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Preparation, Properties and Use of Nanocellulose from Non-Wood Plant Materials

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Abstract

The chapter describes the chemical structure and hierarchical organization of cellulose fibers, characteristics of non-wood plant raw materials (NWPM), and methods for preparing pulp and nanocellulose (NC). NWPM have the necessary reserves and properties to make up for a possible shortage of wood fiber for pulp production. The methodology for evaluating the efficiency of the delignification processes of plant raw materials is presented. A two-stage technology for producing pulp for the preparation of NC by environmentally friendly organosolvent methods of NWPM delignification is proposed. Methods for preparing nanocellulose are described. The technological parameters of the extraction of NC from pulp are discussed. The influence of NC on the properties of composite materials is analyzed. Areas of use for NC from NWPM are shown.

Keywords: non-wood plant, wheat straw, flax, kenaf, miscanthus, pulp, nanocellulose, paper, cardboard, thermoelectric material, composite

1. Introduction

In recent years, there has been a growing interest in the development of new biodegradable materials from environmentally friendly renewable plants. They are able to replace materials made from exhaustible natural resources—oil, gas, coal. Polymers from these fossils take hundreds of years to decompose, causing irreparable damage to the environment. Plastic accounts for 85 percent of all waste in the world's oceans, half of which are disposable plastic products [1, 2].

The European Parliament in March 2019 approved a new law banning single-use plastic products such as plates, cutlery, straws, plastics and food containers and expanded polystyrene cups [3]. Scientists and civil society organizations are working together to create new consumption patterns that meet the needs of all people, while eliminating waste and overconsumption, where the production of consumer goods is less dependent on the use of natural resources and makes the most of recycled materials [4, 5]. The use of natural polymers from cellulosic plant materials is being seen as an alternative to plastics and could be a viable approach to reducing deforestation, increasing the use of agricultural surplus and developing biodegradable materials. The development of environmentally friendly technologies of processing renewable plant sources contribute to the sustainable development of society, solving economic and environmental problems in the production

of consumer goods [6–8]. The processing products of such renewable plant materials are widely used in the chemical, pharmaceutical, paper, medicine, textile and electronic industries [9, 10].

The main component of all plants is cellulose, which is the most abundant renewable biopolymer in nature with an estimated annual production of 1.5×10^{12} ton [11]. Cellulose is a structural component of the cell walls of softwood and deciduous wood, stalks and leaves of non-wood plants. A source of cellulose can be also bacteria, algae, and fungi [12, 13]. Cellulose $(C_6H_{10}O_5)_n$ is a stereoregular, semicrystalline polysaccharide consisting of a linear chain from several hundred to several tens of thousands of repeating units of β -D-glucopyranose (n), covalently linked by 1–4 glycosidic bonds (**Figure 1**).

The number of repeating units n is highly dependent on the source of the original cellulose (e.g. 10,000 in natural wood, 15,000 in cotton and 44,000 in the genus *Valonia*). To a lesser extent, the number of repeating unit n depends on the methods of preparation and purification (e.g., $n = 250$ – 500 in regenerated cellulose and $n = 1000$ in bleached kraft pulp) [11, 14]. The β -D-glucopyranose ring of the middle units of cellulose macromolecules contains three hydroxyl groups, which determine the chemical reactions, the ability to form intramolecular and intermolecular between different chains hydrogen bonds and properties of cellulose - solubility, thermal stability and mechanical properties [13, 15]. In the process of biosynthesis due to enzymatic polymerization of glucose monomers, glucan chains are formed, which independently form chains through van der Waals forces and are held together through hydrogen bonds, forming elementary fibrils. It was found that 36 cellulose chains lead to the production of elementary cellulose fibrils, the cross section of which has a size of 3–5 nm [16]. These elementary fibrils or nanofibrils have highly ordered regions (crystallites) that alternate with less organized (amorphous regions) [16, 17]. Then multiple elementary fibrils are brought together into larger units called microfibrils with a diameter of ~ 20 – 30 nm and length of several micrometers [18, 19]. The hierarchical organization of cellulose macromolecules in elementary fibrils and microfibrils of the plant cell wall is shown in **Figure 2**.

Cellulose is in the form of microfibrils, consisting of amorphous and crystalline domains in combination with other substances such as lignin, hemicelluloses, proteins, extractives and minerals, which constitute the main structural unit of plant cell walls [11], as shown schematically in the **Figure 2**. The proportion of plant fiber constituents depends on parameters like botanical origin, maturation time, climatic conditions, age of the plant etc. [20].

In world practice, the main consumers of cellulose are the pulp and paper industry for the production of paper and cardboard, and the chemical industry for the production of cellulose derivatives. Recently, cellulose has also attracted considerable interest as a source of raw materials for the production of nanocellulose (NC). Nanocellulose belongs to a group of nanomaterials consisting of the nanosized cellulose particles. The NC exhibit unique properties, such as high elastic modulus, high specific surface area, optical transparency, low thermal expansion

Figure 1.
Chemical structure of cellulose.

Figure 2.
 The hierarchical organization of cellulose macromolecules in elementary fibrils and microfibrils of the plant cell wall (adapted from [15, 19]).

coefficient, and chemical reactivity [21–23]. NC has high transparency, biodegradability and biocompatibility, a low lightweight and production cost in comparison with synthetic polymers [24, 25].

