyranose form, the hydroxyl at C-4 can approach the carbonyl at C-1 from either side, resulting in two different stereochemistry at C-1. When the hydroxyl group at C-1 is on the same side of the ring as the C-6 carbon, it is said to be in the α configuration. In cellulose, the C-1 oxygen is in the opposite or β configuration (*i.e.*, cellulose is poly [β-1,4-D-anhydroglucopyranose]). This β configuration, with all functional groups in equatorial positions, causes the molecular chain of cellulose to extend in a more or less straight line, making it a good fiber-forming polymer [13].

Because of the equatorial positions of the hydroxyls on the cellulose chain, they protrude laterally along the extended molecule and are readily available for hydrogen bonding. These hydrogen bonds cause the chains to group together in a highly ordered structure. Since the chains are usually longer than the crystalline regions, they are thought to pass through several different crystalline regions, with areas of disorder in between (“fringed-micelle” model) [14]. The inter-chain hydrogen bonds in the crystalline regions are strong, giving the

resultant fiber good strength and insolubility in most solvents. They also prevent cellulose from melting (non-thermoplastic). In the less ordered regions, the chains are further apart and more available for hydrogen bonding with other molecules, such as water. Most cellulose structures can absorb large quantities of water (hygroscopic). Thus, cellulose swells but does not dissolve in water [13].

The cellulose molecule contains three different kinds of anhydroglucose units, the reducing end with a free hemi-acetal (or aldehyde) group at C-1, the non-reducing end with a free hydroxyl at C-4 and the internal rings joined at C-1 and C-4. But because of long chain length, the chemistry of the alcohol groups of the internal units predominates, so long as the chains are not cleaved by the reaction conditions. However, unlike simple alcohols, cellulose reactions are usually controlled by steric factors than would be expected on the basis of the inherent reactivity of the different hydroxyl groups. C-2, C-3 and C-6 hydroxyls and C-H groups are active sites in cellulose for the incorporation of polymeric chains through grafting. In grafting it has been reported that the reactivity of hydroxyl group at C-6 is far less than those at C-2 and C-3 [13].

2.2 Chemical composition, Structure and Properties of Cellulose Fibers

Cellulose fibers can be classified according to their origin and grouped into leaf: abaca, cantala, curaua, date palm, henequen, pineapple, sisal, banana; seed: cotton; bast: flax, hemp, jute, ramie; fruit: coir, kapok, oil palm; grass: alfa, bagasse, bamboo and stalk: straw (cereal). The bast and leaf (the hard fibers) types are the most commonly used in composite applications [15, 16]. Commonly used plant fibers are cotton, jute, hemp, flax, ramie, sisal, coir, henequen and

kapok. The largest producers of sisal in the world are Tanzania and Brazil. Henequen is produced in Mexico whereas abaca and hemp in Philippines. The largest producers of jute are India, China and Bangladesh [1].

Plant fibers are constitutes of cellulose fibers, consisting of helically wound cellulose micro fibrils, bound together by an amorphous lignin matrix. Lignin keeps the water in fibers, acts as a protection against biological attack and as a stiffener to give stem its resistance against gravity forces and wind. Hemicellulose found in the natural fibers is believed to be a compatibilizer between cellulose and lignin [1]. The cell wall in a fiber is not a homogenous membrane (Fig. 1) [17]. Each fiber has a complex, layered structure consisting of a thin primary wall which is the first layer deposited during cell growth encircling a secondary wall. The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fiber. The middle layer consists of a series of helically wound cellular microfibrils formed from long chain cellulose molecules. The angle between the fiber axis and the microfibrils is called the microfibrillar angle. The characteristic value of microfibrillar angle varies from one fiber to another. These microfibrils have typically a diameter of about 10–30 nm and are made up of 30–100 cellulose molecules in extended chain conformation and provide mechanical strength to the fiber.

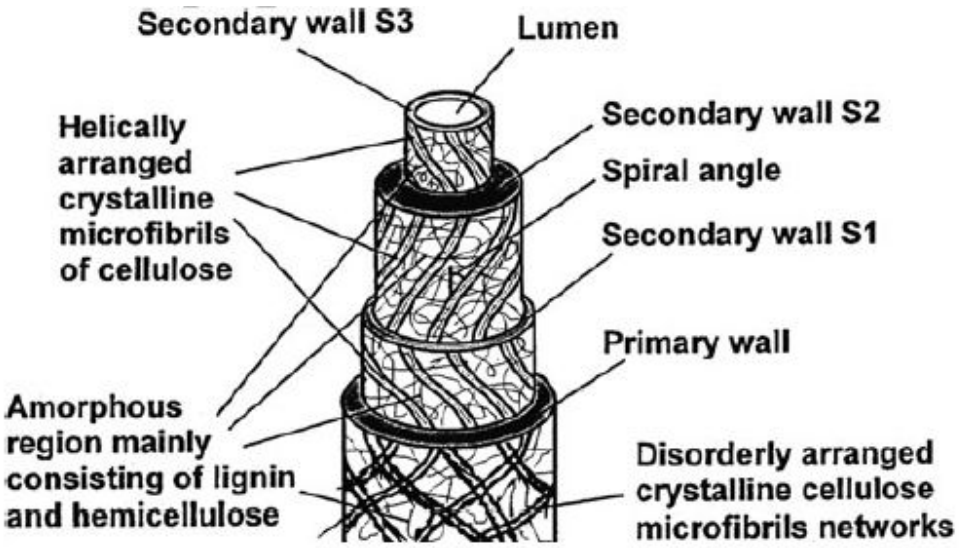


Fig. 1 Structural constitution of natural fiber cell [17]

The properties of cellulose fibers are affected by many factors such as variety, climate, harvest, maturity, retting degree, decortications, disintegration (mechanical, steam explosion treatment), fiber modification, textile and technical processes (spinning and carding) [18]. In order to understand the properties of natural fiber-reinforced composite materials, it becomes necessary to know the mechanical, physical and chemical properties of natural fibers. Flax fibers are relatively strong fibers as compared to other natural fibers. The tensile strength of elementary fibers is in the region of 1500 MPa and for technical fibers a value of circa 800 MPa was observed at 3 mm clamp length [19]. Baley [20] and Lamy and Baley [21] investigated the modulus of flax fibers. The modulus of elementary fibers is dependent on the diameter of fiber and it ranges from 39 GPa for fibers having diameter approximately 35 μm to 78 GPa for fibers having 5 μm diameter. This variation is related to the variation in relative lumen size

between fibers having different diameter. An average Young's modulus of 54 GPa was observed after numerous tensile tests on single flax fibers and the results are within the range of moduli measured on technical fibers. The mechanical, chemical and physical properties of plant fibers are strongly harvest dependent, influenced by climate, location, weather conditions and soil characteristics. These properties are also affected during the processing of fiber such as retting, scotching, bleaching and spinning [22].

Cellulose fibers have relatively high strength, high stiffness and low density [23]. The characteristic value for soft-wood-Kraft-fibers and flax has been found close to the value for E-glass fibers. Different mechanical properties can be incorporated in natural fibers during processing period. The fiber properties and structure are influenced by several conditions and varies with area of growth, its climate and age of the plant [24]. Technical digestion of the fiber is another important factor which determines the structure as well as characteristic value of fiber. The elastic modulus of the bulk natural fibers such as wood is about 10 GPa. Cellulose fibers with moduli up to 40 GPa can be separated from wood by chemical pulping process. Such fibers can be further subdivided into micro fibrils within elastic modulus of 70 GPa. Theoretical calculations of elastic moduli of cellulose chain have been given values upto 250 GPa. However, no technology is available to separate these from microfibrils [25]. The tensile strength of natural fibers depends upon the test length of the specimen which is of main importance with respect to reinforcing efficiency. Mieck et al [26] and Mukherjee et al [27] reported that tensile strength of flax fiber is significantly more

dependent on the length of the fiber. In comparison to this, the tensile strength of pineapple fiber is less dependent on the length, while the scatter of the measured values for both is located mainly in the range of the standard deviation. The properties of flax fiber are controlled by the molecular fine structure of the fiber which is affected by growing conditions and the fiber processing techniques used. Flax fibers possess moderately high specific strength and stiffness.

Quality and other properties of fibers depend on factors such as size, maturity and processing methods adopted for the extraction of fibers. Properties such as density, electrical resistivity, ultimate tensile strength and initial modulus are related to the internal structure and chemical composition of fibers [23]. Desirable properties for fibers include excellent tensile strength and modulus, high durability, low bulk density, good moldability and recyclability.

3. Cellulose Nanofibers

Cellulose nanofibers have a high potential to be used in many different area particularly as reinforcement in development of naocomposites. Many studies have been done on isolation and characterization of cellulose nanofibers from various sources. Cellulose nanofibers can be extracted from the cell walls by simple mechanical methods or a combination of both chemical and mechanical methods.

3.1 Synthesis of Cellulose Nanofibers

Alemdar and Sain [28] have extracted cellulose nanofibers from wheat straw by a chemical treatment, resulting to purified cellulose. To individualize the nanofibers from the cell walls a mechanical treatment (cryocrushing, disintegration and defibrillation steps) was applied to the chemically treated fibers. Cellulose

nanofibers were extracted from the agricultural residues, wheat straw and soy hulls, by a chem-mechanical technique [29]. The wheat straw nanofibers were determined to have diameters in the range of 10–80 nm and lengths of a few thousand nanometers. By comparison, the soy hull nanofibers had diameter 20–120 nm and shorter lengths than the wheat straw nanofibers. Zimmermann et al [30] were separated nanofibrillated cellulose (NFC) at the greatest possible lengths and diameters below 100 nm from different starting cellulose materials by mechanical dispersion and high pressure (up to 1500 bar) homogenization processes. The treatment resulted in nano-scaled fibril networks. Two commercial fibrous celluloses showed bigger cellulose aggregates with micrometer dimensions and a less homogeneous network structure.

The cellulose nanofibers were extracted by Wang and Sain [31] from soybean stock by chemo-mechanical treatments [Fig. 2]. These are bundles of cellulose nanofibers with a diameter ranging between 50 and 100 nm and lengths of thousands of nanometers.

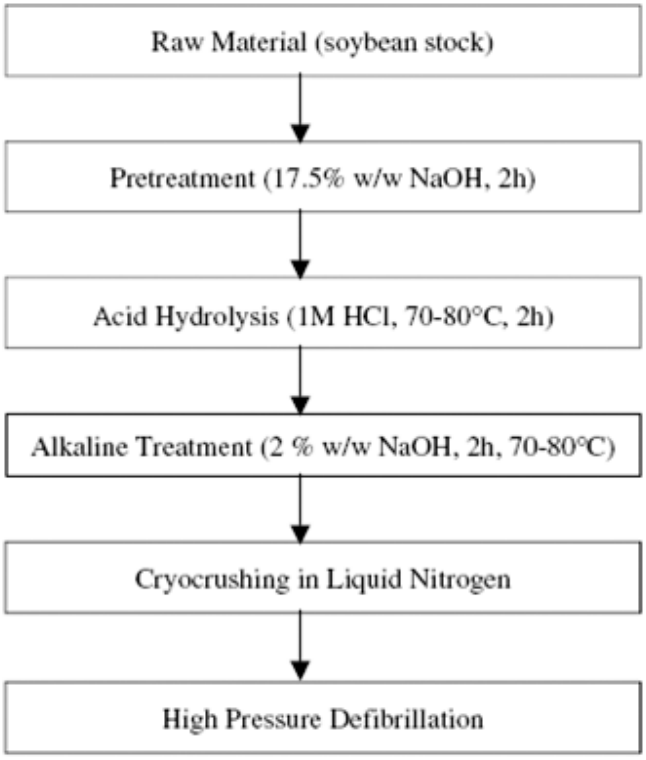


Fig. 2 Isolation of nanofibers by chemo-mechanical treatment [31]

The cellulose nanofibrils were extracted from wheat straw using steam explosion, acidic treatment and high shear mechanical treatment. Alkaline treated pulp was soaked in 8% solution of H_2O_2 (v/v) overnight. Bleached pulp was then rinsed with abundant distilled water. Bleached pulp was then treated with 10% HCl (1N) solution and mixed using ultrasonicator at temperature around 60±1 °C for 5 h. Finally the fibers were taken out and washed several times with distilled water in order to neutralize the final pH and then dried. Fibers were suspended in water and continuously stirred with a high shear homogenizer for 15 min. High shearing action breaks down the fiber agglomerates and result in nanofibrils [32].

3.2 Structure and Properties of Cellulose Nanofibers

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), wide-angle X-ray scattering (WAXS) and NMR spectroscopy have been used to study the structure of cellulose nanofibers [33]. A combination of microscopic techniques with image analysis can provide information about widths of cellulose nanofiber but it is very difficult to find out the lengths of nanofiber because of entanglements and difficulties in identifying both ends of individual nanofibers. It is often reported that MFC suspensions are not homogeneous and that they consist of cellulose nanofibers and nanofiber bundles [2].

Teixeira et al [34] were obtained the suspensions of white and colored nanofibers by the acid hydrolysis of white and naturally colored cotton fibers. Possible differences among them in morphology and other characteristics were investigated. Morphological study of cotton nanofibers showed a length of 85–225 nm and diameter of 6–18 nm. It was found that there were no significant morphological differences among the nanostructures from different cotton fibers. The main differences found were the slightly higher yield, sulfonation effectiveness and thermal stability under dynamic temperature conditions of the white nanofiber. On the other hand, the colored nanofibers showed a better thermal stability than the white in isothermal conditions at 180 ºC.

The structure of the cellulose nanofibers from agricultural residues was investigated by Alemdar and Sain [29]. FT-IR spectroscopic analysis demonstrated that chemical treatment also led to partial removal of hemicelluloses and lignin from the structure of the fibers. PXRD results revealed

that this resulted in improved crystallinity of the fibers. Thermal properties of the nanofibers were studied by the TGA technique and found to increase dramatically.

Stelte and Sanadi [35] have studied the mechanical fibrillation process for the preparation of cellulose nanofibers from two commercial hard- and softwood cellulose pulps. The degree of fibrillation was studied using light microscopy (LM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). LM and SEM images (Fig. 3) of hard- and softwood fibers showed that the hardwood fibers that were fibrillated only on the surface during the refining step are now disintegrated into a network of small fibers. AFM images (Fig. 4) of the final products after high-pressure homogenization showed that the size distribution of the hard- and softwood nanofibers is in the range of 10-25 nm in diameter.

Wang and Sain [31] synthesized soybean stock based nanofibers having a diameter in the range 50–100 nm by chemo-mechanical isolation. X-ray crystallography (Fig. 5) was carried out to investigate the percentage crystallinity after various stages of the chemo-mechanical treatment. It has been found that crystallinity of the samples increased after each stage of nanofiber development.

Fig. 6 shows the network of cellulose nanofibers. The nanofiber suspension obtained after the high pressure defibrillation was analyzed to determine diameters using AFM. The AFM image (Fig. 6) shows the surface of air-dried soybean stock nanofiber. It is seen that the fibers are indeed nanosized and the diameter of nanofibers is within the range 50–100 nm.

