REVIEW OF RECENT RESEARCH IN NANO CELLULOSE PREPARATION FROM DIFFERENT LIGNOCELLULOSIC FIBERS

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Abstract. Lignocellulosic fibers have become the focus of intense interest in recent years. They have attracted the attention of scientists and technologies worldwide because of their tremendous advantages and now it is possible to isolate cellulose nanofibrils and nanowhiskers from various lignocellulosic wastes. Studies in this area have shown that both cellulose nanofibrils and nanowhiskers could be used as reinforcing fillers to improve mechanical and barrier properties of different types of polymer systems which include rubbers, thermoplastics and thermosets. This review paper provides an overview of recent progress made in the area of nanocellulose and nanowhiskers preparation from various natural fibers. A thorough review of the various techniques being currently used for the isolation of cellulose nanofibers and nanowhiskers has been presented. Finally, the emerging applications of these materials in various fields including nanocomposite preparation have been presented.

1. INTRODUCTION

Nanotechnology is the understanding and controlling of matter at dimensions of roughly 1–100 nm, where unique phenomena enable novel applications. Nanomaterials from cellulose and lignocelluloses play a large role in the nanotechnology field. The development of cellulose nanofibers (CNFs) has attracted significant interest in the last few decades due to the unique characteristics they endow such as high surface area-to-volume ratio, high Young's modulus, high tensile strength and low coefficient of thermal expansion [1-3]. For environmental awareness and the international demand for green technology, bio nano composites have the potential to replace present petrochemical based materials. The use of natural fibers instead of traditional reinforcement materials such as glass fibers, carbon and talc provides several advantages including low density, low cost, good specific mechanical properties, reduced tool wear and biodegradability [4].

CNFs have shown great potential in several applications including biomedical, bioimaging, nanocomposite, gas barrier films and optically transparent functional materials [5-11]. Although CNFs can be extracted from algae, tunicates and bacterial cellulose, the main source is natural plant cell walls [12]. Considering the fact that plant fibers are renewable, abundant and low cost and can be extracted into nanofibers thinner than fibers from bacterial cellulose and tunicates, many researchers have

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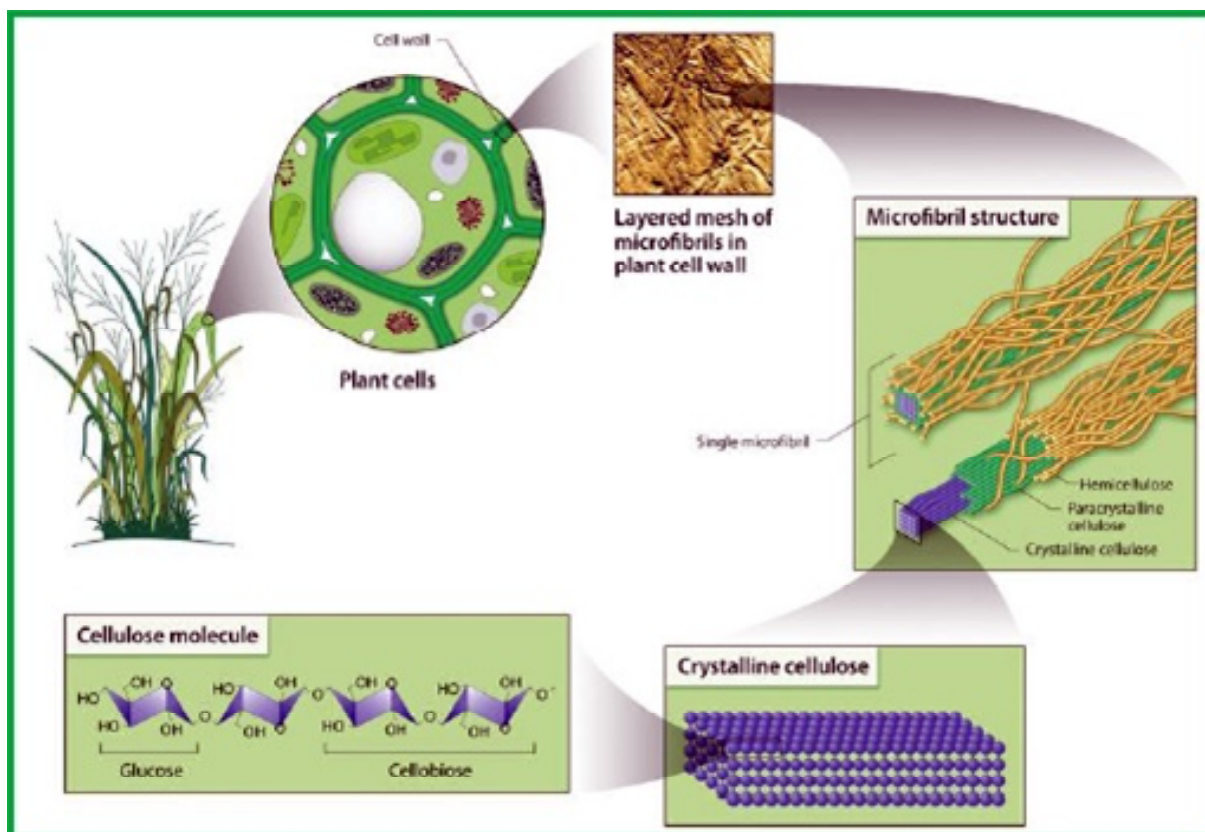
Fig. 1. Scheme of the cellulose cell wall and microfibril organization, Reprinted with permission from G. Siqueira, J. Bras and A. Dufresne, Polymers vol 2, 2010 728, (c) 2010 MDPI.