The main raw material for cellulose production in the world pulp and paper industry is wood. For countries that do not have large reserves of free wood, alternative sources of fibrous raw materials may be non-wood plant raw materials (NWPM) - annual and perennial plants and fibrous waste from agricultural production. For example, in 2014, 172.6 million tons of pulp were produced from wood and only 13 million tons from non-wood fibers [26]. At the same time, in the world, forests occupy 3937 million hectares and agricultural plants 4932 million hectares [27]. World reserves of NWPM are estimated at 2.527 billion tons [28]. Almost half of all NWPM stocks are cereal stalks (1250 million tons), of which about half are wheat straw [29]. Non-wood fibers have a wide range of properties that are used for the production of cellulose-containing products [30].

In general, NWPM can be divided into two broad categories [31]:

- a. common non-forest plants, which are considered as an alternative to deciduous wood, which include: straw of cereals, corn stalks, sorghum, bagasse, reeds, bamboo, esparto, natural herbs, etc.;
- b. special types of plants that are considered as an alternative to coniferous wood, which include: cotton linter, flax, hemp, kenaf, etc.

The first category includes the predominant absolute reserves of non-wood plants. It contains 35 - 62% cellulose, 10 - 25% lignin and 18 - 36% pentosanes.

The fibers in it are shorter than the fibers of the second category and softwood, the length of the fibers of which is 0.3 - 2 mm. Fibers of the second category of plants contain 55 - 85% of cellulose, 1 - 10% of lignin and have stronger and longer (larger than 5 mm) fibers [32, 33]. For most annuals, the average fiber length is close to the length of wood fibers of some deciduous species, but less than the average length of coniferous wood fibers and some industrial crops. The fiber width of annual plants is 2 - 3 times thinner than the fibers of coniferous wood, but the ratio of the length of the fibers to their width in annual plants and in wood have the same order [34].

The chemical composition of the main components of NWPM differs from coniferous and deciduous wood. The content of cellulose, as the main component of raw materials, varies in wide ranges of values from 26% (bamboo) to 98% (cotton). Non-wood plant materials are distinguished by a high content of hemicellulose, especially pentosans to 30% [35]. Most NWPM have a lower lignin content from 6% (hemp) to 24% (bagasse) compared to wood (to 34%), which indicates the possibility of their use for pulp extraction [36]. Lignin of NWPM consists of guaiacylpropane, syringylpropane and oxyparaphenylpropane structural units, connected by simple ether and carbon-carbon bonds [37]. NWPM contain more minerals, but less lignin than wood, which a priori gives reason to expect a lower consumption of reagents for their delignification in comparison with the production of pulp from wood.

2. Preparation of nanocellulose

Properties of NC particles depend on the properties of plant raw materials and methods used for their production [38]. In world practice, for the production of NC, pulp with a minimum content of lignin, mineral and extractive substances, is usually used as a feedstock [39–42]. In this case, such pulp is obtained either by traditional methods of cooking with subsequent bleaching [43], or by environmentally friendly organosolvent methods of delignification [44].

In the global practice of pulp and paper industry, the dominating technologies to obtain pulp are sulphate and sulfite methods, which lead to environmental pollution [45]. Cooking pulp from NWPM in alkaline liquor is predominant because lignin from NWPM has a lower molecular weight than softwood lignin [37]. During cooking in an alkaline solution, the main ingredient of hemicellulose, xylan, is easily dissolved, which also opens additional channels for the cooking solution to penetrate into lignin, thereby facilitating the removal of lignin from the cell wall [46]. Alkaline methods for producing pulp from non-wood plants also include the NACO method based on alkaline oxygen cooking and the SAICA method. Experiments have shown that NACO-derived straw pulp has a lower yield and is inferior to the physico-mechanical properties of soda pulp and pulp obtained by the SAICA method [47, 48].

Alkaline methods include the neutral-sulfite method, which is used to obtain high yield pulp from hardwood and annual plants. Neutral sulfite pulp in comparison with sulphate pulp with the same degree of delignification has a 3–5% higher yield from plant raw materials due to less destruction of hemicelluloses and, therefore, is easier to grind [49]. It should be noted that among the main problems of organizing the process of obtaining pulp from NWPM by alkaline methods is the high content of silicates in them, which turn into black liquor during cooking and require additional technological solutions [45, 46].

Increased environmental requirements to the quality of wastewater and gas emissions of industrial enterprises requires the development of new technologies for processing of plant raw materials with the use of different organic solvents [50–52]. Organic solvents used in organosolvent methods of delignification differ

in the chemistry of interaction with the components of plant raw materials and technological parameters of the pulp cooking process. The most developed organo-solvent methods of plant delignification include the following methods: ASAE [53], ALCELL [54], Acetosolv [55], MILOX [56], Chempolis [57] and CIMV [58]. Each of them has its own advantages and disadvantages, but they are all united by relative environmental safety.

Methods for producing NC include mechanical, chemical, oxidative and enzymatic treatment of cellulose fibers [59–61]. The essence of the mechanical methods is an application of different forces to reduce the size of the natural cellulose fibers to nanoscale. For this, various mechanical processing is used: homogenization, grinding, microfluidization, ultrasonic treatments, ball milling, and cryocrushing [42, 62]. The use of mechanical methods for obtaining nanocellulose is characterized by significant energy consumption, for example, with multiple passages of the cellulose fibers through a high-pressure homogenizer, it is above 25 kW/kg [38]. In [63] have shown that the homogenization process is the most expensive method for nanomaterial isolation. To reduce energy consumption and fiber damage during mechanical processes, various pretreatments of cellulose are used: enzymatic treatment, alkaline treatment and chemical oxidation. As a result of the rupture of strong interfibrillar hydrogen bonding, the power required for the production of NC is significantly reduced, for example, from 20 to 30 kW/kg to 0.5 kW/kg of sulfite pulp [38].