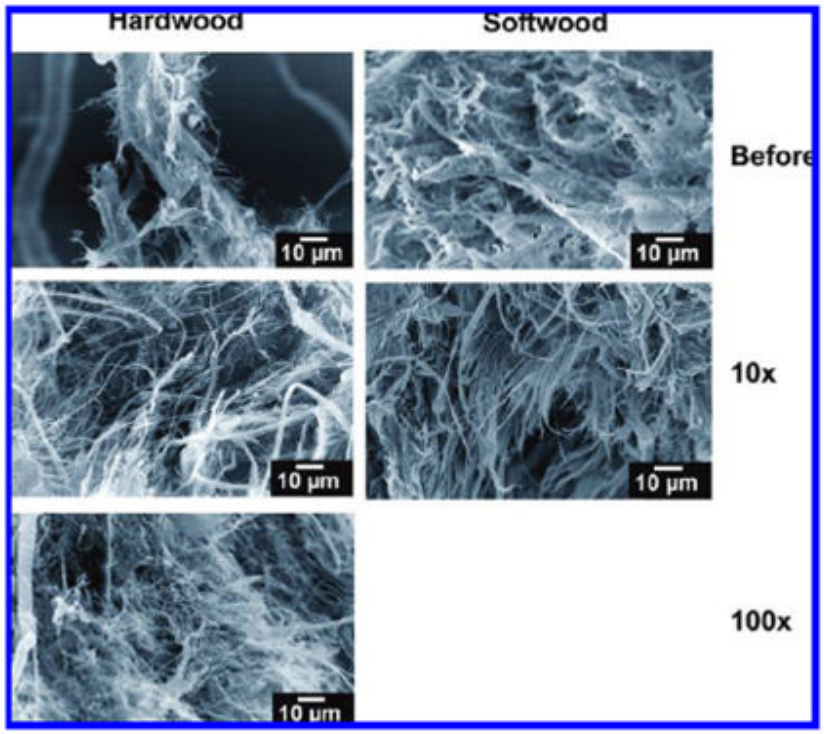


Fig. 3 Scanning electron micrographs of hard- and softwood cellulose fibers, before and after 10 passes through the homogenizer [35]

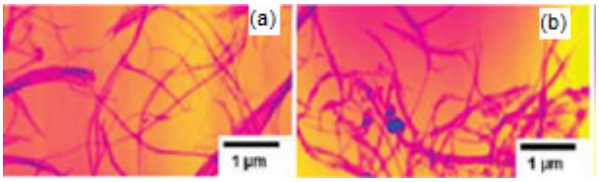


Fig. 4 AFM images (a) hard- and (b) softwood cellulose nanofibers at process equilibrium [35]

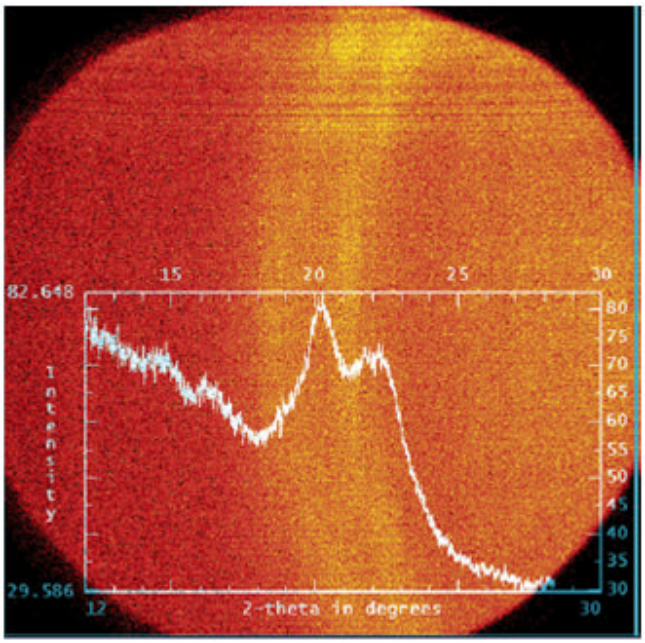


Fig. 5 X-ray pattern to demonstrate the crystallinity of soybean stock nanofibers [31]

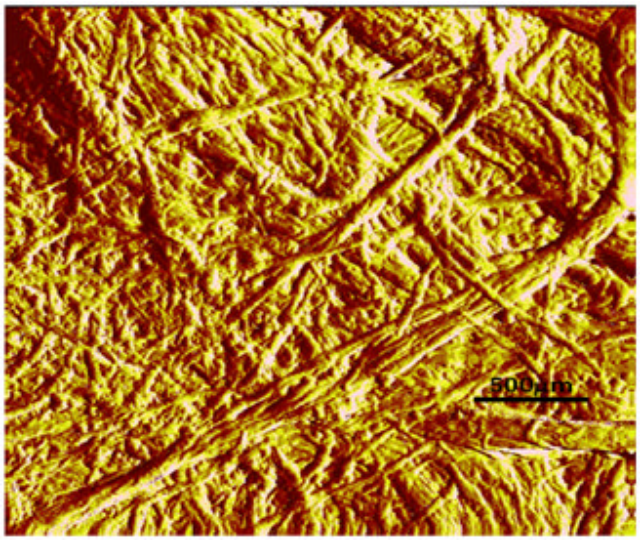


Fig. 6 Atomic force micrograph of soybean stock nanofibers [31]

4. Surface Modification of Cellulose Fibers

In order to develop composites with better mechanical properties and environmental performance, it becomes necessary to increase the hydrophobicity of the cellulose fibers and to improve the interface between matrix and fibers. Lack of good interfacial adhesion, low melting point and poor resistance towards moisture make the use of plant cellulose fiber reinforced composites less attractive. Pre-treatments of the cellulose fiber can clean the fiber surface, chemically modify the surface, stop the moisture absorption process and increase the surface roughness [1, 36]. Among the various pre-treatment techniques, silylation, mercerization, peroxide, benzoylation, graft copolymerization and bacterial cellulose treatment are the best methods for surface modification of natural fibers.

4.1 Silylation, Mercerization and Other Surface Chemical Modifications

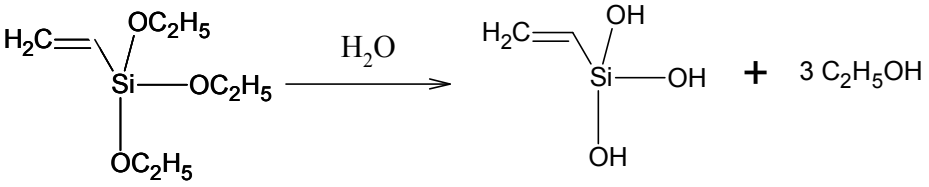
Silane Coupling agents usually improve the degree of cross-linking in the interface region and offer a perfect bonding. Among the various coupling agents, silane coupling agents were found to be effective in modifying the natural fiber-matrix interface. Efficiency of silane treatment was high for the alkaline treated fiber than for the untreated fiber because more reactive site can be generated for silane reaction. Therefore, fibers were pre-treated with NaOH for about half an hour prior to its coupling with silane. Fibers were then washed many times in distilled water and finally dried. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fiber–matrix interface. In the presence of moisture, hydrolizable alkoxy group leads to the formation of silanols. The silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to

the cell wall that are chemisorbed onto the fiber surface [37]. Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fiber by creating a crosslinked network due to covalent bonding between the matrix and the fiber [1].

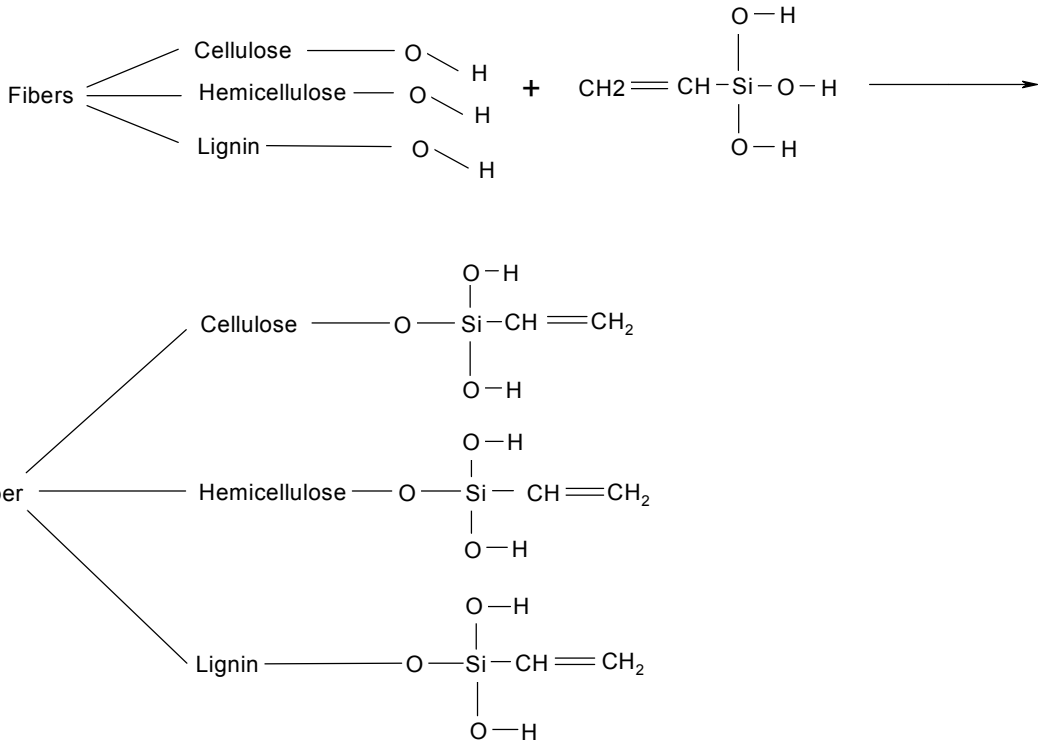
Silanes were effective in improving the interface properties [38-41]. Alkoxy silanes are able to form bonds with hydroxyl groups. Fiber treatment with toluene dissocyanate and triethoxyvinyl silane could improve the interfacial properties. Silanes after hydrolysis undergo condensation and bond formation stage and can form polysiloxane structures by reaction with hydroxyl group of the fibers. The reactions are given in equation 1 and 2 [1, 42].

In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. Hydrogen and covalent bonding mechanisms could be found in the natural fiber-silane system. It is understood that the hydrocarbon chains provided by the silane application influenced the wet-ability of the fibers, thus improving the chemical affinity to polyethylene. 1% solution of three aminopropyl trimethoxy silane in a solution of acetone and water (50/50 by volume) for 2 h was reportedly used to modify the flax surface [43]. Rong et al. [17] soaked sisal fiber in a solution of 2% aminosilane in 95% alcohol for 5 min at a pH value of 4.5–5.5 followed by 30 min air drying for hydrolyzing the coupling agent. Silane solution in water and ethanol mixture with concentration of 0.033% and 1% was also carried by Valadez et al. [44] and Agrawal et al. [37] to treat henequen and oil palm fibers. They modified the short henequén fibers with a silane coupling agent in order to find out its deposition mechanism on the fiber surface and the

influence of this chemical treatment on the mechanical properties of the composite. It was shown that the partial removal of lignin and other alkali soluble compounds from the fiber surface increases the adsorption of the silane coupling agent whereas the formation of polysiloxanes inhibits this process.



(1)

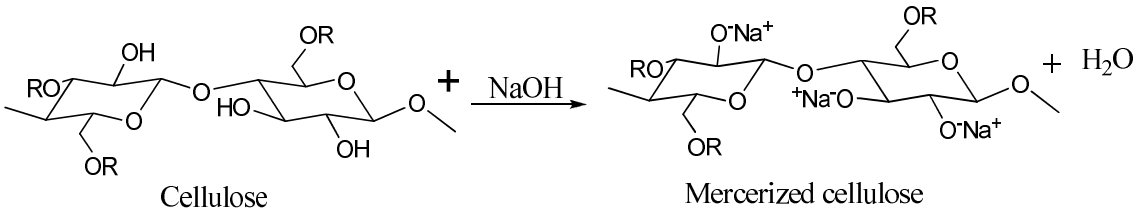


(2)

Mercerization is the common method to produce high quality fibers [45]. Equation 3 shows the probable mechanism of mercerization of cellulose fibers. Mercerization leads to fibrillation which causes the breaking down of the

composite fiber bundle into smaller fibers. Mercerization reduces fiber diameter, thereby increases the aspect ratio which leads to the development of a rough surface topography that results in better fiber-matrix interface adhesion and an increase in mechanical properties [46]. Moreover, mercerization increases the number of possible reactive sites and allows better fiber wetting. Mercerization has an effect on the chemical composition of the flax fibers, degree of polymerization and molecular orientation of the cellulose crystallites due to cementing substances like lignin and hemicellulose which were removed during the mercerization process. As a result, mercerization had a long-lasting effect on the mechanical properties of flax fibers, mainly on fiber strength and stiffness [47]. Sreekala et al. [42] indicated that a 10–30% sodium hydroxide solution produced the best effects on natural fiber properties. Flax fibers were soaked into 2.5, 5, 10, 13, 15, 18, 20, 25, or 30% NaOH solutions and it was found that 5%, 18% or 10% of sodium hydroxide solution were the appropriate concentrations for mercerization. Jute fibers were treated with 5% alkali solution for 0, 2, 4, 6 and 8 h at 30^{o}C by Ray et al [45]. The fibers were then dried at room temperature for 48 h followed by oven drying at 100°C for 6 h. It has been reported by Garcia et al [48] that 2% alkali solution at 200^{o}C and 1.5 MPa pressure for 90 s was suitable for degumming and defibrillation to individual fibers. Several workers have carried out work on alkali treatment and reported that mercerization leads to an increase in the amount of amorphous cellulose at the cost of crystalline cellulose and the removal of hydrogen bonding in the network structure [42, 46]. The jute fibers were washed with detergent (2 vol. % in aqueous solution, 15%

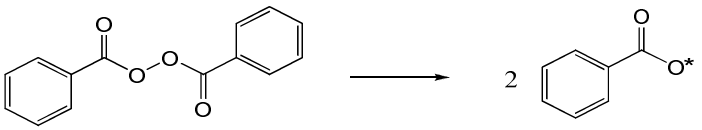
active matter) and then immersed in beakers with a solution of 5 wt. % NaOH for 24 h at room temperature. After that, the fibers were washed thoroughly with distilled water to remove the excess of NaOH and dried at 70°C for 24 h under vacuum [49]. The banana fibers were cleaned and refluxed in 0.25% solution of NaOH for 1 h and then washed in very dilute acid to remove the non-reacted alkali. Washing was continued until the fibers were alkali free. The washed fibers were then dried in an oven at 70°C for 3 h [50].



Cellulose Mercerized cellulose

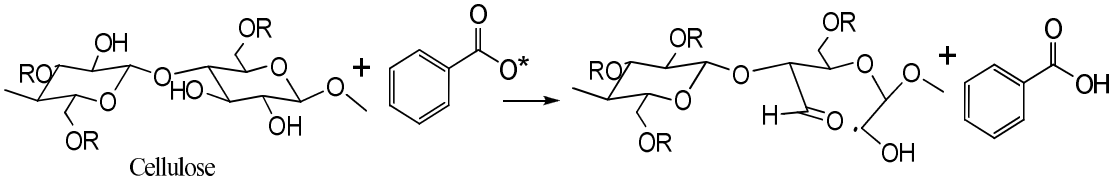
(3)

Peroxide treatment of cellulose fiber has attracted the attention of various researchers due to easy processability and improvement in mechanical properties. Organic peroxides tend to decompose easily to free radicals (RO.), which further react with the hydrogen group of the matrix and cellulose fibers. Equations 4 and 5 show the peroxide treatment reaction onto cellulose fibers [42].



benzoyl peroxide

(4)

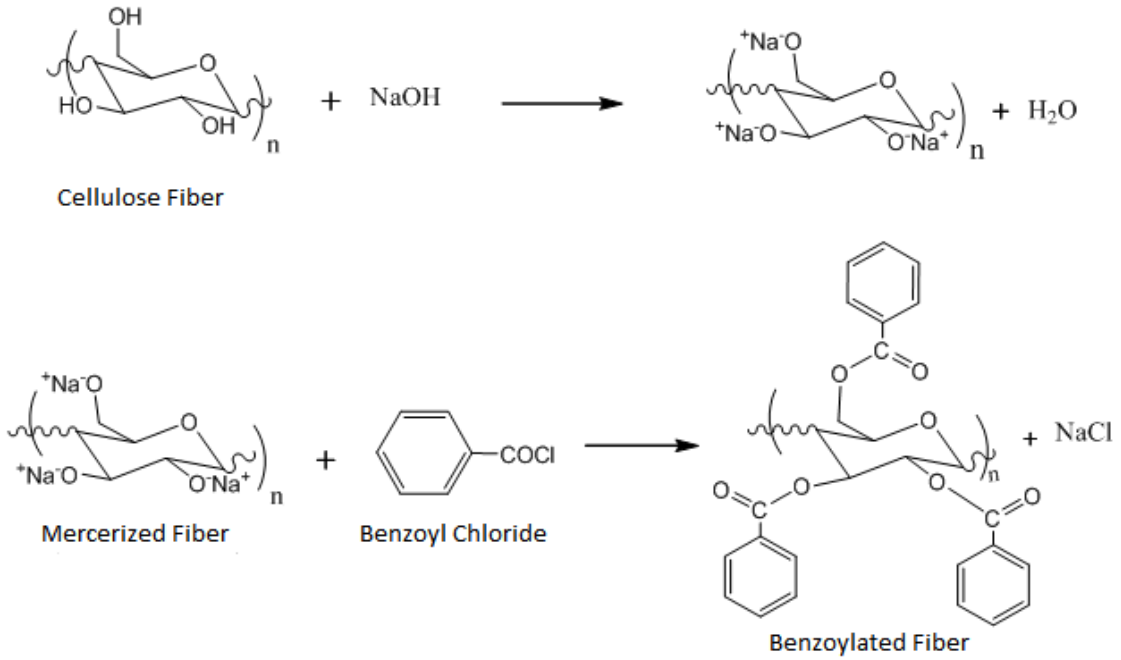


Cellulose

(5)

In peroxide treatment, fibers are treated with 6% benzoyl peroxide or dicumyl peroxide in acetone solution for about 30 min after alkali pre-treatment [42, 51, 52]. Flax fibers were coated with dicumyl peroxide from acetone solution after alkali pre-treatments. Saturated solution of the peroxide in acetone was used. Soaking of the fibers in the solution was conducted at a temperature of 70^{o}C for 30 min. High temperatures were favored for decomposition with the peroxide. The chemically treated fibers were washed with distilled water and placed in an oven at 80^{o}C for 24 h [53].