extensively studied the extraction of nanofibers from the natural plant cellulose fibers. The main aim of this paper is to provide a comprehensive review on different approaches being used to isolate cellulose nanofibrils and nanowhiskers from different lignocellulosic fibers. The morphology and properties of nanofibers and nanowhiskers obtained from various lignocellulosc waste materials (extracted using various techniques) have been discussed and compared. Finally, the applications of these nanoscale materials have been reviewed.

2. STRUCTURE OF LIGNOCELLULOSIC FIBERS

Lignocellulosic fibers are one of the major renewable resource materials throughout the world. There are about 2000 species of useful fibre plants in various parts of the world and these are used for many applications. Now industrialists utilize the locally grown fibres as substitute for expensive synthetic fibres. Natural fibers basically constituted of cellulose, lignin and hemicellulose. Pectin, pigments and extractives can be found in lower quantities.

For this reason natural fibers are also referred as cellulosic fibers [13]. The chemical composition and cell structure of natural fibers are quite complicated. Each fiber is essentially a composite in which rigid cellulose microfibrils are embedded in a soft matrix mainly composed of lignin and hemicelluloses [14]. The properties of cellulosic fibers are strongly influenced by many factors like chemical composition, internal fiber structure, micro fibril angle and cell dimensions which differ from different parts of a plant as well as from different plants. The mechanical properties of natural fibers also depend on their cellulose type because each type of cellulose has its own crystalline organization, which can determine the mechanical properties [15]. An elementary plant fibre is a single cell typically a length from 1 to 50 mm and a diameter of around 10-50 μm. Plant fibres are like microscopic tubes and it consists of several cell walls. These cell walls are formed from cellulose microfibrils of diameter 10-30 nm and are made up of 30-100 cellulose molecules. Fig. 1 shows the scheme of the cellulose cell wall and microfibril organisation. Extraction of fibres from the plant stems is achieved by various methods. Retting is a process of controlled degradation of the plant stem to allow the fibre to be separated from the woody core and thereby improving the ease of extraction of the fibres from the plant stems. Ret-

ting procedures can be divided into biological, mechanical, chemical and physical fibre separation process [16].