Chemical methods are based on the cleavage of 1–4 glycosidic bonds of cellulose chains and isolation of cellulose nanocrystals with the removal of a part of the amorphous cellulose under the action of acids [64, 65]. For these purposes, the different acids are used: sulfuric, hydrochloric, phosphoric, maleic, hydrobromic, nitric, formic, p-toluenesulfonic [66–68]. Sulfuric acid is the most widely used acid for making NC. It reacts with the surface hydroxyl groups of cellulose to form negatively charged sulfonic groups and a stable gel. Otherwise, upon hydrolysis with hydrochloric acid, uncharged nanocellulose particles tend to flocculate in aqueous dispersions [69].

Recently, oxidizing agents such as 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and phthalimide-N-oxyl (PINO) have been used to obtain NC. They improve the environmental friendliness and shorten the duration of the nanocellulose production process compared to hydrolysis, but have a higher cost than the above acids [70–72].

Enzymatic methods are based on the biosynthesis from monosaccharides or decreasing the size of the cellulose fibers by the fermentation. The enzymatic methods are time-consuming and require reagents that are more expensive. However, preliminary treatment of cellulose by enzymes before the mechanical grinding can decrease the energy consumption required for preparation of NC [73, 74]. For these reasons, a pre-treatment of the fibrous material is usually performed in order to decrease the size of the cellulose fibers and to ease the fibrillation and the process of nanocellulose preparation. The method of NC production by combining mechanical, chemical or biological pretreatment with homogenization treatment can not only reduce energy consumption, but also obtain NC with controllable size [75].

The various types of NC can be classified into different subcategories based on their shape, dimension, function, and preparation method, which in turn primarily depend on the cellulosic source and processing conditions [69].

Different terminologies have been used for the various types of NC. The Technical Association of the Pulp and Paper Industry (TAPPI) proposed standard terms and their definitions for cellulose nanomaterial WI 3021, based on the NC size [76]. NC is categorized into following kinds, such as cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), amorphous nanocellulose, and cellulose nanoyarn [78]. CNF consist of a network of intertwined elementary nanofibrils, consisting of alternating crystalline and amorphous areas. CNF particles are

10–60 nm in width, 500–2000 nm in length, and high aspect ratio $L/D > 50$ [77]. CNF is usually obtained by some kind of mechanical treatment of softwood pulp without any pretreatment or after chemical or enzymatic pretreatment. CNC particles are extracted from pulp, usually by hydrolysis, and have a diameter from 4 to 20 nm, a length 100–300 nm, and low aspect ratio $L/D > 5$ [78].

The hydrolysis of cellulosic materials remains the most common commercial-scale CNC production method. The CNC yield after acid hydrolysis of pulp is 30–50% [62], and CNC films have brittle and rigid characteristics, which limits its use, for example, in flexible electronics. CNF has higher yield, good strength and good elasticity [79]. The combination of the intrinsic strength of CNF particles with the strong interaction between nanoparticles during drying makes it possible to obtain a more rigid and flexible film from CNF than from CNC [80].

Typically, higher acid concentrations, longer reaction times, and higher temperatures lead to higher surface charge and narrow sizes, but to lower yield and decreased crystallinity and thermal stability of cellulose nanocrystals [81].

3. Results and discussion

3.1 Methods of obtaining pulp for preparation of nanocellulose

Many factors determine the efficiency of the plant-based pulp production process, to which there has been a lot of research. These include technological, economic and environmental factors [31, 45, 57]. We are proposing to estimate efficiency of processes of delignification of plant raw materials by the diagram of dependence of pulp yield on the maintenance in it of residual lignin. For example, the dependence of pulp yield on the content of residual lignin for different methods of delignification of wheat straw is shown in **Figure 3**.

The proposed methodology for constructing diagram differs from the known lignin-carbohydrate diagrams of Ross, Geertz and Schmidt in the simplicity of construction, the essence of which consists of the following [82]. On the y-axis the pulp yield

Figure 3.

The dependence of the pulp yield on the residual lignin content for different methods of delignification of wheat straw: 1- line of "ideal" delignification; 2 - Acetic; 3 - Ester; 4 - Soda; 5 - two-stage alkali-alc.; 6 - two-stage alkali-alc. + AQ; 7 - Neutral-sulfite; 8 - Bisulfite; 9 - Alkaline-sulfite-alc. + AQ; 10 - Peracetic; 11 - Ammonium-sulfite-alc.; 12 - Ammonium-sulfite-alc. + AQ.

is indicated from 30% (for better visualization on the few percent lesser than cellulose content is in the plant raw material) to 100%. On the y-axis the point corresponding to holocellulose content is also indicated. On the x-axis, the percentage value of the lignin content in pulp is indicated from zero to maximum value in plant raw material. The intersection of horizontal axis at 100% yield and vertical axis of lignin content creates the point corresponding to initial composition of all plant components. The line, which links this point with the point of holocellulose content in plant raw material, can be considered as the line of ideal delignification. It characterizes maximal polysaccharide content for certain residual lignin content in pulp. Further, on the lignin-carbohydrate diagram, the dependencies of the yield on the residual content of lignin in the pulps obtained by different methods are plotted. So the closer the line of certain delignification method is to the line of ideal delignification, the higher is polysaccharide yield in the obtained pulp and thus delignification method is more efficient.