In benzoylation treatment, benzoyl chloride is most often used in fiber pre-treatment and inclusion of benzoyl ($C_6H_5C=O$) group in the fiber is responsible for the decreased hydrophilic nature of the treated fiber [46]. A known amount of washed fibers (35 g) were soaked in 18% NaOH solution for 30 minutes followed by filtration and washing with water. The treated fiber was suspended in 10% NaOH solution and agitated with 50 ml benzoyl chloride. The reaction between the cellulosic –OH group of sisal fiber and benzoyl chloride is shown in Equation 6 as follows [46, 54]:



(6)

Joseph et al. [46] and Kalia et al. [54] used NaOH and benzoyl chloride (C_6H_5COCl) solution for surface treatment of sisal fibers. The fiber was initially alkaline pre-treated in order to activate the hydroxyl groups of the cellulose and lignin in the fiber; then the fiber was suspended in 10% NaOH and benzoyl chloride solution for 15 min. The isolated fibers were then soaked in ethanol for 1 h to remove the benzoyl chloride and finally was washed with water and dried in the oven at 80 °C for 24 h [55].

4.2 Polymer Grafting

Desirable and targeted properties can be imparted to the cellulose fibers through graft copolymerization in order to meet-out the requirement of specialized applications. Graft copolymerization is one of the best methods for modifying the properties of cellulose fibers. Different binary vinyl monomers and their mixtures

have been graft copolymerized onto cellulosic material for modifying the properties of numerous polymer back-bones [1, 56].

During last decades several methods have been suggested for the preparation of graft copolymers by conventional chemical techniques. Creation of an active site on the pre-existing polymeric backbone is the common feature of most methods for the synthesis of graft copolymers. The active site may be either a free-radical or a chemical group which may get involved in an ionic polymerization or in a condensation process. Polymerization of an appropriate monomer onto this activated back–bone polymer leads to the formation of a graft copolymer. Ionic polymerization has to be carried-out in presence of anhydrous medium and / or in the presence of considerable quantity of alkali metal hydroxide. Another disadvantage with the ionic grafting is that low molecular weight graft copolymers are obtained while in case of free radical grafting high molecular weight polymers can be prepared. C_2, C_3 and C_6 hydroxyls and C-H groups are the active cites for grafting in cellulosics [Fig. 7] [57].

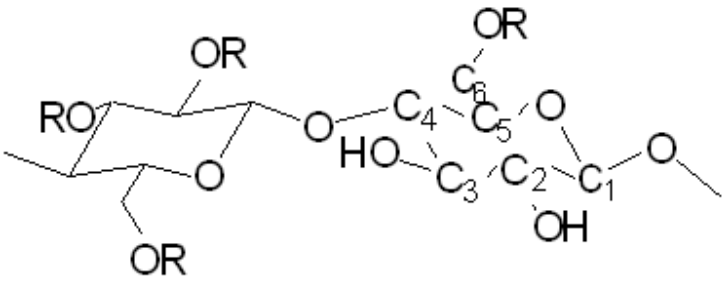


Fig. 7 Structure of Cellulose

The conventional technique of grafting and chemical modification of natural fibers requires significant time and energy. The use of MWR technique to modify the

properties of natural fibers within the textile industry, although somewhat slow and still rather limited, is finding its way into numerous uses in production plants. Microwave radiation technique reduces the extent of physicochemical stresses to which the fibers are exposed during the conventional techniques. Microwave technology uses electromagnetic waves, which passes through material and causes its molecules to oscillate. Microwave energy is not observed by non polar materials to any degree while polar water molecules held within a polymer matrix do absorb energy very proficiently, thus becoming heated [58, 59].

Graft copolymerization of methyl methacrylate onto flax fiber was carried out under three different reaction methods, in air, under pressure and under the influence of micro wave radiations. Grafting through micro-wave radiation technique is an effective method in terms of time consumption and cost effectiveness. Maximum percentage grafting has been observed in case of grafting carried out in air followed by grafting under pressure and under the influence of microwave radiations. Flax fiber faces less surface deformations during grafting process under the influence of microwave radiations as compared to grafting in air and under pressure, thereby retaining better crystalline structure. Morphological and thermal studies showed that surface of sunn hemp fibers becomes rough through graft copolymerization and thermal stability has been found to be increased. Microwave radiation induced grafting showed a diminutive effect on the crystalline behavior of the sunn hemp fibers as optimum time to get maximum grafting is very less (40 minutes) in comparison to conventional grafting [60].

4.3 Bacterial Modification

The coating of bacterial cellulose onto cellulose fibers provides new means of controlling the interaction between fibers and polymer matrices. Coating of fibers with bacterial cellulose does not only facilitate good distribution of bacterial cellulose within the matrix, it also results in an improved interfacial adhesion between the fibers and the matrix. This enhances the interaction between the fibers and the polymer matrix through mechanical interlocking [3, 61]. Surface modification of cellulose fibers using bacterial cellulose is one of the best methods for greener surface treatment of fibers. Bacterial Cellulose has gained attention in the research area for the encouraging properties it possesses; such as its significant mechanical properties in both dry and wet states, porosity, water absorbency, moldability, biodegrability and excellent biological affinity [62]. Because of these properties, BC has a wide range of potential applications.

Acetobacter xylinum (or *Gluconacetobacter xylinus*) is the most efficient producer of bacterial cellulose. BC is secreted as a ribbon-shaped fibril, less than 100 nm wide, which is composed of much finer 2–4 nm nanofibrils. In comparison to the methods for obtaining nanocellulose through mechanical or chemo-mechanical processes, it is produced by bacteria through cellulose biosynthesis and the building up of bundles of microfibrils [63-65].

The cultivation of the cellulose producing bacteria in the presence of natural fibers such as sisal and hemp results in the coating of natural fiber surfaces by bacterial nanocellulose (Fig. 8) [61]. Strong and highly crystalline nanocellulosic fibrils preferentially attached to the surface of natural fibers thereby creating

‘‘hairy fibers’’ (Fig. 9), leading to a nanostructured natural fiber surface. Simply weighing the fibers before and after the BC fermentation process confirmed that between 5 and 6 wt% of bacterial cellulose adhered to the fibers after the surface modification. The strength of attachment of the nanocellulose coating to the fibers can be attributed to strong hydrogen bonding between the hydroxyl groups present in bacterial cellulose and the lignocellulose in natural fibers [66]. The modification process did not affect the mechanical properties of sisal fibers but it significantly reduced the mechanical properties of hemp fibers. Fig. 10 shows the coating of bacterial nanocellulose onto hemp fibers [61].

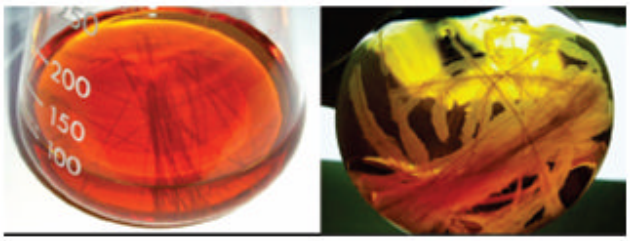


Fig. 8 Photographs of sisal fibers before and after bacterial culture [61]

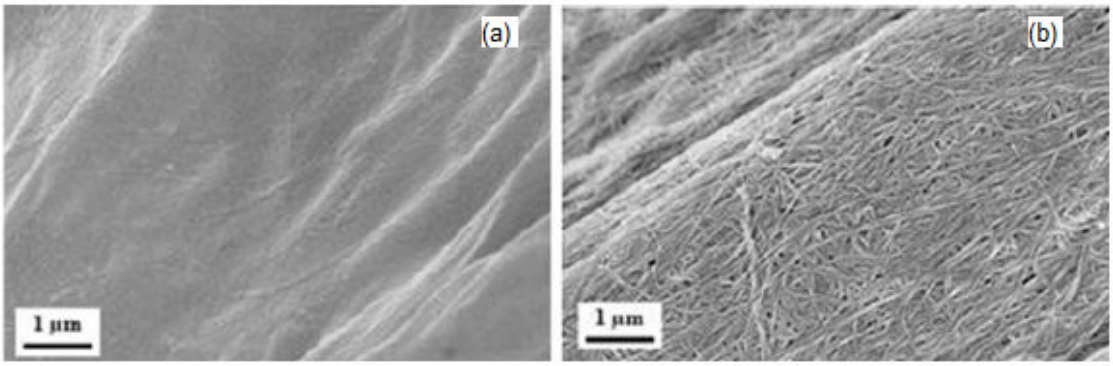


Fig. 9 SEM micrographs (a) sisal fiber and (b) bacterial cellulose coated sisal fiber [61]

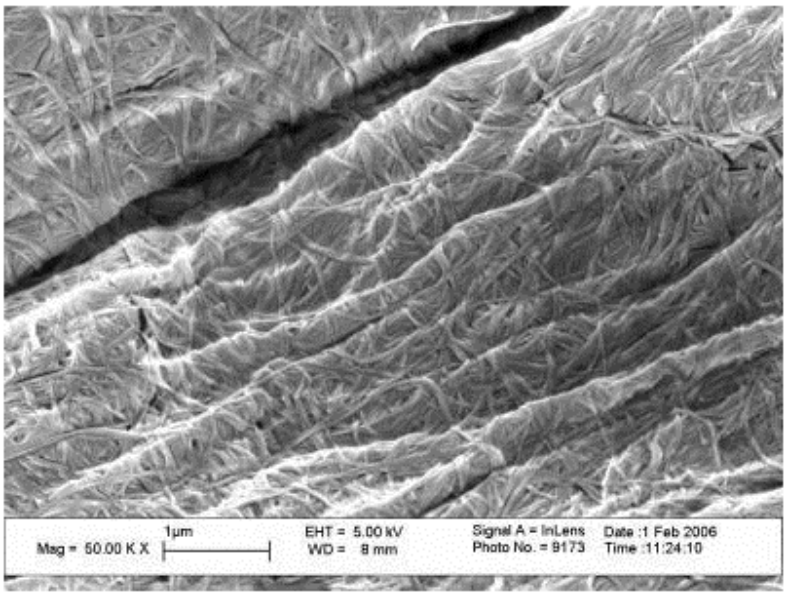


Fig. 10 Hemp fiber after bacterial cellulose modification [61]

To improve the compatibility between natural fibers and hydrophobic polymer matrices, various greener methods have been explored such as fungi, enzymes and bacterial treatments. Kalia and Sheoran [67] have reported cellulase enzyme assisted biopolishing of ramie fibers using bacteria *Streptomyces albaduncus.* Biopolishing of ramie fibers by utilizing cellulase from bacteria Streptomyces albaduncus was observed for 5 days, at the pH 7.4 and 2.0 g glucose, which results in enhanced brightness due to the removal of gum materials and small fibrils protruding from the fiber surface. Bacterial treatment has diminutive effect on thermal stability and crystalline structure of ramie fibers.

5. Cellulose Fiber Reinforced Biocomposites

5.1 Processing Method

Natural fiber composites are prepared using various composites manufacturing methods such as compression moulding, injection moulding, resin transfer moulding (RTM) and vacuum bagging. The preforms are mostly fibers, fabrics or nonwovens. Prepregs are also widely used to prepare composites [68]. Equation (5.1) is commonly used in the preparation of composites.

$$V_f = \frac{W_f/\rho_f}{(W_f/\rho_f)+(W_m/\rho_m)} \qquad (5.1)$$

Where Vf is the fiber-volume fraction, Wf is the weight of fiber and Wm is the weight of matrix. rf and rm are the densities of the fiber and matrix, respectively.

The production of the composites is optimized in relation to temperature, pressure and moulding time. It is often necessary to preheat the natural fibers to reduce the moisture before processing the composites. High temperatures degrade the cellulose; thus, negatively affecting the mechanical properties of the composites. Inefficient fiber dispersion in the matrix causes fiber agglomeration which decreases the tensile strength [68]. Most of the previous research on natural fiber composites has focused on reinforcements such as flax, hemp, sisal and jute, and thermoplastic and thermoset matrices. Some of these composites have been produced using matrices made of derivatives from cellulose, starch and lactic acid to develop fully biodegradable composites or biocomposites [69]. The emerging diversity of applications of natural fiber composites has seen the

production of sandwich structures based on natural fiber composite skins. In some cases, these sandwich composites have been produced from paper honeycomb and natural fiber-reinforced thermoplastic or thermoset skins, depending on the applications.

The main criteria for the selection of the appropriate process technology for natural-fiber composite manufacture include the desired product geometry, the performance needed, the cost and the ease of manufacture. The fabrication methods for natural fiber composites are similar to those used for glass fibers. The most commonly used manufacturing processes are introduced in the followings. Although many variants on these techniques exist, this overview gives a good indication of the production possibilities.

5.1.1 Hand laminating

The fibers are placed in a mould and the resin is later applied by rollers. One option is to cure using a vacuum bag, as then excess air is removed and the atmospheric pressure exerts pressure to compact the part. The simplicity, low cost of tooling and flexibility of design are the main advantages of the procedure. On the other end, the long production time, intensive labour and low automation potential, consist some of the disadvantages.

5.1.2 Resin Transfer Moulding (RTM)

The resin transfer moulding technique requires the fibers to be placed inside a mould consisting of two solid parts (close mould technique). A tube connects the mould with a supply of liquid resin, which is injected at low pressure through the mould, impregnating the fibers. The resulting part is cured at room temperature

or above until the end of the curing reaction, when the mould is opened and the product removed. Parameters such as injection pressure, fiber content or mould temperature have a great influence on the development of the temperature profiles and the thermal boundary layers, especially for thin cavities. This technique has the advantage of rapid manufacturing of large, complex and high performance parts. Several types of resins (epoxy, polyester, phenolic and acrylic) can be used for RTM as long as their viscosity is low enough to ensure a proper wetting of the fibers. Parameters such as injection pressure, fiber content or mould temperature have a great influence on the development of the temperature profiles and the thermal boundary layers, especially for thin cavities. Good knowledge of all the operating steps is very important to obtain high-quality parts [68].

An alternative variant of this process is the vacuum injection or vacuum assisted resin transfer moulding (VARTM), where a single solid mould and a foil (polymeric film) are used. The VARTM process is a very clean and low cost manufacturing method: resin is processed into a dry reinforcement on a vacuum bagged tool, using only the partial vacuum to drive the resin. As one of the tool faces is flexible, the moulded laminate thickness depends partially on the compressibility of the fiber–resin composite before curing and the vacuum negative pressure.