3. STRUCTURAL ORGANIZATION OF CELLULOSE

Cellulose is considered to be the most abundant renewable polymer on earth. This structural material is organized as microfibrils linked together to form cellulose fibers. It is biosynthesized by a number of living organisms ranging from higher to lower plants, some amoebae, sea animals, bacteria and fungi [17]. Cellulose consists of a linear homopolysaccharide composed of D-glucopyranose units linked together by β-1-4-linkages. Each monomer bears three hydroxyl groups and these hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystalline packing and also governing the physical properties of cellulose [18]. Cellulose micro fibrils are the basic structural component of cellulose formed during the biosynthesis. The chains of poly- β-(1→4)-D-glucosyl residues aggregate to form a fibril which is a long thread-like bundle of molecules laterally stabilized by intermolecular hydrogen bonds [19-21]. Individual cellulose microfibrils have diameters ranging from 2 to 20 nm. Each microfibril can be considered as a string of cellulose crystals linked along the micro fibril axis by disordered amorphous domains [22]. The anomalies exist in the literature regarding the nomenclature applied to cellulosics are reviewed by Siro and Plackett 2010 [3]. The term microfibril is generally used to describe the 2–10 nm thick fibrous cellulose structures with the length of several microns formed during cellulose biosynthesis in higher plants. Depending on their origin the micro fibril diameters may vary. Nanofibrils and nanofibers are also used as synonyms for micro fibril. Even though the thickness of MFC nano-elements is as small as 3–10 nm it is typically in the range of 20–40 nm since MFC usually consists of aggregates of cellulose microfibrils [23]. When subjected to acid hydrolysis, cellulose microfibrils undergo transverse cleavage along the amorphous regions and the use of sonication results in a rod-like material with a relatively low aspect ratio referred as cellulose whiskers [24]. Other synonyms for cellulose whiskers include nanowhiskers [25], nanorods [26], and rod-like cellulose crystals [27]. Strong hydrogen bonding between the individual cellulose crystals promotes re-aggregation [28] which leads to another cellulose structure called microcrystalline cellulose (MCC). MCC is a commercially available material

mainly used as a rheology control agent and as a binder in the pharmaceutical industry [29].

4. ISOLATION OF MICROCRYALLINE CELLULOSE, CELLULOSIC NANOFIBRILS AND NANOCRYSTALS

Methods for producing MFC were first reported by Herrick et al. [30] and Turbak et al. The principle of their methods was to pass dilute cellulosic wood pulp-water suspensions through a mechanical homogenizer, in which a large pressure drop facilitated micro fibrillation [3]. The manufacture of MFC is now generally performed by a mechanical treatment consisting of refining and high pressure homogenizing process [21,32-33]. Cryocrushing is an alternative method for producing nanofibers in which fibers are frozen using liquid nitrogen and high shear forces are then applied. Alemdar and Sain (2008) extracted MFC from wheat straw and soy hulls via mechanical treatment. In such equipment the cellulose slurry is passed between a static grind stone and a rotating grind stone revolving at 1500 rpm [35]. A major obstacle that needs to be overcome is the high energy consumption connected to the mechanical disintegration of the fibers to MFC. By combining the mechanical treatment with certain pre-treatments it is possible to decrease the energy consumption. Before mechanical processing, a number of researchers have applied alkaline treatment of fibers in order to disrupt the lignin structure and help to separate the structural linkages between lignin and carbohydrates [20,36]. Purification by mild alkali treatment results in the solubilisation of lignin, pectins and hemicelluloses. Oxidation pre-treatment is another method. Saito et al. (2006) introduced an oxidation pre-treatment of cellulose, applying 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals before mechanical treatment [37]. Softwood and hardwood celluloses were oxidized by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation. The TEMPO-oxidized cellulose fibers were converted to transparent dispersions in water, which consisted of individual nanofibers 3"4 nm in width. Films were then prepared from the TEMPO-oxidized cellulose nanofibers (TOCN) and characterized from various aspects. AFM images showed that the TOCN film surface consisted of randomly assembled cellulose nanofibers [9]. Systematic diagram of individualization of nano-sized plant cellulose fibrils by surface carboxylation using TEMPO catalyst is shown in Fig. 2. TEMPO-mediated oxidation is a promising method for sur-
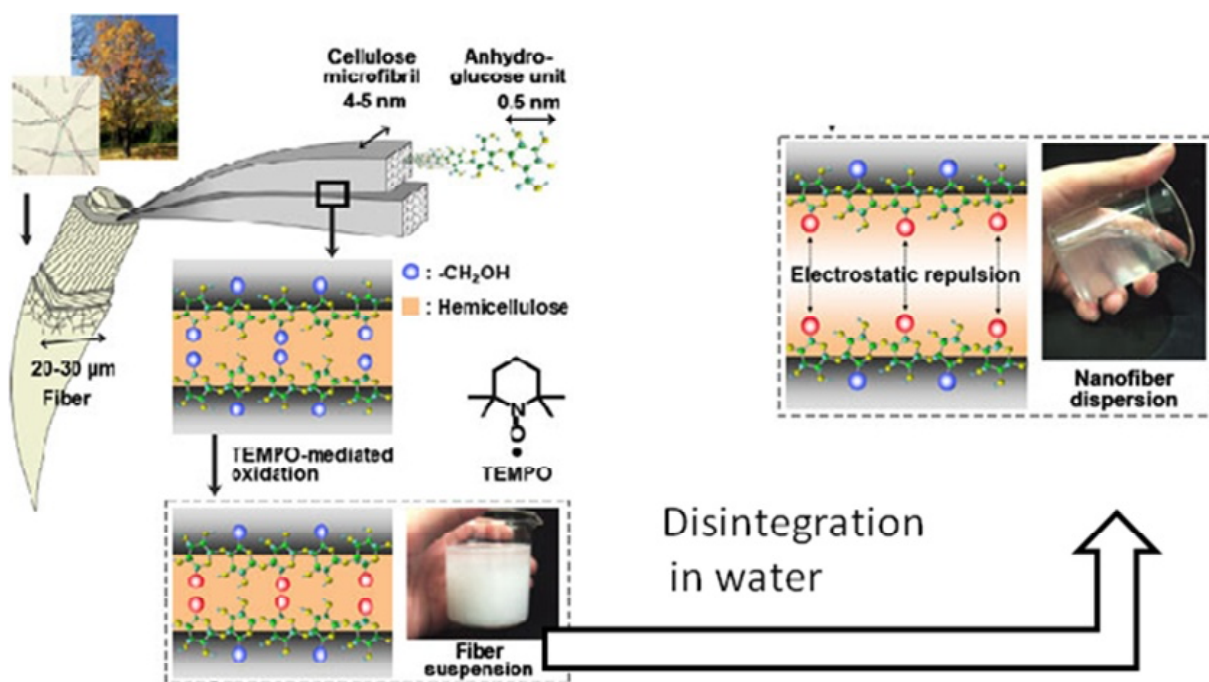
Fig. 2. Systematic diagram of individualization of nano-sized plant cellulose fibrils by surface carboxylation using TEMPO catalyst. (Image: Dr. Isogai/University of Tokyo), Reprinted with permission from H. Fukuzumi, T. Saito, T. Iwata, Y. Kumamoto and A. Isogai, Biomacromolecules vol 10, 2009, p. 162, (c) 2010 Americal Chemical Society.