The dependencies presented in the diagram (**Figure 3**) allowed concluding that investigated delignification methods with approaching to the line of ideal delignification, i. e. with the increased efficiency of obtaining pulp from wheat straw, can be located in following sequence: Acetic – Ester – Soda – Neutral- sulfite – Bisulfite – two-stage alkali-alcohol – two-stage alkali-alcohol + AQ - Alkaline- sulfite-alcohol + AQ – Peracetic – Ammonium-sulfite-alcohol – Ammonium-sulfite-alcohol + AQ. This methodology is applicable to assess the efficiency of the processes of obtaining pulp from one type of raw material using different methods [83], and for a comparative assessment of the delignification of various types of plant raw materials by one method [84].

To obtain cellulose with a minimum residual content of lignin and minerals, we used a two-stage method of delignification of NWPM [85–89]. Peracetic acid (PAA) was used as a reagent for the delignification of NWPM, which has bleaching properties. PAA leads to minimal fiber damage and is environmentally friendly [90]. We have already demonstrated the possibility of obtaining straw pulp by means of organosolv delignification in the system of isobutyl alcohol–H₂O–KOH–hydrazine, which makes it possible to reuse the organic component and waste cooking liquor without regeneration [85]. At the same time, the waste liquor is divided into two layers: the upper organic solvent layer and the lower aqueous layer to which has moved the bulk of soluble minerals and organic substances from plant raw material (lignin, hemicelluloses, and extractives). The use of potassium and nitrogen compounds in the cooking liquor allows the use of waste liquor in the manufacture of fertilizers. **Table 1** shows the stages of preparation and indicators of the pulps from various plants, which were used to obtain nanocellulose.

The data in **Table 1** show that carrying out the two-stage thermochemical treatment of NWPM makes it possible to almost completely remove lignin and minerals and obtain a pulp with a content of non-cellulose components of no more than 1%. The obtained organosolvent pulps are not inferior in quality, if not superior, to bleached sulphate pulp from softwood, and therefore were used for the production of nanocellulose.

3.2 Properties of nanocellulose

We obtained nanofibrillated cellulose from air-dry bleached sulphate pulp of softwood using mechanochemical treatment [91]. It was carried out on grinding equipment, and hydrolysis with sulfuric acid solutions of various concentrations at temperatures from 20 to 60° C for 5–60 minutes. An increase of the acid concentration from 18–43% has led to an increase of the mechanical properties of the nanocellulose films. Further increase of the acid concentration above 50% leads to a sharp decrease of all strength properties and led to the formation of films with the

Pulp from a plant and a method of obtaining	Stages of preparation of pulp	Yield, %	Lignin, %	Ash, %
Wheat straw, isobutanol* [85]	I – isobutanol	49.0	1.1	1.63
	II – PAA**	41.5	0.2	0.2
Wheat straw, PAA** [86]	I – NaOH***	54.9	9.8	0.98
	II - PAA	51.1	0.4	0.09
Flax fiber, PAA [87]	I – PAA	68.2	1.7	0.5
	II - NaOH	52.8	0.02	0.04
Kenaf, PAA [88]	I – PAA	61.2	0.37	0.24
	II - NaOH	51.2	0.29	0.18
Miscanthus, PAA [89]	I – PAA	50.7	0.25	0.96
	II - NaOH	57.0	0.08	0.04
Bleached sulphate softwood pulp	I – grinding to 93 °SR	—	0.23	0.21

*isobutanol: mixture of isobutanol-KOH-hydrazine, 120 min at 95 ± 2°C.
**PAA: mixture of acetic acid and hydrogen peroxide in a volume ratio of 70:30%, 120 min, at 95 ± 2°C.
***- solution 5% NaOH, 120 min, at 95 ± 2°C.

Table 1.
Indicators of pulps from various plant materials for the production of nanocellulose.

brownish color. We recommended a reduced sulfuric acid concentration of 43% at 60°C during 60 minutes as the main process parameters for the production of NC by hydrolysis of organosolvent pulp from NWPM [87–89]. Such conditions agree well with data in [92] and are economically more favorable than traditional conditions for hydrolysis of cellulose with 60–65% sulfuric acid at 40–50°C for 1–2 h [93]. We used never-dried organosolvent pulps from NWPM to prepare NC. Never dried pulp is better than once dried sample, as the drying process leads to cornification of the fibers, which reduces the impregnation of the fibers with chemicals during their hydrolysis. Using of never-dried pulp does not require the consumption of energy for drying and grinding since dried cellulose fibers lose the ability to swell and percolate due to irreversible cornification.

Hydrolyzed NC was washed three times with distilled water by centrifugation at 8000 rpm, followed by dialysis to achieve a neutral pH and ultrasonic treatment during 30–60 min. As a result, the suspension took the form of a homogeneous gel-like dispersion and was stored in sealed containers for further research in order to determine the physical and mechanical characteristics of the NC. The prepared suspensions were poured into Petri dishes and dried in the air at a room temperature to obtain NC films. The structural change and crystallinity index of organosolvent pulps and NC were studied by means of SEM and XRD techniques. TEM and AFM methods were used to determine the particle size of nanocellulose (**Figure 4**). Transparency of the NC films was determined by electron absorption spectra, and tensile strength - according to ISO 527-1. The indicators of the obtained NC from NWPM is shown in the **Table 2**.