5.1.3 Compression Moulding

Compression moulding is another major technique for the construction of fiber reinforced polymers, which involves a semi-finished composite sheet widely

known as sheet moulding compound (SMC) that is later moulded into the final parts by compression. For the SMC the process consists of a rolling film of resin on which fibers are added. A second film of resin is then added, so as to later be compressed in a composite sheet that may be stored for few days. To get the final product the reinforced sheet is then placed into a press to take its desired shape.

Advantages of compression moulding are the very high volume production ability, the excellent part reproducibility, the short cycle times and the low crap arising. Processing times of < 2 min are reached during the compression moulding of three-dimensional components with a high forming degree. It has also been shown that the adhesion of natural fibers and matrix resin is important in order to obtain good mechanical properties of natural fiber composites, and the mechanical properties were improved by the moulding condition, the moulding pressure and temperature. A big concern with compression moulding that needs always to be considered is the maximum pressure before the damage of the fibers and the structure.

5.1.4 Injection Moulding

Injection moulding process is suitable to form complex shapes and fine details with excellent surface finish and good dimensional accuracy for high production rate and low labour cost. In the injection moulding resin granules and short fibers are mixed into a heated barrel and transported to the mould cavity by a spindle. Injection moulding is another process among the most important for the

manufacturing of plastics/composites, and can produce from very small products such as bottle tops to very large car body parts.

5.1.5 Pultrusion

Pultrusion is a continuous process to manufacture composite profiles at any length. The impregnated fibers are pulled through a hole (mandrel) which is shaped according to the desired cross-section of the product. The resulting profile is shaped until the resin is dry. Advantages of this process are the ability to build thin wall structures, the large variety of cross-sectional shapes and the possibility for high degree of automation.

5.2 Interfacial Interactions

All natural fibers are (in different extent) hydrophilic in nature. This is attributed mainly to the lignocellulose into their structure, which contain strongly polarized hydroxyl groups [68]. These fibers, therefore, are inherently incompatible with many well known and popular in composite manufacturing resins. Only some thermosets such as the phenol-formaldehyde and related polymers are less hydrophilic and thus less problematic.

This discrepancy leads often to the formation of ineffective interface between the fibers and the matrix. The major limitations of using these fibers as reinforcements in such matrices include poor interfacial adhesion between polar-hydrophilic fibers and non-polar-hydrophobic matrix, and difficulties in mixing due to poor wetting of the fibers with the matrix. The role of the matrix in a fiber-reinforced composite is to transfer the load to the stiff fibers through shear

stresses at the interface. This process requires a good bond between the polymeric matrix and the fibers [70].

Poor adhesion at the interface means that the full capabilities of the composite cannot be exploited and leaves it vulnerable to environmental attacks that may weaken it, thus reducing its life span. Insufficient adhesion between the polymer and the fibers results in poor mechanical properties of the natural fiber-reinforced polymer composites.

Pre-treatments of the fibers can clean the fiber surface, chemically modify the surface, stop the moisture absorption process and increase the surface roughness [71, 72]. These properties may be improved by both physical treatments like cold plasma treatment or corona treatment, and chemical treatment such as maleic anhydride, organosilanes, isocyanates, sodium hydroxide, permanganate and peroxide.

5.2.1 Physical treatment

Physical treatments change the structural and surface properties of the fibers and thereby influence the mechanical bonding to polymers. Corona treatment is one of the most popular techniques for surface oxidation activation through electric discharge that changes the surface energy of the cellulose fibers. Cold plasma treatment is another electric discharge technique and can have the same surface effects and increase the fiber matrix adhesion [72]. A traditional physical method is mercerization. In this process the fibers are treated with an aqueous solution of a strong base (alkali treatment) so as to produce great swelling that

result in changes of their structure, dimensions, morphology and mechanical properties [72].

5.2.2 Chemical Treatment

Among the most effective methods of chemical treatment is graft copolymerization [68, 72]. The cellulose is treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Under the radiation the cellulose molecule cracks and radicals are formed. Using then a suitable (compatible with the matrix) solution it is possible to create a co-polymer with properties and characteristics of both the fibers and the matrix. Graft copolymers of natural fibers with vinyl monomers provide better adhesion between matrix and fiber. Gauthier et al. [73] reported that adhesion may be improved by using coupling agents like maleic anhydride to incorporate hydroxyl groups on the matrix through hydrophilization and consequently enhancing the wetting effect of the resin on the fibers. The hydroxyl groups then interact with –OH molecules on the lignocellulosic fibers via hydrogen bonding thus producing a stronger bond. George et al. [74] reviewed the physical and chemical treatments that may improve the fiber-matrix adhesion and manufactured biocomposites by applying an alkaline solution to the fibers. Natural fibers are mainly composed of cellulose, whose elementary unit, anhydro d-glucose, contains three hydroxyl (OH) groups. These hydroxyl groups form intramolecular and intermolecular bonds, causing all vegetable fibers to be hydrophilic. The alkaline solution regenerated the lost cellulose and dissolved unwanted microscopic pits or cracks on the fibers resulting in better fiber–matrix adhesion.

Coupling agents are based on the concept that when two materials are incompatible, a third material with intermediate properties can bring the compatibility to the mixture [72]. The coupling agents have two functions: to react with OH groups of the cellulose and to react with the functional groups of the matrix with the goal of facilitating stress transfer between the fibers and the matrix. Numerous studies [68, 72] have been conducted on the use of coupling agents including organosilanes, tryazine and maleic-anhydride (MAH). For instance, Xie et al. [75] used silane coupling agents in natural fiber/polymer composites and concluded that proper treatment of fibers with silanes can increase the interfacial adhesion and improve the mechanical performance of the resulting composites. Gassan et al. [76] improved the tensile and flexural strength and stiffness of jute/epoxy composites by treating the fibers with silane. Acetylation, isocyanate treatment and treatment with stearic acid are some more chemical methods for modification and preparation of the fiber/matrix adhesion.

5.3 Characterization

Plant fibers are basically composite materials designed by nature, and consist of a collection of long and thin cells made up of hollow cellulose fibrils held together by a lignin and hemicellulose matrix [77]. The strength and stiffness of the fibers are provided by hydrogen bonds and other linkages. The overall properties of the fibers depend on the individual properties of each of its components. Hemicellulose is responsible for the biodegradation, moisture absorption and thermal degradation of the fiber. On the other hand, lignin (or pectin) is thermally

stable but is responsible for UV degradation of the fiber. On average, natural fibers contain 60–80% cellulose, 5–20% lignin (or pectin) and up to 20% moisture.

On a composite the properties of the fibers are combined with those of the matrix, which is responsible to transfer the external loads to the stiff fibers through shear stresses at the interface as well as keep the fibers together in a specific structural form. Thus the properties of the composite are a combination of the properties of the ingredients and their prediction and estimation becomes a difficult job.

5.3.1 Stiffness & Strength

The mechanical properties of natural fiber composites are much lower than those of glass fibers. However their specific properties, especially stiffness, are comparable to the stated values of glass fibers. Moreover, natural fibers are about 50% lighter than glass, and in general cheaper. It is widely acknowledged that natural fiber composites combine good mechanical properties with a low specific mass and offer an alternative material to glass fiber-reinforced plastics in some technical applications. For example, Bledzki and Gassan [72] observed that the characteristic values of natural fibers are comparable to those of glass fibers. Experimental data giving the tensile strength, flexural strength, modulus, impact force and compressive force are available in the literature for different types of natural-fiber composites.

The ultimate strength of any composite depends on several factors, most important of which are the properties of the components and the volume fraction.

Wambua et al. [70] studied the importance and effect of the volume fraction on the tensile strength of natural fiber composites. They reported that an increase in the fiber weight fraction produces an increase in the tensile strength. Testing different fiber reinforcement they also found that hemp/ polypropylene (PP) composites with a 30% volume fraction displayed a tensile strength of 52MPa, higher than equivalent glass reinforced composites with the same volume fraction. Further, hemp and kenaf – polypropylene composites registered a high tensile modulus of 6.8 GPa compared to 6.2 GPa of equivalent glass composites. The increase of the modulus and the tensile strength with increase of the volume or weight fraction was also showed by Bos [78, 79] on flax/PP composites with maleic-anhydride grafted polypropylene for improved adhesion.

Studies and results of tensile tests on flax-fiber reinforced PP composites were conducted by Garkhail et al. [80] which concluded that fiber length affect the strength and modulus of the composites for small fiber lengths whilst after a specific value for the length the two parameters are constant. The stiffness of a flax/PP composite was shown to be comparable to E-glass based composite, especially when the specific properties are concerned due to the very low density of flax. However the results also depicted a relatively low tensile strength.

Nishino [81] studied the mechanical properties of kenaf/poly-L-lactide (PLLA) composites. He concluded that the modulus of the composites increases with the increase of the volume fraction, but only up to a certain level. When this threshold is achieved further increase of the fiber fraction leads to a dramatic reduction of the composite properties.

Water content has also a dramatic effect on the properties of natural-fiber composites. Espert et al. [82] showed this effect on cellulose/PP composites by submerging samples into distilled water under different temperatures. The samples were removed from the water at certain times and the water absorption was measured. The results of tensile tests showed a significant effect of the water content to the young's modulus of the samples, and an even bigger effect on the tensile strength. The studies also concluded that the effect of the water to the properties is highly influenced by the fiber content, the matrix and mainly the temperature. Thwe et al. [83] investigated the same effect on bamboo-fiber composites and resulted that both the tensile strength and modulus have decreased after aging in water at 25 and 75 ^{o}C for prolonged period. The extent of strength and stiffness loss depends on the aging time and temperature. They also concluded that tensile strength and stiffness are enhanced by inclusion of a coupling agent, maleic anhydride polypropylene (MAPP), in matrix material as a result of improved interfacial bonding.

5.3.2 Impact performance

There are only few studies known about the impact behaviour of natural fiber reinforced composites. The impact performance of several natural fiber composites was compared and reviewed by Wambua et al. [70]. Using kenaf, coir, sisal, hemp, and jute reinforced polypropylene the study concluded that natural fiber composites display low impact strengths compared to glass composites, whereas their specific impact strength can be comparable with those

of glass mat composites. Among the materials studied, sisal and hemp showed the higher impact strength.

Pavithran et al. [84] determined the fracture energies for sisal, pineapple, banana and coconut fiber – polyester composites in a Charpy impact test. They concluded that increased fiber toughness results in increased fracture energy, and found that fibers with higher fibril angles have higher fracture-toughness than those with small spiral angle.

Fiber content and fiber length have also a contribution to the impact performance of the composite. Tobias et al. [85] examined this influence with banana-fiber composites and concluded that, smaller fiber lengths have higher impact strength which also increases for higher fiber content. Contradictorily the fiber length was also studied by Garkhail et al. [80] on flax/PP composites. The results showed that (as in glass fiber composites) the impact strength increases with increasing fiber length until a plateau level is reached. After that level the impact performance drops depending on the pre-treatment of the fibers and the adhesion of the fiber/matrix interface.

Dieter [86] investigated the effect of several material parameters on the impact strength of compression moulding components of hemp, flax and kenaf – polypropylene composites. The studies showed a strong influence of the thermal process conditions during the moulding. He concluded that for every material studied there is an optimum temperature that results to a peak of the impact strength. Higher and lower processing temperature resulted in lower mechanical values that could be explained by a thermal decomposition of the fibers. Strong

impact of the fiber fineness was also proved, with the impact performance getting higher from composites with fiber of higher fineness.

The effect of temperature and water on the impact properties of natural-fiber thermoplastics were reviewed by Bruijn [87], and showed not significant effect on the impact properties of the composites. However the results showed that the impact strength was 20 to 25% to that of glass reinforced thermoplastics.

A significant contribution of coupling agents on the impact strength has also been reported. When the composites have no coupling agent a part of the energy is lost in the interface, by for example debonding and friction effects. Maleic-anhydride - treated jute composites showed higher impact strength than untreated samples made out of the same process.

5.3.3 Fatigue behaviour

The cyclic loading of natural fiber composites is still poorly investigated. Gassan [88] investigated the fatigue behaviour of flax and jute epoxy resin composites. Fiber type, textile architecture, interphase properties, fiber properties and content were found to affect the fatigue behaviour strongly. It was also found that natural fiber reinforced plastics with higher fiber strength and modulus, stronger fiber–matrix adhesion or higher fiber fractions possess higher critical loads for damage initiation and higher failure loads. In addition, damage propagation rates were reduced. Furthermore, unidirectional composites were less sensitive to fatigue induced damage than woven reinforced ones.

Savastano et al. [89] presented the results of experimental studies of resistance-curve behaviour and fatigue crack growth in cementitious matrices reinforced

with natural fibers such as sisal, banana and bleached eucalyptus pulp. Fatigue crack growth was observed to occur in three stages: an initial decelerated growth, a steady-state growth, and a final catastrophic crack growth. In the case of the composites reinforced with sisal and banana fibers, most of fatigue life was spent in the second stage of steady-state crack growth. The results showed that fatigue crack growth in the composites occurred via matrix cracking, crack deflection around fibers, and crack-bridging by un-cracked fibers and ligaments, whilst fiber pull-out was also observed.

The fatigue performance of sisal/epoxy composites was also studied by Towo et al. [90, 91] which looked into the effect of surface modification on the fatigue performance of the composite. The results show that a NaOH surface treatment has a significant effect on the tensile modulus and strength of the material but the fatigue life is not highly influenced, especially in low stress levels. Their conclusion states that the behaviour of sisal fiber composites is similar to that of conventional synthetic fiber composites and static and fatigue strengths are suitably high for many commercial applications. Towo et al. also studied the fatigue properties of flax/polyester with alkali-treated and untreated fibers. In this case they observed a high influence of the treatment on the fatigue life of the components and they also underlined that the polyester matrix samples had lower life than the epoxy samples.

A comparison between hemp and flax reinforced polyester composites with focus on the fatigue behaviour was conducted by Yuanjian et al. [92]. A steeper gradient of the S–N curve for the hemp fiber composite was indicative of a higher

rate of reduction in fatigue strength. However the fatigue performance levels of this hemp mat composite were comparable and slightly greater than those of the glass fiber composite.

6. Cellulose Nanofiber Reinforced Nanocomposites

The potential of nanocomposites in various sectors of research and application is promising and attracting increasing investments. In the nanocomposite industry, a reinforcing particle is usually considered as a nanoparticle when at least one of its linear dimension is smaller than 100 nm. Owing to the hierarchical structure and semicrystalline nature of cellulose, nanoparticles can be extracted from this naturally occuring polymer. Native cellulose fibers are built up by smaller and mechanically stronger long thin filaments, the microfibrils consisting of alternating crystalline and non-crystalline domains. Multiple mechanical shearing actions can be used to release more or less individually these microfibrils. This material is usually called microfibrillated cellulose (MFC). Figure 11 [93-96] shows transmission electron micrographs from dilute suspensions of MFC obtained from different sources.

Longitudinal cutting of these microfibrils can be performed by submitting the biomass to a strong acid hydrolysis treatment, allowing dissolution of amorphous domains. The ensuing nanoparticles occur as rod-like nanocrystals or whiskers with dimensions depending on the source of cellulose and preparation procedure. Examples are shown in Fig. 12 [97-104]. The typical geometrical characteristics for nanocrystals derived from different species and reported in the literature are collected in Table 1.