face modification of native celluloses by which carboxylate and aldehyde functional groups can be introduced into solid native celluloses under aqueous and mild conditions [38].

Enzymatic pre-treatment is another method for reducing energy consumption. Henriksson et al. (2007) and Paakko et al. (2007) found that endoglucanase pre-treatment facilitates disintegration of wood fiber pulp into MFC nanofibers. Moreover, the MFC produced from enzymatically pre-treated cellulosic wood fibers showed more favourable structure than nanofibers produced by acid hydrolysis [33,39]. Literature study reveals that different preparation methods were adopted for the isolation of cellulose nanofibrils. Dufresne et al. (2000) tried mechanical treatment on bleached potato and obtained nanofibers with a dimension 5 nm in width [40]. Iwamoto et al. (2005) obtained nanofibers with a width of 50–100 nm from kraft pulp by passing through a refiner of gap 0.1 mm (30 times) followed by homogenization [41]. Wang and Sain (2007) used cryocrushing method for soybean stock and obtained nanofibers of width 50–100 nm [36]. In another study Alemdar and Sain (2008) obtained nanofibers from wheat straw by cryocrushing followed by fibrillation and subsequent homogenization. The nanofibrils have 20–120 nm in width the majority around 30–40 nm [35]. Chen et al. (2011) individualized cellulose nanofibers from poplar wood

in two distinct stages. Initially wood fibers were subjected to a chemical process to eliminate lignin and hemicellulose [42]. Then these fibers were mechanically separated into nanofibers using high intensity ultrasonication as shown in Fig. 3. The diameter distributions of the resulting nanofibers were dependent on the output power of the ultrasonic treatment. They also isolated cellulose nanofibers (CNFs) by chemical ultrasonic treatment from four kinds of plant cellulose fibers and made a comparative study. The chemical composition, morphology, crystalline behaviour, and thermal properties of the nanofibers and their intermediate products were characterized and compared [43]. The CNFs extracted from wood, bamboo, and wheat straw fibers had uniform diameters of 10–40 nm, whereas the flax fibers were not uniformly nanofibrillated because of their initially high cellulose content.