As can be seen from **Figure 4** and the data in **Table 2**, the process of hydrolysis and ultrasonic treatment of pulps leads to the formation of nanosized particles. NC had homogeneous and stable nanocellulose suspension. The nature of stabilization of the colloidal suspension is explained by the presence of charged groups on the surface of nanocellulose, which are formed by the interaction of cellulose with sulfate acid due to the esterification reaction. The structure of the NC films, according to SEM, TEM and AFM data, was similar to the structure of the film obtained from nanofibrillar cellulose [95]. The obtained NC had high tensile strength from 42.3 to 70 MPa and Young’s modulus from 8.9 to 11.45 GPa. The obtained samples

Figure 4. TEM images of nanocellulose prepared by hydrolysis from bleached sulphate pulp (a) and organosolvent wheat straw pulp (b); AFM images of nanocellulose from kenaf (c) and lateral size of its nanocellulose surface (d); and AFM images of nanocellulose from miscanthus: The lateral size of the nanocellulose surface (e) and 3D projection (f) with definition of sample height tapping mode.

of NC from NWPM physical and mechanical parameters, comparable to the values obtained by other researchers. For instance, Young's modulus values of films generated from nanofibrillated bleached pulp, wheat straw, and recycled newspaper were between 6,0 and 9,0 GPa [96]. The positive results of obtaining NC from NWPM are given in other sources [97–99]. The properties of NC from NWPM exhibit great potential for their application to new nanocomposite materials and consumer goods.

3.3 Application of nanocellulose

Due to its unique properties, nanocellulose is widely used in various fields: in the production of electronic devices and composites, as a natural material for replacing synthetic reinforcing substances in the paper, chemical, pharmaceutical, cement

Nanocellulose from plant	Density, g/cm ³	Particle diameter, nm	Tensile strength, MPa	Crystallinity index, %	Transparency, %
Wheat straw isobutanol [94]	1.3	10–40	42	72.2	70
Wheat straw PAA [86]	1.27	16–20	123	71.3	78
Flax [87]	1.37	20–60	70	62.0	60
Kenaf [88]	1.39	10–28	65	80.0	72
Miscanthus [89]	1.32	10–18	62	76.7	74
Bleached sulphate softwood pulp [91]	1.38	15–30	88	79.8	78

Table 2.
The indicators of the obtained nanocellulose from NWPM.

industries [100–104]. In the last few years, the cellulosic biopolymer-based green electronics is supplemented by lightweight, portable, flexible NC-based power generators to provide energy to wearable electronics through harvesting mechanical energy in triboelectric and piezoelectric appliances [105, 106]. Huge ecological advantage of the NC-based electronic and thermoelectric devices is their inherent biodegradability. As these devices have become ubiquitous in modern society, and are prevalent in every facet of human activities, and the lifetime of electronics get shorter and shorter, the pressure on electronic waste (e-waste) management systems is mounting with no abate insight. This poses a growing ecological problem, and an alternative to traditional electronics is biodegradable electronics as the most viable replacement to address the issue of uncontrollable e-waste to reduce the environmental footprint of devices [107, 108]. Recently, nanocellulose is used for the preparation of porous carbon that be used as a high-performance supercapacitor electrode [109–111].

The use of nanocellulose in energy harvesting is illustrated in the following articles [112–114]. We used conversion of solar energy into chemical energy of biomass of fast-growing perennial herb *Miscanthus* to fabricate via an environmentally friendly method of organosolvent delignification low-cost NC films used as substrates for the creation of new biodegradable thin film thermoelectric material [115]. To do this, we applied a 0.72- μm CuI film onto a 12- μm NC substrate using a low-temperature, low-cost and scalable sequential ion layer adsorption method and thus obtained a lightweight and flexible biodegradable CuI thermoelectric material CuI/NC. We found out that nanostructured p-type semiconductor CuI film in the CuI/NC thermoelectric material is quite dense and completely covers the NC surface. The determined value of the Seebeck coefficient (S) is about $228\ \mu\text{VK}^{-1}$ more than an order of magnitude higher than the Seebeck coefficients that were measured earlier for the nanocellulose-derived organic and composite materials contained poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS), silver nanoparticles and carbon nanotubes [116]. The coefficient S obtained by us even exceeds the S values for the different thin-film composites of such well-known inorganic thermoelectric material as Bi_2Te_3 [117]. At that, S is constant in the temperature range 290–335 K, which is favorable for the use of CuI/NC as new thermoelectric material for an in-plane design of biodegradable flexible thin film thermoelectric generator. The thermoelectric power factor of CuI/NC is about $36\ \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ is higher than that of the best examples bacterial nanocellulose films with embedded highly dispersed carbon nanotubes networks ($20\ \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$) in article [118]. At temperature gradient of 50 K, the single p -CuI thermoelectric

leg made from CuI/NC generates $V_{oc} = 8.4 \text{ mV}$. It corresponds to the power density $10 \text{ } \mu\text{W/m}^2$. Due to the complex of these properties, the developed environmentally friendly biodegradable flexible thin-film thermoelectric material can be effectively used to convert low-grade waste heat into electricity at temperatures close to room temperature [115].

The use of NC during paper formation or even coating of dry formed paper can improve interfiber bonding, softness and printability and, consequently, physical-mechanical properties [119–121]. **Figures 5–7** show the results of using NC from NWPM for the production of mass grades of paper and cardboard [122, 123].