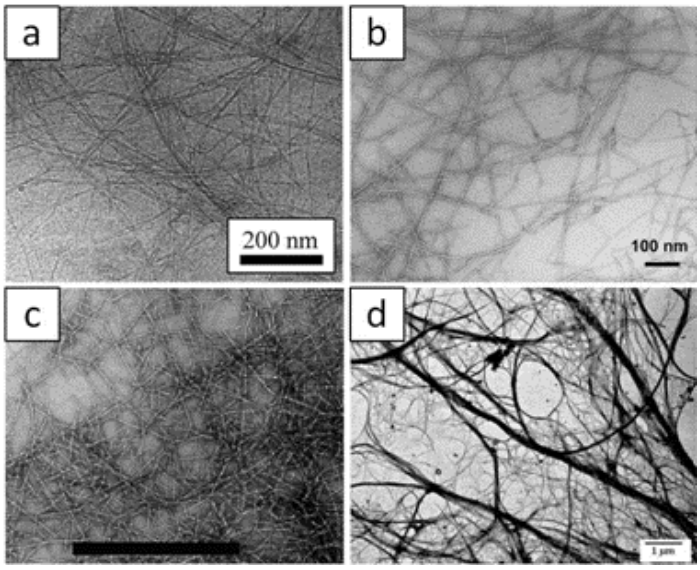


Fig. 11 Transmission electron micrographs from dilute suspension of MFC obtained from wood fibers by mechanical processing combined to (a) enzymatic [93], (b) TEMPO-mediated oxidation [94], (c) carboxylmethylation pretreatment [95], (d) extracted from Opuntia ficus-indica [96]

Table 1. Geometrical characteristics of cellulose nanocrystals from various sources: length (L), cross section (D) and aspect ratio (L/d).

Source	L (nm)	D (nm)	L/D	Ref.
Acacia pulp	100-250	5-15	_	[105]
Alfa	200	10	20	[106]
Algal (*Valonia*)	> 1,000	10-20	∞	[107, 108]
Bacterial	100-several 1,000	5-10 × 30-50	_	[98, 109, 110]
Banana rachis	500-1,000	5	_	[111]
Bio-residue from wood bioethanol production	several 100	10-20	_	[112]
Capim dourado	300	4.5	67	[113]

Cassava bagasse	360-1,700	2-11	_	[114]
Cladophora	-	20 × 20	_	[115]
Coconut husk fibers	80-500	6	39	[116]
Cotton	100-300	5-15	10	[117-119]
Cottonseed linter	170-490	40-60	_	[120]
Curaúa	80-170	6-10	13-17	[121]
Date palm tree (rachis/leaflets)	260/180	6.1	43/30	[122]
Eucalyptus wood pulp	145	6	24	[123]
Flax	100-500	10-30	15	[124]
Grass Zoysia	200-700	10-60	_	[125, 126]
Hemp	several 1,000	30-100	_	[127]
Luffa Cylindrica	242	5.2	47	[128]
MCC	150-300	3-7	_	[100]
Mulberry	400-500	20-40	_	[129]
Pea hull	240-400	7-12	34	[130]
Ramie	350-700	70-120		[97, 131, 132]
	150-250	6-8		
Recycled pulp	100-1,800	30-80	_	[133]
Sisal	100-500	3-5	60/43	[99, 134, 135]
	215	5		
Sugar beet pulp	210	5	42	[101]
Sugarcane bagasse	200-310	2-6	64	[136]
Tunicin	100-several 1,000	10-20	67	[137]
Wheat straw	150-300	5	45	[103]
Wood	100-300	3-5	50	[115, 138, 139]

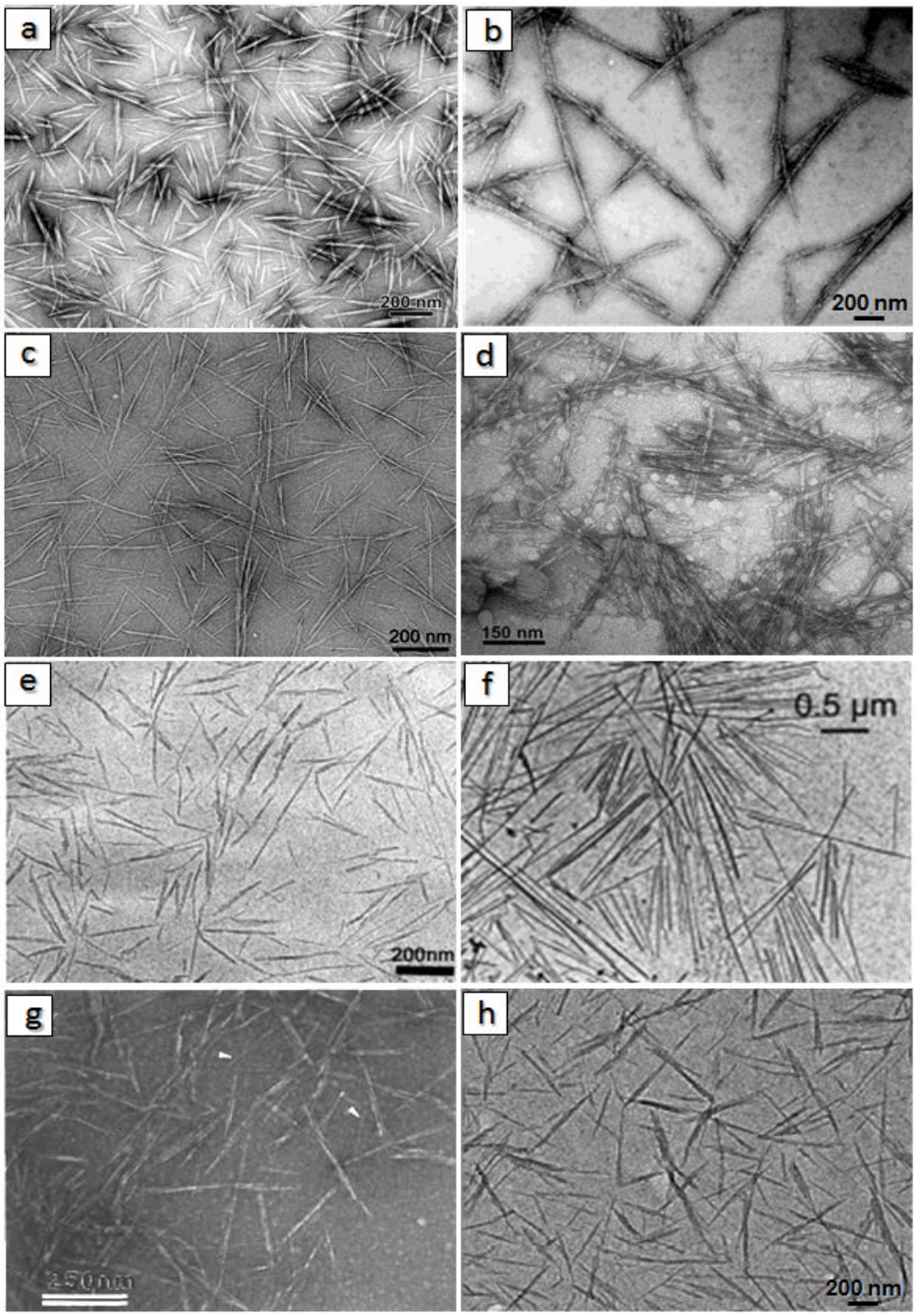


Fig. 12 Transmission electron micrographs from dilute suspension of cellulose nanocrystals from: a) ramie [97], b) bacterial [98], c) sisal [99], d) microcrystalline cellulose [100], e) sugar beet pulp [101], f) tunicin [102], g) wheat straw [103] and h) cotton [104]

Impressive mechanical properties and reinforcing capability, abundance, low weight, and biodegradability of cellulose nanocrystals make them ideal candidates for the processing of polymer nanocomposites [140-143]. With a Young's modulus around 150 GPa and a surface area of several hundred $m^2.g^{-1}$ [144], they have the potential to significantly reinforce polymers at low filler loadings. A broad range of applications of nanocellulose exists even if a high number of unknown remains at date. Tens of scientific publications and experts show its potential even if most of the studies focus on their mechanical properties as reinforcing phase and their liquid crystal self-ordering properties. However, as for any nanoparticle, the main challenge is related to their homogeneous dispersion within a polymeric matrix.

6.1 Nanocomposite Processing

Cellulose nanoparticles are obtained as stable aqueous suspensions and most investigations focused on hydrosoluble (or at least hydrodispersible) or latex-form polymers. The main advantage is that the dispersion state of the nanoparticles is kept when using an aqueous medium for the processing.

After dissolution of the hydrosoluble or hydrodispersible polymer, the aqueous solution can be mixed with the aqueous suspension of cellulosic nanoparticles. The ensuing mixture is generally cast and evaporated to obtain a solid nanocomposite film. It can also be freeze-dried and hot-pressed. The preparation of cellulose nanofiber reinforced starch [145-150], silk fibroin [151], poly(oxyethylene) (POE) [152-156], polyvinyl alcohol (PVA) [157-161],

hydroxypropyl cellulose (HPC) [157, 158], carboxymethyl cellulose (CMC) [162] or soy protein isolate (SPI) [163] has been reported in the literature.

The first publication reporting the preparation of cellulose nanocrystals reinforced polymer nanocomposites was carried out using a latex obtained by the copolymerization of styrene and butyl acrylate (poly(S-co-BuA)) and tunicin (the cellulose extracted from tunicate – a sea animal) whiskers [137]. The same copolymer was used in association with wheat straw [103, 164] or sugar beet [101] cellulose nanocrystals. Other latexes such as poly (□-hydroxyoctanoate) (PHO) [165-167], polyvinylchloride (PVC) [168-171], waterborne epoxy [172], natural rubber (NR) [122, 173, 174], and polyvinyl acetate (PVAc) [99] were also used as matrix. Recently, stable aqueous nanocomposite dispersions containing cellulose whiskers and a poly(styrene-co-hexyl-acrylate) matrix were prepared via miniemulsion polymerization [106]. Addition of a reactive silane was used to stabilize the dispersion. Solid nanocomposite films can be obtained by mixing and casting the two aqueous suspensions followed by water evaporation.

The possibility of dispersing cellulosic nanofibers in non-aqueous media has been investigated using surfactants or chemical grafting and it opens other possibilities for nanocomposites processing. Cellulose nanoparticles possess a reactive surface covered with hydroxyl groups, providing the possibility to extensive chemical modification. Although this strategy decreases the surface energy and polar character of the nanoparticles, improving by the way the adhesion with non polar polymeric matrix a detrimental effect is generally reported for the mechanical performances of the composite. This unusual

behavior is ascribed to the originality of the reinforcing phenomenon of polysaccharide nanocrystals resulting from the formation of a percolating network thanks to hydrogen bonding forces. Therefore, grafting of long chains instead of small molecules can be used to preserve the mechanical properties of the material.

Very few studies have been reported concerning the processing of cellulose nanofibers reinforced nanocomposites by extrusion methods. The hydrophilic nature of cellulose causes irreversible agglomeration during drying and aggregation in non-polar matrices because of the formation of additional hydrogen bonds between amorphous parts of the nanoparticles. Therefore, the preparation of cellulose whiskers reinforced PLA nanocomposites by melt extrusion was carried out by pumping the suspension of nanocrystals into the polymer melt during the extrusion process [175]. An attempt to use PVA as a compatibilizer to promote the dispersion of cellulose whiskers within the PLA matrix was reported [176]. Organic acid chlorides-grafted cellulose whiskers were extruded with LDPE [177]. The homogeneity of the ensuing nanocomposite was found to increase with the length of the grafted chains. Polycaprolactone-grafted cellulose nanocrystals obtained by ring-opening polymerization of the corresponding lactone were also used as “masterbatches” by melt blending with a PCL matrix [178].

An attempt to use a recently patented concept (Dispersed Nano-Objects Protective Encapsulation - DOPE process) intended to disperse carbon nanotubes in polymeric matrices was reported. Physically cross-linked alginate

capsules were successfully formed in the presence of either cellulose whiskers or microfibrillated cellulose [179]. The ensuing capsules have been extruded with a thermoplastic material.

6.2 Interfacial Interactions

Strong interactions between cellulose nanofibers prepared from cottonseed linters and between the filler and the glycerol plasticized starch matrix were reported to play a key role in reinforcing properties [120]. In non-percolating systems, for instance for materials processed from freeze-dried cellulose nanocrystals, strong matrix/filler interactions enhance the reinforcing effect of the filler. This observation was reported using EVA matrices with different vinyl acetate contents and then different polarities [180]. Improvement of matrix/filler interactions by using cellulose whiskers coated with a surfactant was shown to play a major role on the non linear mechanical properties, especially on the elongation at break [181]. Grunert and Winter (2002) [98] founded a higher reinforcing effect for unmodified cellulose whiskers than for trimethylsilylated whiskers. Apart the fact that 18% of the weight of the silylated crystals was due to the silyl groups, they attributed this difference to restricted filler/filler interactions.

6.3 Mechanical Performance

The first demonstration of the reinforcing effect of cellulose nanocrystals in a poly(S-co-BuA) matrix was reported by Favier et al. (1995) [137]. The authors measured by DMA in the shear mode a spectacular improvement in the storage modulus after adding tunicin whiskers even at low content into the host polymer.

This increase was especially significant above the glass-rubber transition temperature of the thermoplastic matrix because of its poor mechanical properties in this temperature range. Figure 13 shows the isochronal evolution of the logarithm of the relative storage shear modulus (log G'_T/G'_{200}, where G'_{200} corresponds to the experimental value measured at 200 K) at 1 Hz as a function of temperature for such composites prepared by water evaporation. In the rubbery state of the thermoplastic matrix, the modulus of the composite with a loading level as low as 6 wt% is more than two order of magnitude higher than the one of the unfilled matrix. Moreover, the introduction of 3 wt% or more cellulosic whiskers provides an outstanding thermal stability of the matrix modulus up to the temperature at which cellulose starts to degrade (500K).

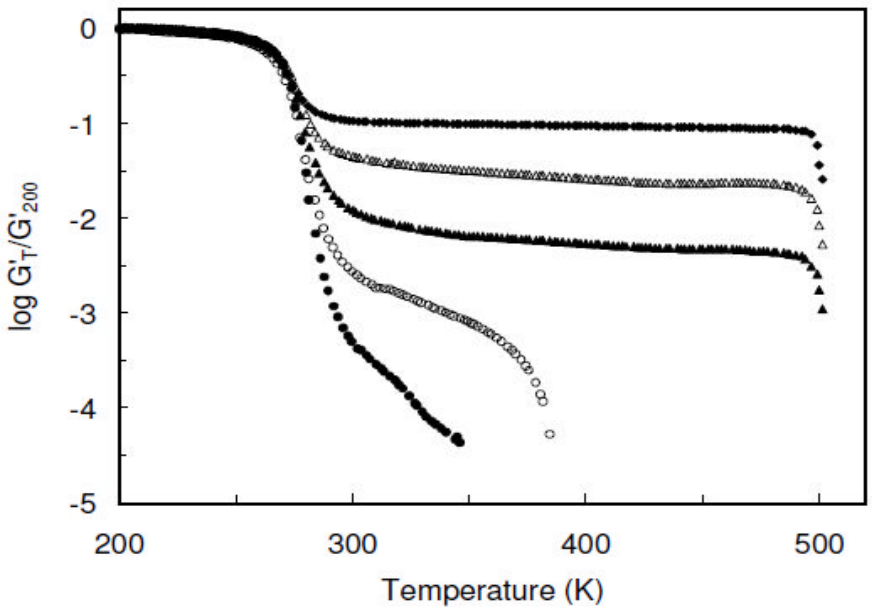


Fig. 13 Logarithm of the normalized storage shear modulus (log G'_T/G'_{200}, where G'_{200} corresponds to the experimental value measured at 200 K) vs temperature at 1 Hz for tunicin whiskers reinforced poly(S-co-BuA) nanocomposite films

obtained by water evaporation and filled with 0 (●), 1 (○), 3 (▲), 6 (△) and 14 wt% (♦) of cellulose whiskers [140]

The macroscopic behavior of cellulose nanofibers based nanocomposites depends as for any heterogeneous materials, on the specific behavior of each phase, the composition (volume fraction of each phase), the morphology (spatial arrangement of the phases) and the interfacial properties. The outstanding properties observed for these systems were ascribed to a mechanical percolation phenomenon [137]. A good agreement between experimental and predicted data was reported when using the series-parallel model of Takayanagi modified to include a percolation approach. Therefore the mechanical performances of these systems were not only due to the high mechanical properties of the reinforcing nanoparticles. It was suspected that the stiffness of the material was due to infinite aggregates of cellulose whiskers. Above the percolation threshold the cellulosic nanoparticles can connect and form a 3D continuous pathway through the nanocomposite film. For rod-like particles such as tunicin whiskers with an aspect ratio of 67, the percolation threshold is close to 1 vol%. The formation of this cellulose network was supposed to result from strong interactions between nanofibers, like hydrogen bonds. This phenomenon is similar to the high mechanical properties observed for a paper sheet, which result from the hydrogen-bonding forces that hold the percolating network of fibers. This mechanical percolation effect allows explaining both the high reinforcing effect and the thermal stabilization of the composite modulus for evaporated films.