Leyva et al. (2011) produced cellulose nanofibers from durum wheat straw and characterized it to study its potential as reinforcement fibers in biocomposites [44]. Cellulose nanofibers were produced via an electrospinning method using trifluoroacetic acid (TFA) as the solvent. The nanofibers were approximately 270 nm in diameter. Alemdar et al. (2007) extracted cellulose nanofibers from the agricultural residues (wheat straw and soy hulls) by a chemimechanical technique and the structure of nanofibers were investigated by transmission electron micros-
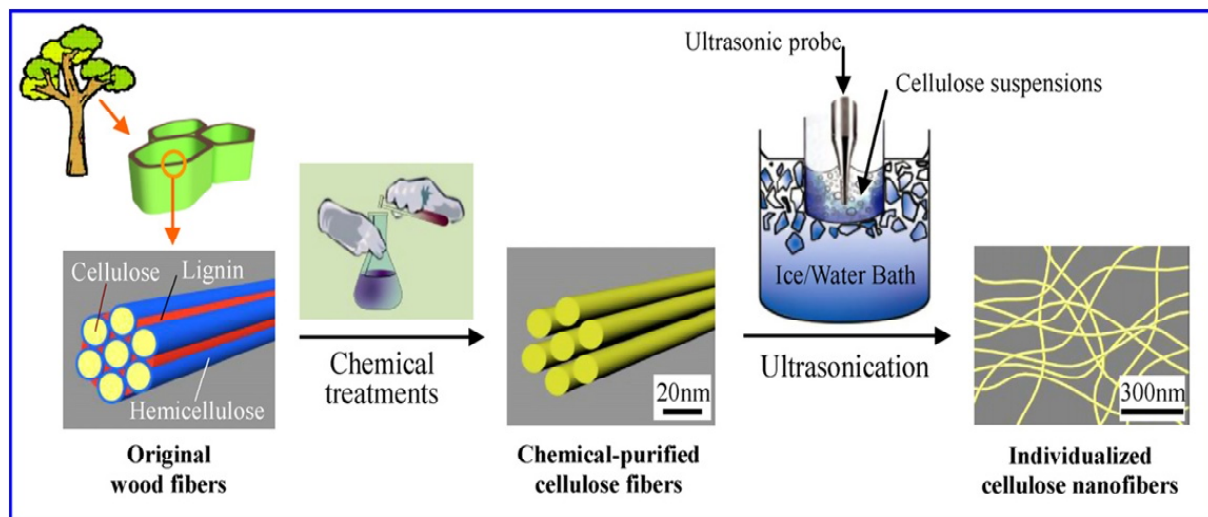
Fig. 3. Procedure for the separation of cellulose nanofibers from polar wood, Reprinted with permission from W. Chen, H. Yu, Y. Liu and Y. Hai, Carbohydrate Polymers vol. 83, 2011, p. 1804, (c) 2011 Elsevier.

copy [35]. The wheat straw nanofibers have diameters in the range of 10-80 nm and lengths of a few thousand nanometers. By comparison it is found that the soy hull nanofibers had diameter 20-120 nm and shorter lengths than the wheat straw nanofibers. In another study, Mandal et al. (2011) synthesized nanocellulose with a reasonable content of cellulose II from waste sugarcane baggase, by acid hydrolysis. They obtained it in the form of a stable suspension where the surface anionic charges help to bring the necessary stabilization of the nanoculelulose [45]. Leitner et al. (2007) isolated cellulose from sugar beet chips, a by-product of sugar production by wet chemistry [46]. Further processing of the cellulose with a high-pressure homogenizer led to the disruption of cell walls into nanofibrils. Cellulose sheets obtained by casting and slow evaporation of water showed higher strength and stiffness when compared to unhomogenised cellulose. The addition of prepared cellulose nanofibrils to a polyvinyl alcohol and a phenol-formaldehyde matrix respectively demonstrated excellent reinforcement properties. Abraham et al. (2011) obtained an aqueous stable colloid suspension of cellulose nano fibrils from three different lignocellulosic fibres namely banana, jute and pineapple leaf fibre (PALF) using steam explosion technique along with mild chemical treatment [47]. These processes included chemical procedures such as alkaline extraction, bleaching, and acid hydrolysis. On removing the noncellulosic constituents of the fibres by chemical treatment, the degree of crystallinity changed and the trend was same in all these three fibres. The removal of surface impurities on plant fibres is advantageous in fibre–matrix adhesion, as