As can be seen from the data in **Figures 5–7**, the application of NC to the surface of paper and cardboard has a positive effect on their physical and mechanical properties. Low consumption of NC allows production of the paper and cardboard with properties that meet the requirements to appropriate standards and replacement of synthetic reinforcing materials [123]. The increase in the values of the indicators of paper and cardboard occurs due to the creation of new hydrogen bonds between the fibers of cellulose and NC, which is confirmed by other authors [124, 125]. NC often replaces such well-known material, as glass and certain polymers, which are not biodegradable at ambient conditions. Modern technologies allow use NC

Figure 5. Properties of paper for corrugating (a, b, c) and paper for bags (d, e, f) from waste paper (I) and unbleached pulp (II) with different consumption (g/m²) of nanocellulose from NWPM per paper surface; asterisk or dotted line - line of standards requirements.

Figure 6. Properties of cardboard for flat layers of corrugating cardboard with different consumption of sizing agents on 1 m²: Without application (1); 7 g of glue (2); 3.5 g of nanocellulose (3); 3.5 g of glue and 3.5 g of nanocellulose (4); 7 g of nanocellulose (5); asterisk: Line of standard requirements.

Figure 7. Properties of recycled cardboard with different nanocellulose consumption; asterisk: Line of standard requirements.

in energy storage systems [126], biosensors [127], as well as in various electronic and optoelectronic devices [128, 129]. Among them, transparent transistors, light emitting diodes, solar cells, antennas and radiofrequency identification devices, high-performance loudspeakers, and lightweight actuators [130, 131].

Nano-sized cellulose fibers are considered as promising candidates for the production of nanocomposites. NC was added to polymer matrices to obtain reinforced composites with mechanical strengths from ten to one hundred times and to improve barrier properties [132–134].

Loading of structural materials with NC particles makes it possible to reduce their weight while maintaining the strength of the composites [135, 136]. For instance, addition of 6.5% nanofibrils improved the tensile strength and elongation at the break of the nanocomposite from cassava starch and polyvinyl alcohol by 24% and 51%, respectively. At the same time, the water vapor permeability and water solubility of the nanocomposite containing high contents of nanofibrils decreased up to 20% and 30%, respectively, in relation to the control blend [137]. A high effect of reinforcement was observed even at a low content of CNC when used to obtain nanocomposites with a matrix of natural rubber. With the addition of only 2.5 wt % CNC, which were isolated from soybean husks by acid sulfur hydrolysis, the elastic modulus of the composite was about 21 times higher than that of a pure rubber matrix [138]. In [139] it was shown that the addition of 10% NC from miscanthus to a composite based on epoxy resin Eposir-7120 with a polyethylene polyamine

hardener increases the elastic modulus of the composite by 12.2% with respect to the control mixture. Otherwise, adding 5% NC from Colombian fique to acrylic hydrogels made it possible to obtain a reinforced hydrogel with 2.5 times higher compression resistance values than the resistance of the original hydrogel [140].

4. Conclusions

With the increasing requirements for environmental protection, there is a need to replace exhaustible sources - oil, gas, coal, and existing forest resources with biodegradable and renewable, including non-wood plant raw materials (NWPM). NWPM have the necessary reserves and properties to make up for a possible shortage of wood fiber for pulp production. To obtain pulp suitable for the production of nanocellulose (NC), a two-stage technology for delignification of NWPM with reagents that does not contain sulfur and chlorine has been proposed. NC has unique physical and mechanical properties and can replace well-known materials such as glass and some polymers, which are not biodegradable under ambient conditions. Methods for preparing nanocellulose are described. The influence of the main technological parameters of the cellulose hydrolysis process on the properties of nanocellulose is discussed. It is proposed to carry out the hydrolysis of cellulose using 43% concentration of sulfuric acid. Examples of the use of nanocellulose in various industries are given.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] Zarfl C, Flet D, Fries E, et al. Microplastics in oceans. *Marine Pollution Bulletin*. 2011;62:1589-1591. DOI: 10.1016/j.marpolbul.2011.02.040
- [2] Jambeck JR, Andrady A, Geyer, R., Narayan, R., Perryman, M., Siegler, T., Wilcox, C., Lavender Law, K. Plastic waste inputs from land into the ocean, *Science*. 2015;347:768-771. <https://jambeck.engr.uga.edu/landplasticinput>
- [3] Schlanger Z. The problem with turning to paper after the EU's plastic ban. 2019. [Internet]. Available from: <https://qz.com/1582520/the-problem-with-turning-to-paper-after-the-eus-plastic-ban>. [Accessed: 2020-07-23]
- [4] Haggith M, Kinsella S, Baffoni S, Anderson P, Ford J, Leithe R, Neyroumande E, Murtha N, Tinhout B. The state of the global paper industry. *Environmental Paper Network*. 2018. 89 p. <http://www.environmentalpaper.org>
- [5] Huang C, Wang X, Liang C, Jiang X, Yang G, Xu J, Yong Q. A sustainable process for procuring biologically active fractions of high-purity xylooligosaccharides and water-soluble lignin from Moso bamboo prehydrolyzate. *Biotechnology for Biofuels*. 2019;12(1):189. DOI: 10.1186/s13068-019-1527-3
- [6] Baghban MH, Mahjoub R. Natural Kenaf Fiber and LC3 Binder for Sustainable Fiber-Reinforced Cementitious Composite: A Review. *Appl. Sci*. 2020;357:1-15. DOI: 10.3390/app10010357.
- [7] Dong H, Zeng L, Yu P, Jiang Q, Wu Y, Huang C, Yin B. Characterization and application of lignin-carbohydrate complexes from lignocellulosic materials as antioxidant for scavenging in vitro and in vivo reactive oxygen species. *ACS Sustainable Chemistry & Engineering*. 2019;8(1):256-266. DOI: 10.1021/acssuschemeng.9b05290
- [8] Jasmani L, Thielemans W. Preparation of nanocellulose and its potential application. *Forest Res*. 2018;7:1-8. DOI: 10.4172/2168-9776.10002 22
- [9] Sagar NA, Pareek S, Sharma S, Yahia EM, Lobo MG. Fruit and vegetable waste: bioactive compounds, their extraction, and possible utilization. *Compr Rev Food Sci Food Saf*. 2018;17:512-531. DOI: 10.1111/1541-4337.12330
- [10] Thomas B, Raj MC, Athira KB, Rubiyah MH, Joy J, Moores A, Drisko GL, Sanchez C. Nanocellulose, a versatile green platform: from biosources to materials and their applications. *Chem Rev*. 2018;118(24):11575-11625. DOI: 10.1021/acs.chemrev.7b00627
- [11] Klemm D, Heublein B, Fink H-P, Boh A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chem. Int. Ed*. 2005;44:3358-3393. DOI: 10.1002/anie.200460587
- [12] Henriksson M, Berglund LA. Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. *J Appl Polym Sci*. 2007;106:2817-2824. DOI: 10.1002/app.26946
- [13] Iwamoto S, Nakagaito AN, Yano H. Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites. *Appl Phys A Mater*. 2007;89:461-466
- [14] Calvin P. The Influence of Levelling-off Degree of Polymerisation on the Kinetics of Cellulose Degradation. *Cellulose*. 2005;12(4):445-447. DOI: 10.1007/s10570-005-2206-z
- [15] Dufresne A. Nanocellulose: from nature to high performance tailored