Any factor that affects the formation of the percolating whiskers network or interferes with it changes the mechanical performances of the composite [141]. Three main parameters were reported to affect the mechanical properties of such materials, viz. the morphology and dimensions of the nanoparticles, the processing method, and the microstructure of the matrix and matrix/filler interactions.

6.4 Thermal Stability

Thermogravimetric analysis (TGA) experiments were performed to investigate the thermal stability of tunicin whiskers/POE nanocomposites [152-153]. No significant influence of the cellulosic filler on the degradation temperature of the POE matrix was reported. Cotton cellulose nanocrystals content appeared to have an effect on the thermal behavior of CMC plasticized with glycerin suggesting a close association between the filler and the matrix [162]. The thermal degradation of unfilled CMC was observed from its melting point (270°C) and had a very narrow temperature range of degradation. Cellulose nanocrystals were found to degrade at a lower temperature (230°C) than CMC, but shown a very broad degradation temperature range. The degradation of cellulose whiskers reinforced CMC was observed between these two limits, but of interest was the lack of steps. Composites were reported to degrade as a unit.

7. Applications of Polymer Composites

7.1. Biocomposites

Regular polymer composites are non-biodegradable and pollute the environment. There is an increasing movement of scientists and engineers who are dedicated

to minimizing the environmental impact of polymer composite production. Environmental footprints must be diminished at every stage of the life cycle of the polymer composite. Using natural fibers with polymers based on renewable resources will allow many environmental issues to be solved. By embedding biofibers with renewable resource–based biopolymers such as cellulosic plastics; polylactides; starch plastics; polyhydroxyalkanoates (bacterial polyesters); and soy-based plastics, the so-called green Biocomposites could soon be the future.

Nowadays, biocomposites have been the subject of extensive research, specifically in construction and building industry due to their many advantages such as lower weight, and lower manufacturing costs. Currently, not only builders, but also many home owners are interested in using biocomposites for different products such as decking, fencing, and so on. Biocomposites may be classified, with respect to their applications in building industry into two main groups: structural and nonstructural biocomposites [182].

7.1.1. *Structural Application*

A structural Biocomposite can be defined as one that is needed to carry a load in use. For instance, building industry, load-bearing walls, stairs, roof systems and sub - flooring are examples of structural biocomposites. Structural biocomposites can range broadly in performance, from high performance to low performance materials. Bio-based composite materials have been tested for suitability in roof structure (Figure 14) [183]. Structural beams have been designed, manufactured and tested, yielding good results. Soy oil-based resin and cellulose fibers, in the

form of paper sheets made from recycled cardboard boxes may be used for the manufacture of the composite structures.



Fig. 14 Bio-based composite roof panels; one of them is mounted on a demonstration house made of timber [183]

Figure 15 represents, Stay-in-place bridge forms (SIP) are utilized to span the distance between bridge girders. The SIP forms made from biocomposites have many benefits in comparison to steel forms. Biocomposite-based SIP forms are porous or breathable. Therefore, this lets water to evaporate through the form and to avoid any rebar corrosion. The form is also biodegradable; a bio-based form has the potential to break down in the future, allowing underside inspection of the bridge deck. In addition, the form is lighter compared to a steel form, allowing faster and cheaper installations.

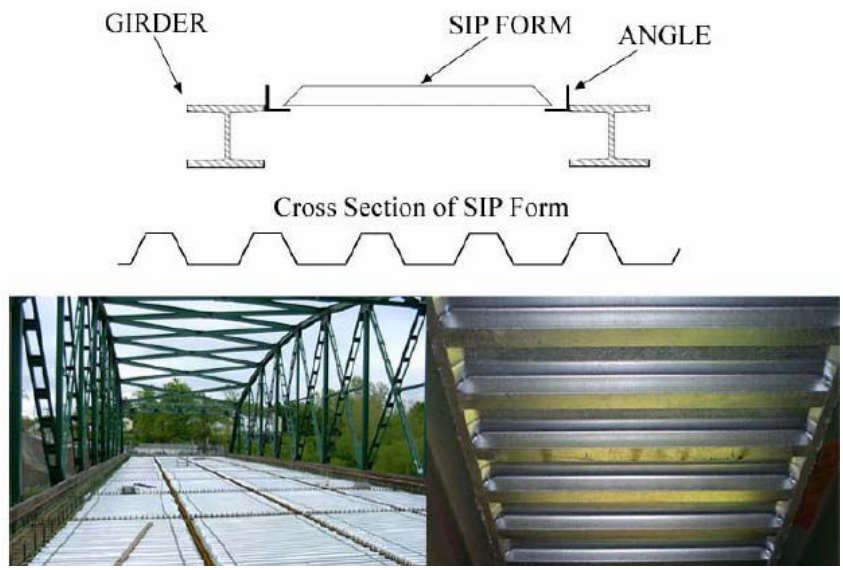


Fig. 15 Stay-In-Place Bridge Form

7.1.2. Nonstructural Application

A nonstructural biocomposite can be defined as one that need not carry a load during service. Materials such as thermoplastics, wood particles, and textiles are used to make this kind of Biocomposites. Nonstructural biocomposites are used for products such as ceiling tiles, furniture, windows, doors, and so on.

Wood fiber plastic composites are made in standard lumber profile cross-section dimensions in exterior construction. These bioproducts are utilized as dock surface boards, deck, picnic tables, landscape timbers, and industrial flooring. Many manufacturers recommend that biocomposites need gaps on both edges and ends for their thermal expansion. Furthermore, wood-based bioproducts are gapped for expansion due to the moisture absorption.

Clear ponderosa pine is utilized in clad components. Currently, it is becoming limited and expensive. In addition, ponderosa pine needs broad cutting, edge

gluing, and finger jointing to get clear sections for window and door fabrication. Also, the glued up material have to be milled to the accurate cross section to be used in the assembly which results in increasing cost and waste wood. Therefore, manufacturers use wood fiber plastic composites as an alternative for solid wood in clad components.

Biocomposites are utilized for the construction of Composite Panels. There are three types of panels: fiberboard, particleboard, and mineral-bonded panels. Bagasse fibers are used for particleboards, fiberboards, and composition panel production. Cereal straw is the second most usual agro-based fiber in panel production. The high percentages of silica in cereal straw make them naturally fire resistant. Also, the low density of straw panels has made them resilient. Results show that houses built by these panels are resistant to earthquake. Straw is also used in particleboards. Rice husks are also fibrous and need little energy input to make the husks ready for use. Rice husks or their ash are used in fiber cement blocks and other cement products. The presence of rice husks in building products helps to increase acoustic and thermal properties. A stress-skin panel-type product has been made by using polyurethane or polyester foam in the core and ply-bamboo in the faces [184]. Figure 16 indicates performance of cellular biocomposite panels against conventional slab and panel systems for commercial and residential construction [185].

7.2. Nanocomposites

The potential applicability of nanocelulose is widely extended. Applications of nanocellulose are mainly considered to be in paper and packaging products,

although construction, automotive, furniture, electronics, pharmacy and cosmetics are also being considered. For companies producing electroacoustic devices, nanocellulose is used as a membrane for high quality sound. Additionaly, nanocellulose is applied in membrane for combustible cells (hydrogen); additives for high quality electronic paper (e-paper); ultra-filtrating membranes (water purification) and membranes used to retrieve mineral and oils [186], and nowadays, nanocellulose has been greatly discussed and researched a huge variety of applications. The high strength and stiffness as well as the small dimensions of nanocellulose may well impart useful properties to composite materials reinforced with these fibers, which could subsequently be used in wide range of applications.

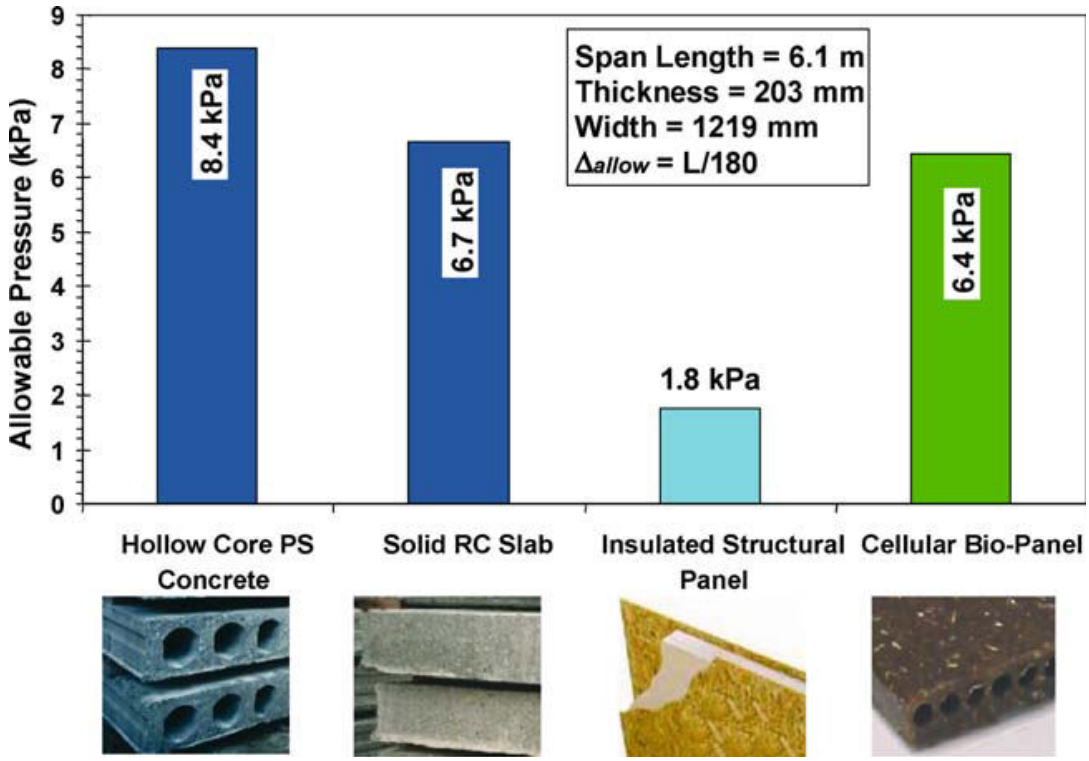


Fig. 16 Performance of cellular biocomposite panels against conventional slab and panel systems for commercial and residential construction [185]

7.2.1. Electronic Industry

7.2.1.1. Diaphragms

Among various applications studied so far, which has already reached the level of practical use is related to acoustic diaphragms, nanocellulose has been found to bear two essential properties: high sonic velocity and low dynamic loss; In fact, the sonic velocity of pure film was almost equivalent to those of aluminium and titanium [63]. Jonas and Farah (1998) [187] stated that SONY® had already been using it in headphones diaphragm (Figure 17). The nanocellulose diaphragms are developed by dehydration and compressed to a thickness of 20 microns in a diaphragm die. The advantage of the ultra-thin nanocellulose diaphragm is that it can produce the same sound velocity as an aluminum or titanium diaphragm, along with the warm, delicate sound that a paper diaphragm provides. Trebles are sparkling clear, and bass notes are remarkably deep and rich in these types of headphones.



Fig. 17 Nanocellulose diaphragm used in SONY® headphones

7.2.1.2. Digital displays

Cellulose has always been the prime medium for displaying information in our society; nowadays, efforts have been made to find dynamic display technology, for example in electronic paper. Nanocellulose is dimensionally stable and has a paper-like appearance which puts it into the leading role for the electronic paper`s basic structure [188]. Shah and Brown [188] proved the concept in a device that holds many advantages such as: high paper-like reflectivity, flexibility, contrast and biodegradability. Figures 18 and 19 shows the fabrication process of display device using nanocellulose.



Fig. 18 Fabrication process of the display using nanocellulose

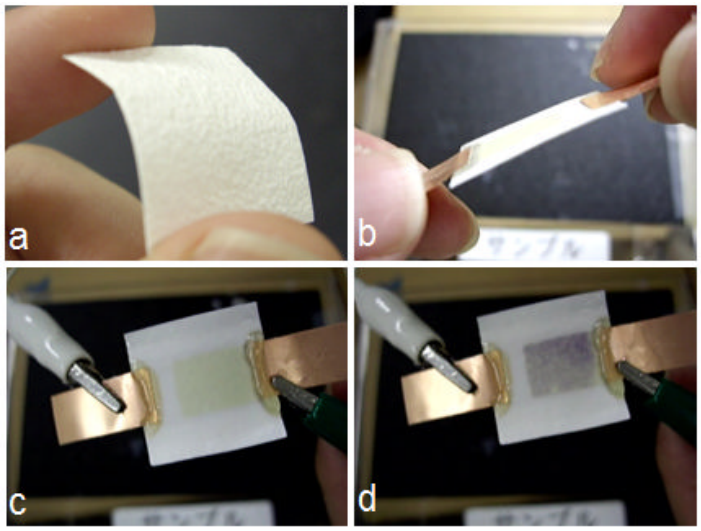


Fig. 19 a) the paper made of nanocellulose; b) display device; c) and d) show the result of the Chromogenic testing [188]

Summarizing, the whole idea is to integrate an electronic dye into the nanostructure of the microbial cellulose, and when integrated, a simple pixel can reversibly switch from the ON to the OFF state. The pixel size is controlled by the minimum addressing resolution of back-plane drive circuits [188]. Yano et al (2005) [189] has shown nanocellulose extraordinary potential as a reinforcement material in optically transparent plastics, for instance, as a substrate for bendable displays. According to the author, the composite remained optically transparent even at high fiber contents.



Fig. 20 Cellulose Nanocomposite based Flexible Organic Light Emitting Diode (FOLED)

Legnani et al (2009) [190] developed biodegradable and biocompatible Flexible Organic Light Emitting Diode (FOLED) (Figure 20) based on nanocellulose (NC) membrane as substrate. Nanocomposite substrates based on nanocellulose (NC) and Boehmite-siloxane systems with improved optical transmittance in the visible region were used as flexible substrate for OLED applications. The nanocomposites formations improve the optical transmittance in visible range. Transmittance of 66% at 550nm was found for the NC-nanocomposite/ITO

(Indium Tin Oxide) substrate when compared to the 40% value at the same wavelength for the NC/ITO substrate. ITO film was deposited at room temperature onto membranes and glass using rf magnetron sputtering with a rf power of 60 W and at pressure of 1 mtorr in Ar atmosphere.

7.2.1.3. Other electronic usages

Evans et al. (2003) [191] found that nanocellulose catalyzed the deposition of metals within its structure, thus a finely divided homogeneous catalyst layer is generated. Experimental data suggested that nanocellulose possessed reducing groups capable of initiating the precipitation of palladium, gold, and silver from aqueous solution. Thus, the structure is suitable for the construction of membrane electrode assemblies. Olson et al (2010) [192] shown that freeze-dried cellulose nanofibril aerogels can be used as templates for making lightweight porous magnetic aerogels, which can be compacted into a stiff magnetic nanopaper.

7.2.2. Pharmaceutical

Cellulose has a long history of use in the pharmaceutical industry. The material has excellent compaction properties when blended with other pharmaceutical excipients so that drug-loaded tablets form dense matrices suitable for the oral administration of drugs. Polysaccharides, natural polymers, fabricated into hydrophilic matrices remain popular biomaterials for controlled-release dosage forms and uses of a hydrophilic polymer matrix is one of the most popular approaches in formulating an extended release dosage forms [193-195]. This is due to the fact that these formulations are relatively flexible and a well designed

system usually gives reproducible release profiles. Drug release is the process by which a drug leaves a drug product and is subjected to absorption, distribution, metabolism, and excretion (ADME), eventually becoming available for pharmacologic action. Crystalline nanocellulose offers several potential advantages as a drug delivery excipient. Crystalline nanocellulose and other types of cellulose in advanced pelleting systems whereby the rate of tablet disintegration and drug release may be controlled by microparticle inclusion, excipient layering or tablet coating [196-197].