it facilitates both mechanical interlocking and the bonding reaction due to the exposure of the hydroxyl groups to chemicals such as resins and dyes. The percentage crystallinity in fibers was in the order PALF > banana > jute and this order agrees with the values of cellulose content determined in these samples. Cherian et al. (2010) employed steam explosion process for the successful extraction of cellulose nanofibrils from pineapple leaf fibers [48]. Steam coupled acid treatment on the pineapple leaf fibers is found to be effective in the depolymerisation and defibrillation of the fibre to produce nanofibrils. The developed nanocellulose promises to be a very versatile material having wide range of biomedical applications and biotechnological applications. Das et al. (2010) extracted spherical and elliptical shaped jute nanofibers from jute fibers by acid hydrolysis and were incorporated as reinforcing filler in a biocopolymer matrix by the melt mixing method [49]. Jute nanofibers (JNFs) were prepared by treating jute fibers with alkali and dimethyl sulfoxide (DMSO) and then applying acid hydrolysis. Biocopolyester matrix was reinforced with JNFs at three different loadings (5, 10, and 15 wt.%) and the JNF-loaded biocomposites were characterized by different techniques. The enhancement in properties was highest for 10 wt.% JNF-loaded composites indicating the most uniform dispersion in this material.

Deepa et al. (2011) extracted cellulose nanofibers from banana fibers by steam explosion technique and these banana fiber specimens were thermo gravimetrically analyzed to compare the degradation characteristics of the chemically treated fibers with the untreated fiber [50]. The fibers exhibited three main weight loss regions. The initial weight

loss in the region 50–100 °C was mainly due to moisture evaporation. The temperature region ranging from 220–300 °C was mainly attributed to thermal depolymerisation of hemicellulose and the cleavage of glycosidic linkages of cellulose. The broad peak in the region from 200 to 500 °C was due to lignin components. And they also found there is a shift in the major decomposition temperature from 374 to 380 °C as we go from raw fiber to acid treated banana fiber. Alkali treatment coupled with high pressure defibrillation and acid treatment have been tried on banana fibers obtained from the pseudo stem of the banana plant Musa sapientum by Cherian et al. (2008) [51]. The structure and morphology of the fibers have been found to be affected on the basis of the concentration of the alkali and acid and also on the pressure applied. Steam explosion in alkaline medium followed by acidic medium is found to be effective in the depolymerisation and defibrillation of the fiber to produce banana nanowhiskers. Besbes et al. (2011) isolated cellulose nanofibers with diameter ranging from 5 to 20 nm from three different sources of fibers- alfa, eucalyptus and pine [52]. A TEMPO oxidation treatment at neutral conditions was carried out on the fibers to increase the carboxyl content in order to facilitate the fibrillation process during the high pressure homogenization. Syverud et al. (2011) made a comparison between eucalyptus and pinus radiata pulp fibers, as raw materials for producing nanofibrils [53]. The cellulose nanofibrils were produced mechanically and chemi mechanically. Then the fibers were subjected to a TEMPO mediated oxidation to facilitate the homogenization. The contents of carboxyl acids after the pre-treatment indicated a favourable situation for producing nanofibrils using eucalyptus pulp fiber as raw material. Films made from nanofibrils evidenced less shrinkage and higher transparency levels, which were related to a higher fibrillation of the pulp fibers.

Morais et al. (2010) prepared cellulose nanocrystals with rod, sphere and network morphologies by acid hydrolysis of cotton cellulose followed by freeze drying [54]. Hydrolysis with sulphuric acid introduced sulphate groups to these nanocrystals surfaces permitting their dispersion in aqueous as well as organic media. Pasquini et al. extracted cellulose whiskers from cassava baggase, a by-product of cassava starch industrialization as a new raw material to extract cellulose whiskers by acid hydrolysis [55]. Then these cellulose whiskers with high aspect ratio were used to process nanocomposite films with a natural rubber matrix. Rosa et al. (2010) prepared cellulose nanowhiskers by sulphuric acid hydrolysis from coconut husk fibers which had previously been submitted to a delignification process [56]. Fig. 4 shows transmission electron micrographs of cellulose whiskers. The microscopic images showed that it was possible to obtain ultrathin cellulose nanowhiskers with diameters as low as 5 nm and aspect ratio of up to 60. These images evidenced the efficiency of the acid hydrolysis treatment, confirming that the aqueous suspensions contained coconut cellulose nanowhiskers consisting mostly of individual fibrils and some aggregates. Higher residual lignin content was found to increase thermal stability indicating that by controlling reaction conditions one can tailor the thermal properties of the nanowhiskers.