materials. De Gruyter; 2012. 460 p.
 DOI: 10.1515/9783110254600

[16] Moon RJ, Martini A, Nairn J, Simonsen J, Youghblood J. Cellulose nanomaterials review structure, properties and nanocomposites. *Chemical Society Reviews*. 2011;40:3941-3994. DOI: 10.1039/c0cs00108b

[17] Chen H. *Biotechnology of lignocellulose: theory and practice*. Beijing: Chemical Industry Press; 2014. 211 p.

[18] Kumar R, Sharma RK, Singh AP. Cellulose based grafted biosorbents- Journey from lignocellulose biomass to toxic metal ions sorption applications-a review. *J.Mol. Liq.* 2017;232:62-93. DOI: 10.1016/j.molliq.2017.02.050

[19] Ritter SK. Sustainability. *Chemical & Engineering News*. 2008;86:59-68.

[20] Céline A, Fréour S, Jacquemin F, Casari P. The hygroscopic behavior of plant fibers: a review. *Frontiers in Chemistry*. 2013;1:43. DOI: 10.3389/fchem.2013.00043

[21] Neto WP, Silvério HA, Dantas NO, Pasquini D. Extraction and characterization of cellulose nanocrystals from agroindustrial residue-soy hulls. *Ind Crop Prod*. 2013;42:480-488. DOI: 10.1016/j.indcrop.2012.06.041

[22] Nie S, Hao N, Zhang K. et al. Cellulose nanofibrils-based thermally conductive composites for flexible electronics: a mini review. *Cellulose*. 2020;27: 4173-4187. DOI: 10.1007/s10570-020-03103-y

[23] Clemons C, Sedlmair J, Illman B, Ibach R, Hirschmug C. Chemically imaging the effects of the addition of nanofibrillated cellulose on the distribution of poly(acrylic acid) in poly(vinyl alcohol). *Polymer*. 2013;54(8):2058-2061. DOI: 10.1016/j.polymer.2013.02.016

[24] Mondal S. Preparation, properties and applications of nanocellulosic materials. *Carbohydr Polym*. 2017;163:301-316. DOI: 10.1016/j.carbpol.2016.12.050

[25] Phanthong P, Reubroycharoen P, Hao X, Xu G, Abudula A, Guan G. Nanocellulose: Extraction and application. *Carbon Resources Conversion*. 2018;1:32-43. DOI: 10.1016/j.crcon.2018.05.004

[26] FAOSTAT Resources. ResourceSTAT data archives, Land, Updated 30 April 2009. Available from: <http://faostat.fao.org/site/377/default.aspx#ancor>

[27] FAO, Yearbook 2015 Forest products, [Internet]. Available from: <http://www.fao.org/3/a-i5542m.pdf>

[28] Fahmy Y, Fahmy TY, Mobarak F, El-Sakhawy M, Fadl M. Agricultural Residues (Wastes) for Manufacture of Paper, Board, and Miscellaneous Products: Background Overview and Future Prospects. *Int. J. ChemTech Res*. 2017;2(10):424-448.

[29] Hunter RW. Non-wood Fiber – 2010 and beyond. Prospects for non-wood paper production in Asia Pacific. *APPITA*. 2010;56.