The very large surface area and negative charge of crystalline nanocellulose suggests that large amounts of drugs might be bound to the surface of this material with the potential for high payloads and optimal control of dosing. Other nanocrystalline materials, such as nanocrystalline clays have been shown to bind and subsequently release drugs in a controlled manner via ion exchange mechanisms and are being investigated for use in pharmaceutical formulations [198]. The established biocompatibility of cellulose supports the use of nanocellulose for a similar purpose. The abundant surface hydroxyl groups on crystalline nanocellulose provide a site for the surface modification of the material with a range of chemical groups by a variety of methods. Surface modification may be used to modulate the loading and release of drugs that would not normally bind to nanocellulose, such as nonionized or hydrophobic drugs. For example, Lonnberg et al suggested that poly(caprolactone) chains might be conjugated onto nanocrystalline cellulose for such a purpose [199].

Additionally, since crystalline nanocellulose is a low-cost, readily abundant material from a renewable and sustainable resource, its use provides a substantial environmental advantage compared with other nanomaterials.

7.2.3. Medical

Recently nanocellulose has been called as the eyes of biomaterial highly applicable to biomedical industry which includes skins replacements for burnings and wounds; drugs releasing system; blood vessel growth; nerves, gum and dura-mater reconstruction; scaffolds for tissue engineering; stent covering and bone reconstruction [200-204]. Figure 21 shows some applications for nanocellulose within biomedical field.

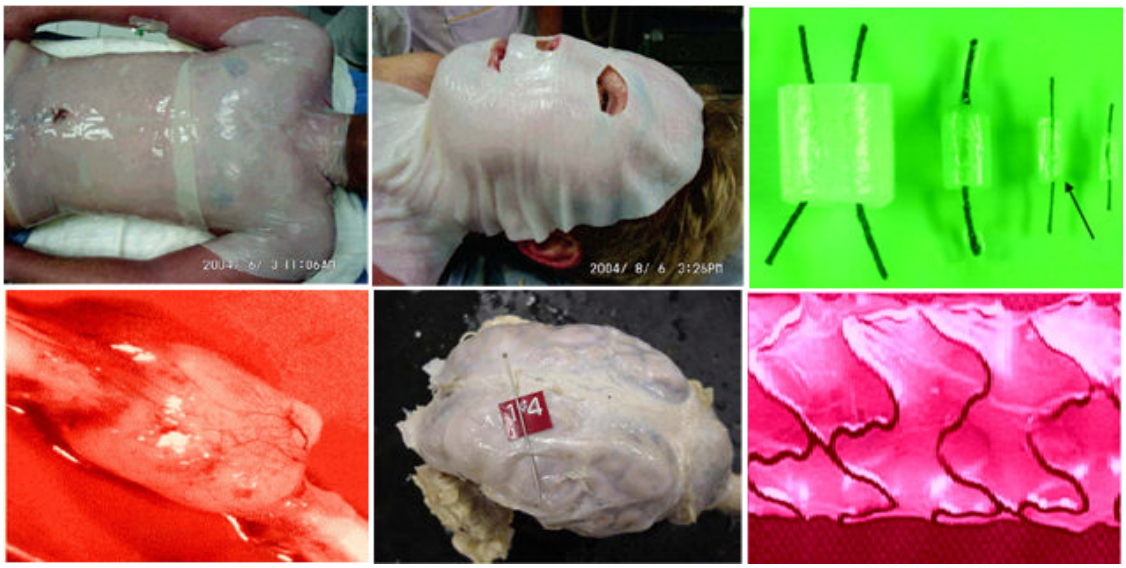


Fig. 21 Biomedical applications of nanocellulose (a) and (b) never dried nanocellulose membrane [202]; (c) and (d) Artificial blood vessels [204]; (e) Dura mater reconstruction [201] (f) covering Stents [203]

Tissue engineering looks for new material and devices which could interact positively with biological tissues [205], either working as an in vitro basis for cell growth or rearranging and developing tissue about to be implanted. They also aim new classes of degradable biopolymers that are biocompatible and whose activities are controllable and specific [206], more likely to be used as cell scaffolds [207], or in vitro tissue reconstruction.

As described above, a great variety of biomaterials have been developed recently. They have all sorts of properties (physical/chemical and mechanical) depending mostly in the final application (tissue regeneration, medication holding and releasing, tissue grafting, or scaffolding) [202]. The scaffold's success depends much on the cellular adhesion and growth onto the surface, thus biopolymer's chemical surface can dictates cellular response by interfering in cellular adhesion, proliferation, migration and functioning.

The surface-cell interaction is extremely important in implant effectiveness, including its rejection. Since the interaction is fully understood in a cell level, new biomaterials and products can be easily developed [208]. The problems still arise due to some methods inefficiency such as cell seeds and sources, scaffolding, ambient, extracellular matrix producing, analysis and appropriate models [209].

On the other hand, to regenerate tissues, three specific foundations are taken: cells, support and growth factors. Cells synthesize the matrix for the new tissues, support holds and keeps the ambient proper for the growth, while the growth factors facilitate and promote the cell regeneration [209]. Material used for implants cannot be either rejected or causes inflammatory response, in others, it

should be biocompatible. Furthermore, it should promote regeneration and if necessary, be absorbed after a while or biodegradable [210]. Studies on support-cell interactions are crucial to implants viability. Many cell responses are observed out of different materials, so the cell ability to discriminate and adapt to it whether adhere or not to its surface [211]. This is crucial as it will direct further responses as cell proliferation, migration and viability.

Due to the clinical importance of skin lesions, many laboratories had been aroused to the search for healing products having benefits including immediate pain relief, close adhesion to the wound bed, and reduced infection rate. The nanocellulose developed having huge superficial area gives great water absorption capacity and elasticity. These are characteristics from an ideal healing bandage. On the other hand, it holds no microbial activity. Nanocellulose mats is very effective in promoting autolytic debridement, reducing pain, and accelerating granulation, all of which are important for proper wound healing. These nanobiocellulose membranes can be created in any shape and size, which is beneficial for the treatment of large and difficult to cover areas of the body.

Barud (2009) [212] has created a biological membrane with bacterial cellulose and standardized extract of propolis. Propolis has many biological properties including anti-microbial and anti-inflammatory activities. All the above mentioned characteristics present, which make the membrane (Figure 22) a good treatment for burns and chronic wounds.

Odontology is challenged to find ideal materials to replace the bones in several procedures, as bones malformation, maxillary and facial deformities. The biggest

challenge is the loss of alveolar bone. Nanocellulose having suitable porosity which gives the mat an infection barrier, loss of fluids, painkiller effect, allows medicines to be easily applied and it also absorbs the purulent fluids during all inflammatory stages, expelling it later on in a controlled and painless manner [213].



Fig. 22 Nanocellulose and propolis based bandage

Polyvinyl alcohol (PVA) is a hydrophilic biocompatible polymer with various characteristics desired for biomedical applications. PVA can be transformed into a solid hydrogel with good mechanical properties by physical crosslinking, using freeze-thaw cycles. Hydrophilic nanocellulose fibers of an average diameter of 50 nm are used in combination with PVA to form biocompatible nanocomposites. According to Millon and Wan (2006) [214] the resulting nanocomposites possess a broad range of mechanical properties and can be made with mechanical properties similar to that of cardiovascular tissues, such as aorta and heart valve leaflets. On their studies, the stress–strain properties for porcine aorta are matched by at least one type of PVA–nanocellulose nanocomposite in both the

circumferential and the axial tissue directions. A PVA–Nanocellulose nanocomposite with similar properties as heart valve tissue is also developed. Relaxation properties of all samples, which are important for cardiovascular applications, were also studied and found to relax at a faster rate and to a lower residual stress than the tissues they might replace. So, finally the new PVA–Nanocellulose composite is a promising material for cardiovascular soft tissue replacement applications.

According to Cai and Kim (2010) [215], have three different methods to prepare Nanocellulose/PEG composite. In the method I, PEG was incorporated in nanocellulose hydrogels by adding PEG solution to the culture medium for Gluconacetobacter xylinus. In the method II, suspensions of microbial cellulose nanofibers are mixed with PEG solution with mechanical stirring followed by freezing-thawing process. The composite is a hydrogel and can be used for soft tissue replacement devices. In the method III, a previously produced nanocellulose hydrogel was soaked with PEG solution, allowing the PEG molecules to penetrate the nanocellulose [216]. The third method seems simple and effective. It has also been used to prepare other nanocellulose based composite. For instance, nanocellulose has been soaked into hydroxyapatite to develop a composite scaffold for bone regeneration [217]. Nanocellulose has also been augmented by immersion in solutions of polyacrylamide and gelatin, yielding hydrogels with improved toughness [218]. Similarly, immersion of nanocellulose into poly (vinyl alcohol) has yielded hydrogels having a wide range of mechanical properties of interest for cardiovascular implants [214]. In this

study, authors reported method III. SEM images showed that PEG molecules were not only coated on the nanocellulose fibrils surface but also penetrated into the nanocellulose fiber networks. The prepared scaffold has very well interconnected porous network structure and large aspect surface. The TGA results prove the improved thermal stability. Tensile test results indicated that the Young's Modulus and tensile strength tended to decrease while the elongation at break had a slight increase. It showed much better biocompatibility compared with the pure nanocellulose. Thus, the prepared Nanocellulose/PEG composite scaffolds are suitable for cell adhesion/attachment, suggesting these scaffolds can be used for wound dressing or tissue-engineering applications.

Lin et al. (2009) [219] used gelatin and its enzymatically modified form (EMG) to prepare nanocellulose nanocomposites in an attempt to enhance the property of rehydration ability of nanocellulose. Referencing SEM photographs of the low Gelatin/Nanocellulose composites (LG/NC), gelatin is shown to lodge in nanocellulose networks and wrap up parts of cellulose ribbons (Figure 23a). As gelatin content in this sample was around 50% (less than in high Gelatin/Nanocellulose composites (HG/NC), a certain quantity of cellulose ribbons emerged. EMG filled up some of the space in the nanocellulose network and some thickened cellulose ribbons could be observed in EMG/NC composites (Figure 23b). Film-like structures were observed only less in non-polar EMG/Nanocellulose (NPEMG/NC) and polar (PEMG/NC) composites. Porous networks and thickened cellulose ribbons could be found in these two composites (Figure 23c and d). It appears that NPEMG and PEMG permeated

into the network and adsorbed on the cellulose ribbons, allowing the continuance of porous structures in these composites. According to the results, they concluded that gelatin and its hydrolysates in combination with nanocellulose can effectively improve the rehydration properties of composites. The polar functional groups of gelatin and EMG as well as nanocellulose porous networks with lower level of crystallinity contributed to the rehydration ability of composites. Nanocellulose immersed in 0.5% EMG solution was sufficient to prepare the desirable composites and may be applied in a rehydratable membrane.

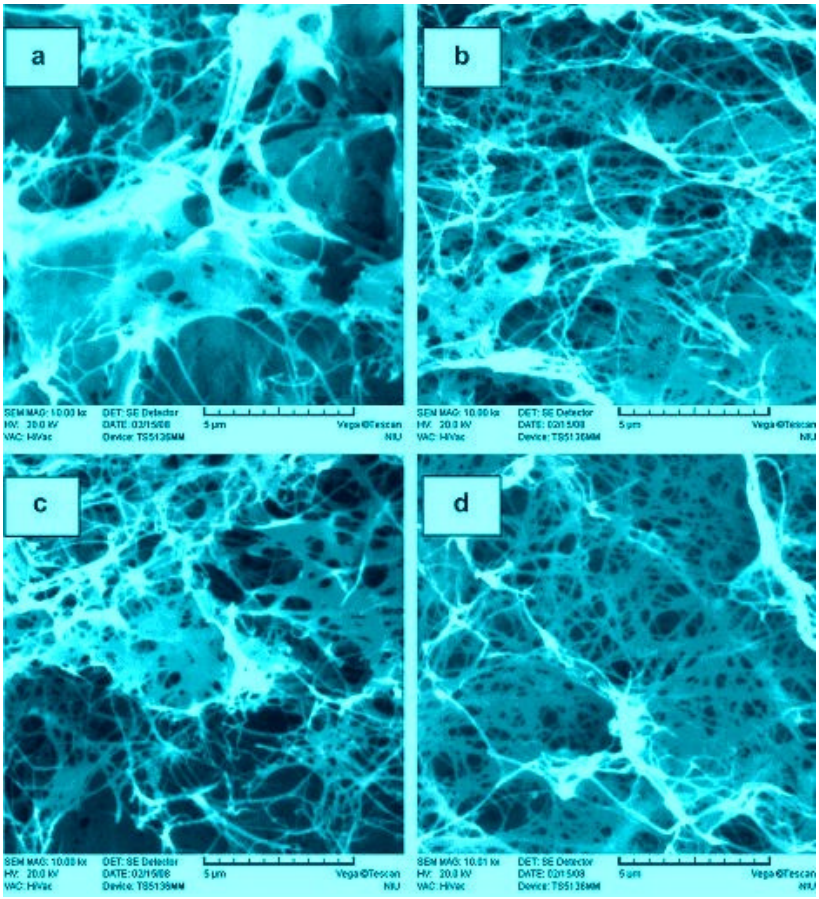


Fig. 23 SEM photographs (10000X) of LG/NC (a) Gelatin/NC (b) EMG/NC (c) NPEMG/NC (d) PEMG/NC

In ophthalmologist area, Huia et al. (2009) [220] explored the potentiality of nanocellulose applied as the scaffold of tissue engineering cornea. They studied the growth of human corneal stromal cells on nanocellulose. The ingrowth of corneal stromal cells into the scaffold was verified by Laser Scanning Confocal Microscope. The results suggest the potentiality for this biomaterial as a scaffold for tissue engineering of artificial cornea. The surface of nanocellulose is lumpy with rills. In Figure 24A and B, the red regions are corneal stromal cells immunofluorescent stained by Vim and the blue region is the nanocellulose scaffold. It is clearly illustrated that corneal stromal cells ingrew into the scaffold.