Rodriguez et al. (2006) used sisal as a novel source for cellulose nanowhiskers by acid hydrolysis method. Analysis of the resulting whiskers revealed rod-like particles and statistical averages for length and diameter were around 250 and 4 nm, respectively [25]. This high aspect ratio, when compared to other polysaccharide nanowhiskers, and coupled with the low cost and widespread availability of the sisal source material, makes these particular nanowhiskers very attractive as reinforcement for polymeric materials. Rice husk is a raw biomass material with high potential for manufacturing value-added products. Luduena et al (2011) prepared nanocellulose from rice husk [57]. The nanocellulose samples were prepared by acid hydrolysis of sub products of rice husk obtained from several chemical treatments. Li et al. (2009) extracted cellulose whiskers from the branch barks of mulberry by an alkali treatment and subsequently sulphuric acid hydrolysis [58]. The obtained whiskers have potential applications in the fields of composites as a reinforcing phase, as well as pharmaceutical and optical industries as additives. Jonoobi et al. (2010) isolated cellulose nanofibers from kenaf core fibers by employing chemo-mechanical treatments [59]. Nanofiber morphologies were examined in every stage. The transmission electron microscopy results showed that most of the nanofibers isolated from kenaf core fibers had diameters in the range of 20 to 25 nm. Chemical analysis of the fibers after each stage of treatment indicated increase in their cellulose contents and decrease in their lignin and hemicelluloses contents relative to the corresponding contents before each respective treatment.

5. NOVEL MATERIALS BASED ON CELLULOSE NANO FIBERS

The use of natural fibers instead of traditional reinforcement materials provides several advantages. Biodegradable composites are one of the important
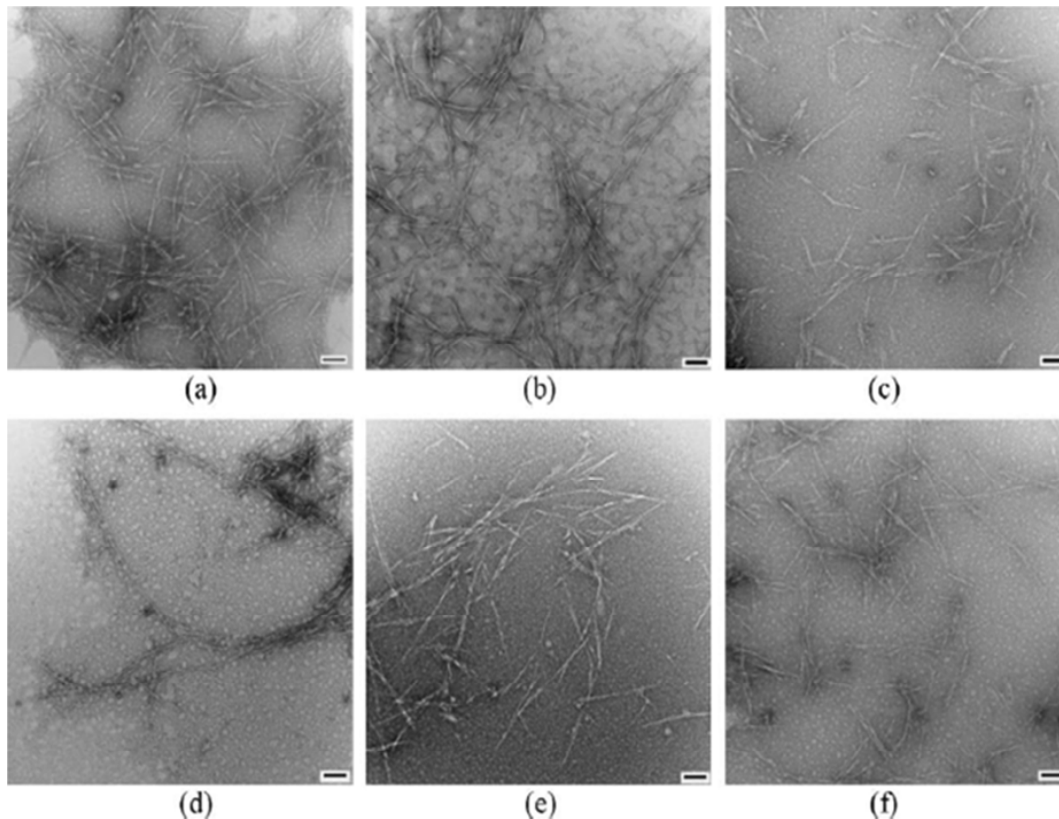
Fig. 4. Transmission electron micrographs of cellulose whiskers. (a) 1B (bleaching), 120 min (treatment time); (b) 1B, 150 min; (c) 1B, 180 min; (d) 4B, 120 min; (e) 4B, 150 min; (f) 4B, 180 min. Scale bars: 100 nm, Reprinted with permission from M.F. Rosa, E.S Medeiros, J.A. Malmonged and K.S. Gregorski, Carbohydrate Polymers vol. 81, 2010, 83, (c) 2010 Elsevier.