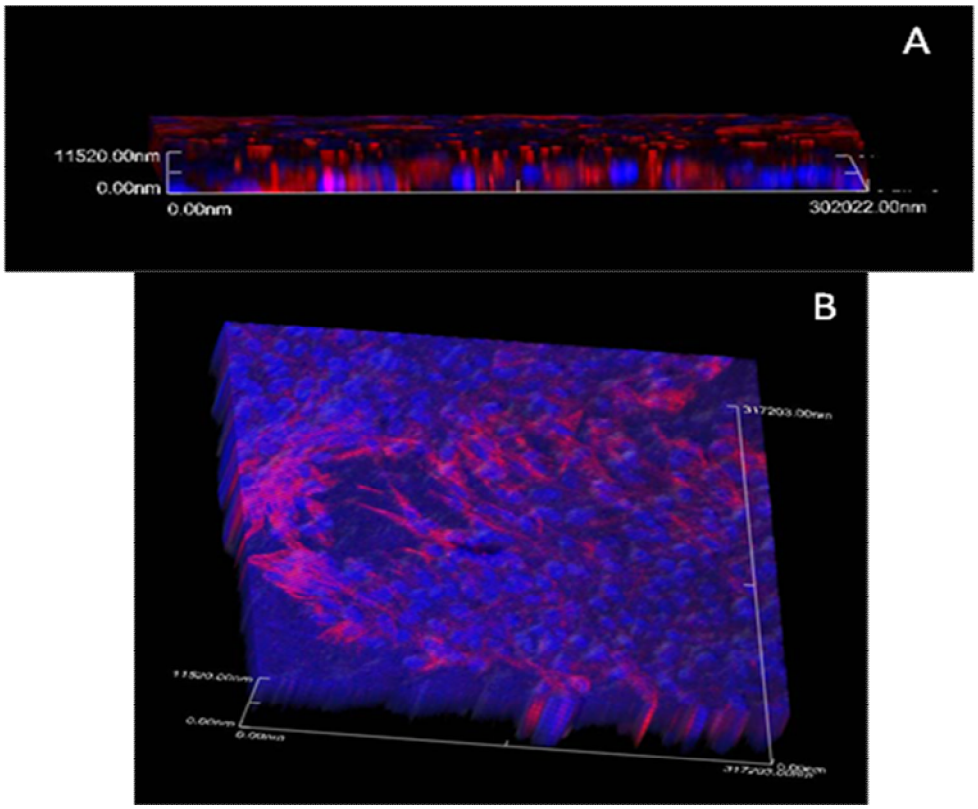


Fig. 24 Growth of Vim Immune Fluorescent Stained human corneal stromal cells in nanocellulose scaffold, observed by LSCM (X400)

For otorhinolaryngologist, surgery of the lateral wall of the nose is common procedure in the ENT specialty and was recommended for resection of soft lush, removal of tumors or to promote aeration of the sinuses. The evolution of surgical techniques provided increased safety to patients, drastically reducing the complications and postoperative morbidity. The nasal bleeding, surgical wound infections, local pain and the presence of adhesions are the major complicating factors related to nasal surgery. Several types of materials have been developed in order to prevent these complications. Nasal packing has been used in these post-surgical procedures and, although effective in preventing bleeding, requires removal causing great discomfort to the patient. Moreover, their presence has been associated with systemic infections graves. The use of a material that, in addition to preventing bleeding, could provide more rapid healing without the formation of crusts and prevent infection without the need for removal would be of great aid in the postoperative period of patients undergoing resection of the lower nasal concha and other nasal surgeries. In 1984, microbiologist Louis Farah Fernando Xavier was able, through the fermentation of bacteria of the genus Acetobacter to produce bacterial cellulose. The resulting film of this synthesis, after processing, is endowed with selective permeability, allowing passage of water vapour but preventing the passage of microorganisms. It is semitransparent, homogeneous, with an average thickness of 0.05 mm and visually very similar to human skin. Schumann et al. (2009) [221] studied the artificial vascular implants from nanocellulose by two studies. In a first microsurgical study, the nanocellulose implants were attached in an artificial

defect of the carotid artery of rats for 1 year. These long term results show the incorporation of the nanocellulose under formation of neointima and ingrowth of active fibroblasts. In a second study, the grafts were used to replace the carotid arteries of pigs. After 3 months, these grafts were removed and analyzed both macro and microscopically. Seven grafts (87.5%) were patent whereas one graft was found occluded. These data indicate that the innovative nanocellulose engineering technique results in the production of stable vascular conduits and confirm a highly attractive approach to in vivo tissue engineered blood vessels as part of programs in cardiovascular surgery. The Figure 25 shows the untreated segment of carotid artery revealing a homogeneous endothelialization inside the grafts with an almost smooth transition to the artery.

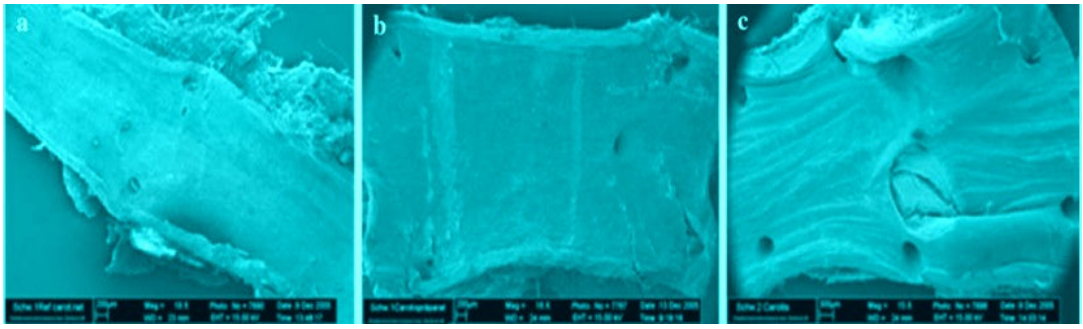


Fig. 25 SEM (magnification 169 to 199): (a) untreated segment of the carotid artery, (b) and (c) good endothelialization of nanocellulose grafts

Another use of nanocellulose is for nasal reconstruction. The desire for an ideal shape has always been part of mankind. Nose, centrally located in the face, is better susceptible to traumas, deformities, thus social disorders. Even since having a major breathing function, it has a great esthetic function, highlighting face's genetics. Amorim et al. (2009) [222] evaluated the tissue response to the

presence of nanocellulose in the nose bone (Figure 26). It had been used 22 rabbits, being that, in 20 a cellulose blanket was implanted in the nasal dorsum, 2 were kept as control group. After three and six months, the back bone was extirpated for further histopathological study, parameter were such as blood vessels clogging, inflammation intensity and presence of purulent fluids.

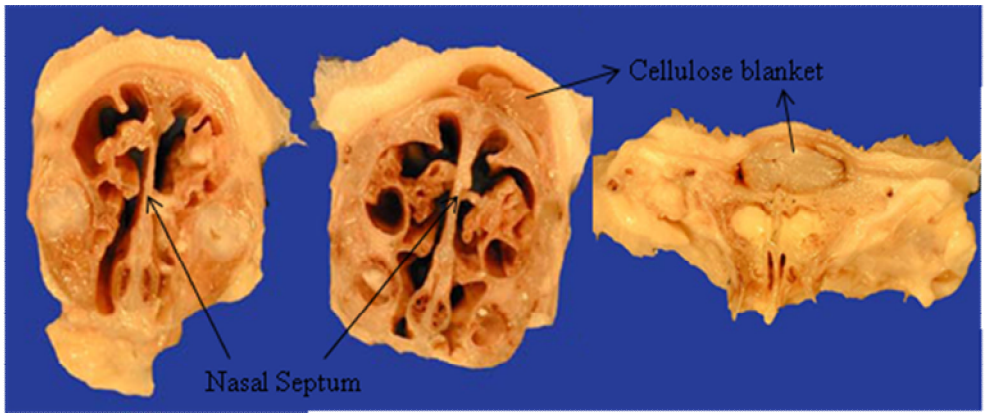


Fig. 26 Serial cut from the nasal septum and front part of the nose showing the cellulose blanket in the nose bone structure

Inflammation was found to be stable, which is probably due to the surgical procedure itself and not to the cellulosic blanket. For the other parameters, there was no statistical significance. Nanocellulosic blanket showed good biocompatibility and did not change over time, thus an excellent material to elevate the nose bone.

7.2.4. Veterinary

Hart et al (2002) [223] studied the pellicle and its ability to promote fibroblast migration and cellular proliferation in diabetic rats. The treatment accelerated the wound healing for the diabetic rats, and improved histological outcome. Diabetic

rat is a recognized model for chronic wounds, thus sharing some features with the chronic human wound. So they could predict the applicability in humans.

Helenius et al. (2006) [224] studied for the first time the in vivo biocompatibility of nanocellulose systematically. Thus, in the development nanocellulose membrane was implanted into the subcutaneous space of rats for 1, 4, and 12 weeks. The implants were evaluated in aspects of chronic inflammation, foreign body responses, cell ingrowth, and angiogenesis, using histology, immunohistochemistry, and electron microscopy. There were no macroscopic signs of inflammation around the implants (redness, edema or exudates) (Figure 27). There were no microscopic signs of inflammation either (i.e., a high number of small cells around the implants or the blood vessels). No fibrotic capsule or giant cells were present. Fibroblasts infiltrated nanocellulose (Figure 28), which was well integrated into the host tissue, and did not elicit any chronic inflammatory reactions, so, the biocompatibility of nanocellulose is proved and the material has potential to be used as a scaffold in tissue engineering.



Fig. 27 Explantation of implants after 1 week

Helenius et al., (2006) [224] brought up more knowledge on biomaterial and its interaction with the cell. In their study, membranes of nanocellulose had been implanted into rats and the biocompatibility was evaluated in vivo. Implants didn't cause 'foreign body reaction', fibrosis or encapsulation, and the rat's conjunctive tissues were well integrated to nanocellulose. Some weeks after the implantation, the rearrangement kept on happening and fibroblasts were fully integrated to the cellulosic structure, they had started to synthesize collagen. Helenius et al. (2006) [224] had also shown that the density influenciates the morphology and cell penetration: as density increased, cell migration lowed. It was observed that nucleus morphology depends on the direction taken by the cellulosic nanofiber, blood flow was also observed.

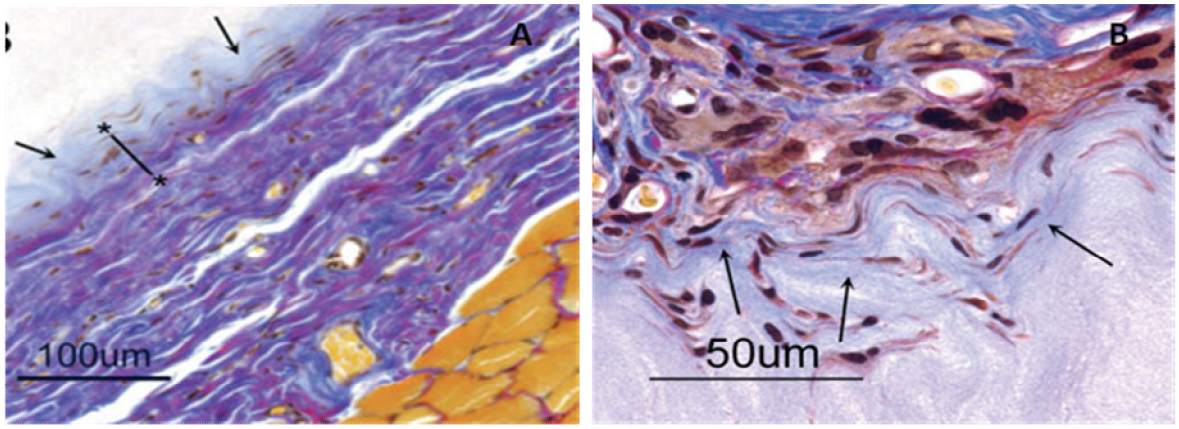


Fig. 28 Ladewig's trichrome staining. (A) The compact side after 12 weeks. Fewer cells are present compared to that after 1 and 4 weeks and the fibroblasts inside the nanocellulose have synthesized collagen (B) High magnification of the interface area at the porous side of nanocellulose after 12 weeks. Arrow heads show collagen synthesized by the fibroblasts

Silva (2009) [225] had evaluated the biological behavior of synthetic hydroxyapatite (HAP-91) when implanted in the dental cavities and covered by nanocellulose. Membranes were shaped into triangles fully covering the cavities avoiding the contact between hydroxyapatite and the oral cavity (a source of contaminants, Figure 29). Silva found that nanocellulose associated to the HAP promoted faster bone regeneration if compared with the control group. 8 days after procedure and a delay of 30 days, although after 50 days they had tissues alike.

Costa e Souza (2005) [226] studied the skin healing in swine; they underwent thermal abrasion, (metal temperature at 100ºC). Comparing Bionext® to the daily healing bandage, all the animals had the healing process completed equally. No differences were seen between the daily bandage and the cellulose pellicle (Bionext®).

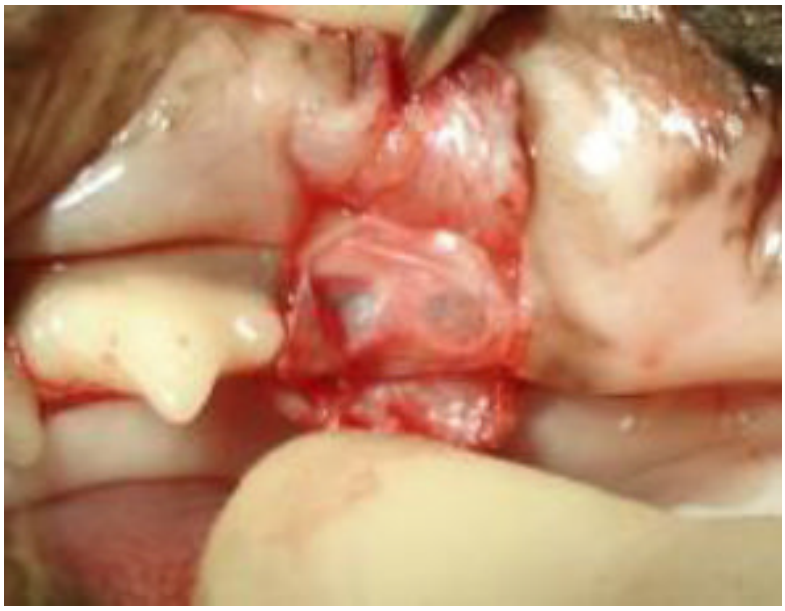


Fig. 29 Cellulosic membranes used as dental cavities covering in cats

For dogs whose peritoneum had been replaced, it was observed that 45 days after the implant, fibroblasts and blood vessels numbers increased. After 90 days collagen and fibroblasts penetrated into nanocellulose and 180 days after implantation nanocellulose formed a net along the conjunctive tissue, little evidence of neovascularization was found [227].

7.2.5. Dental

Nanocellulose was tested in dental tissue regeneration. Microbial cellulose produced by the Glucanacetobacter xylinus strain, can be used to regenerate dental tissues in humans (Figure 30). Nanocellulose product Gengiflex® and Gore-Tex® has intended applications within the dental industry. It was developed to aid periodontal tissue recovery [228]. A description was given of a complete restoration of an osseus defect around an IMZ implant in association with a Gengiflex® therapy. The benefits included the reestablishment of aesthetics and function of the mouth and that a reduced number of surgical steps were required.



Fig. 30 Nanocellulose used in dental tissue regeneration in 39-year-old female patient

The bandage, called Gengiflex®, consists of two layers: the inner layer is composed of microbial cellulose, which offers rigidity to the membrane, and the outer alkali-cellulose layer is chemically modified [229]. Salata et al. (1995) [230] compared the biological performance of Gengiflex® and Gore-Tex® membranes using the *in-vivo* non-healing bone-defect model proposed by Dahlin et al. (1988) [231].

The study showed that Gore-Tex® membranes (a composite with polytetrafluoroethylene, urethane and nylon) were associated with significantly less inflammation and both membranes promoted the same amount of bone formation during the same period of time. A greater amount of bone formation was present in bone defects protected by either Gore-Tex® or microbial cellulose membrane, when compared to the control sites. Gore-Tex® is better tolerated by the tissues than Gengiflex®. Recently, in a similar vein, Macedo et al (2004) [232] also compared bacterial cellulose and polytetrafluoroethylene (PTFE) as physical barriers used to treat bone defects in guided tissue regeneration. In this study, two osseous defects (8 mm in diameter) were performed in each hind-foot of four adult rabbits, using surgical burs with constant sterile saline solution irrigation. The effects obtained on the right hind-feet were protected with PTFE barriers, while Gengiflex® membranes were used over wounds created in the left hind-feet. After 3 months, the histological evaluation of the treatments revealed that the defects covered with PTFE barriers were completely repaired with bone tissue, whereas incomplete lamellar bone formation was detected in defects

treated with Gengiflex® membranes, resulting in voids and lack of continuity of bone deposition.

Nanocellulose with its characteristics like nanofibers size and distribution, mechanical properties, compatibility and ability to mold create it a unique biomaterial indispensable in health area. The nanocellulose composite scaffolds are biocompatible with less rejection with cellular contact and blood contact cells interaction, to be a promissory biomaterial and may be suitable for cell adhesion/attachment suggesting that these scaffolds can be used for wound-dressing or tissue-engineering scaffolds.

Conclusions

The potential applicability of nanocelulose is widely extended. Applications of nanocellulose are mainly considered to be in paper and packaging products, although construction, automotive, furniture, electronics, pharmacy and cosmetics are also being considered. The high strength and stiffness as well as the small dimensions of nanocellulose may well impart useful properties to composite materials reinforced with these fibers, which could subsequently be used in wide range of applications.

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