applications. Lars Berglund and co-workers have been developing a number of novel materials based on cellulose nanofibers like foams, aerogels, nanopaper, and starch–nanocellulose composites. Polymer foams are of interest in various applications. Svagan et al. (2007) prepared biofoams based on amylopectin rich potato starch and cellulose nanofibers from wood pulp [23]. This novel concept of cellulose nanocomposite biofoams is of interest in biomedical applications as well as in packaging material applications. Aerogels are a new class of materials for catalysis applications and in structures for liquid storage. They have exceptional thermal insulation properties. In the study by Paakko et al. (2007) aerogels were prepared by freeze drying of cellulose nanofibril water suspensions [33]. Cellulose nanofibril suspensions can also be converted to nanopaper structures. In the study by Henriksson et al. (2008) the remarkable potential of such nanopaper ie, exceptional mechanical performance was observed [60]. The ability of cellulose nanopaper to maintain its integrity at high strains is demonstrated in the study by Svagan et al. [23]. Recent developments have shown the possibility to increase

paper strength with additive of nanocellulose particles or nanofibrillated cellulose to paper compositions [65]. Henriksson et al. (2008) reported the formation of very dense nano papers (density 1-1.2 g/cm^3) from the dispersion of nanofibrillated cellulose with excellent mechanical properties like Young modulus of 10-14 GPa and tensile strength of 130-214 MPa [60]. These characteristics are like that of regenerated cellulose films and 2-5 times higher than that of common papers formed after conventional beating process. Nanocellulose can also be used as a reinforcing filler to prepare composites with solutions of water soluble polymers, as well as with acrylic and other latex to change the viscosity and increase mechanical properties of dry composites. Another application is the addition of nanocellulose to biodegradable polymers, permitting both the improvement of mechanical properties and acceleration in the rate of biodegradation [61]. Nanocellulose in its pure state is harmless for people and is biocompatible. So it can be used for health care applications like personal hygiene products, cosmetics and biomedicine. Nanocellulose dispersions can be used for stabilization of medical suspensions

against phase separation and sedimentation of heavy ingredients. Chemically modified cellulose can be a promising carrier for immobilization of enzymes and other drugs [62]. Due to its nano size, such a carrier drug complex can penetrate through skin pores and treat skin diseases. And also it can be used as a peeling agent in cosmetics [63].

6. CONCLUSIONS

Literature studies reveal that cellulose nanofibers were isolated from a variety of natural fibers by chemical treatments. Different methods adopted were mechanical treatments such as cryocrushing, grinding, high pressure homogenization, acid hydrolysis, enzyme-assisted hydrolysis, ultrasonication, TEMPO-mediated oxidation, steam explosion and electrospinning methods. Nanofibers with diameters ranging from 10 to 80 nm were successfully isolated from these natural fibers. By means of transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), fourier transform infra red spectroscopy (FT-IR), X-ray diffraction analysis(XRD), thermogravimetric analysis (TGA), and light scattering techniques it is possible to characterize the obtained cellulose and analyze the presence of lignin and hemicellulose. The potential availability and economics of using natural fibers far outweigh their limitations. An increasing population and constraints on using natural resources to grow fiber crops make agro-based fibers the most promising alternative to natural fibers. Development of nanocomposite based on nano cellulosic materials is a rather new but rapidly evolving research area. Cellulose is abundant in nature, biodegradable and relatively cheap, and is a promising nano-scale reinforcement material for polymers. The combination of biodegradable cellulose and biodegradable-renewable polymers is particularly attractive from an environmental point of view. Furthermore, application of nano cellulosic fillers such as micro fibrillated cellulose improves polymer mechanical properties such as tensile strength and modulus in a more efficient manner than is achieved in conventional micro- or macro-composite materials at very low volume fraction.

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