[30] Alireza A. Nonwood fibers a potential source of raw material in papermaking. *Journal of Macromolecular Science: Part D–Reviews in Polymer Processing*. 2006;45(10):1133-1136. DOI: 10.1080/03602550600728976

[31] El-Sayed ES, El-Sakhawy M, El-Sakhawy MA-M. Non-wood fibers as raw material for pulp and paper industry. *Nordic Pulp & Paper Research Journal*. 2020;35(2):215-230. DOI: 10.1515/npprj-2019-0064

[32] Zeng Y, Himmel ME, Ding S. Visualizing chemical functionality in plant cell walls. *Biotechnol Biofuels*. 2017;10:263. DOI: 10.1186/s13068-017-0953-3

- [33] Sorieul M, Dickson A, Hill SJ, Pearson H. Plant Fibre: Molecular Structure and Biomechanical Properties, of a Complex Living Material, Influencing Its Deconstruction towards a Biobased Composite. *Materials*. 2016;9(8):618. DOI: 10.3390/ma9080618
- [34] Jawaid M, Abdul Khalil HPS. Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review. *Carbohydr Polym*. 2011;86:1-18. DOI: 10.1177/0731684413516393
- [35] Atchison JE. Twenty five years of global progress in non-wood plant fibre pulping - historical highlights, present status and future prospects. In: *Proceedings of TAPPI pulping conference (Book 1)*; 1995; TAPPI Press, Atlanta, GA, USA; 1995. p. 91-101.
- [36] Pande H. Non-wood fiber and global fiber supply. *Unasylva*. 1998;193: 44-50
- [37] Tarasov D, Leitch M, Fatehi P. Lignin-carbohydrate complexes: properties, applications, analyses, and methods of extraction: a review. *Biotechnol Biofuels*. 2018;11:269. DOI: 10.1186/s13068-018-1262-1
- [38] Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, Dorris A. Nanocelluloses: a new family of nature-based materials. *Angew. Chem. Int. Edn*. 2011;50:5438-66. DOI: 10.1002/anie.201001273
- [39] Chunhong W, Suyue B, Xinmin Y, Long B. Relationship between chemical composition, crystallinity, orientation and tensile strength of kenaf fiber. *Fibers Polymers*. 2016;17(11):1757-1764. DOI: 10.1007/s12221-016-6703-5
- [40] Płazek A, Dubert F, Kopeć P, et al. In vitro-propagated *Miscanthus x giganteus* plants can be a source of diversity in terms of their chemical composition. *Biomass and Bioenergy*, 2015;75:142-149. DOI: 10.1007/s42452-020-2529-2
- [41] Silva LE, Claro PI, Sanfelice RC, Junior MG, Oliveira JE, et al. Cellulose nanofibrils modification with polyaniline aiming at enhancing electrical properties for application in flexible electronics. *Cellulose Chem Technol*. 2019;53(7-8):775-785
- [42] Rol F, Belgacem MN, Gandini A, Bras J. Recent advances in surface-modified cellulose nanofibrils, *Progress in Polymer Science*. 2019;88:241-264. DOI: 10.1016/j.progpolymsci.2018.09.002
- [43] Li W, Wang R, Liu S. Nano-crystalline cellulose prepared from softwood kraft pulp via ultrasonic-assisted acid hydrolysis. *Bioresources*. 2011;6(4):4271-4281. DOI: 10.15376/biores.6.4.4271-4281
- [44] Hernández J, Romero V, Escalante A, Toriz G, Rojas O, Sulbarán B. Agave tequilana bagasse as source of cellulose nanocrystals via organosolv treatment. *BioRes*. 2018;13(2):3603-3614. DOI: 10.15376/biores.13.2.3603-3614
- [45] Smook G.A. *Handbook for Pulp & Paper Technologists*. 3rd edition, Angus Wilde Publications, Inc.; 2003, 425 p.
- [46] Liu Z, Wang H, Hui L. *Pulping and Papermaking of Non-Wood Fibers*. Chapter 1: Intechopen; 2018. p. 1-31. DOI: 10.5772/intechopen.79017
- [47] Fiala W, Nardi F. The NACO Process, *Pap. Technol. Ind*. 1985;26(2):75-79
- [48] Leponiemi A. Non-wood pulping possibilities – a challenge for the chemical pulping industry. *Appita J*. 2008;61(3):234-243
- [49] Nassar MM. High yield acid and neutral sulfite cooking of rice straw. *Cellul. Chem. Technol*. 2004;37(5-6):487-495
- [50] Saberikhan E, Rovsesh JM, Rezayati-Charani P. Organosolv pulping

of wheat straw by glycerol. *Cellul Chem Technol.* 2011;45(1-2):67-75

[51] Correia VC, dos Santos V, Sain M, Santos SF, Leão AL, Savastano JH. Grinding process for the production of nanofibrillated cellulose based on unbleached and bleached bamboo organosolv pulp. *Cellulose.* 2016;23:2971-2987

[52] Sarkanen KV. Chemistry of solvent pulping. *Tappi J.* 1990;73(10):215-219

[53] Usta M, Eroglu H, Karaoglu C. ASAE pulping of wheat straw (*Triticum aestivum* L.). *Cellul. Chem. Technol.* 1999;33(1-2):91-102

[54] Winner SR, Minogue LA, Lora JH. ALCELL pulping of annual fibers. In: *Proceedings of 9th International symposium on wood and pulping chemistry*; December 1997; Montreal. Poster presentation; 1997. p. 120-1-120-4 1997:120-1 –120-4

[55] Nimz HH. Pulping and bleaching by the Acetosolv process, *Papier.* 1989;43(10A):102-108

[56] Sundquist J, Poppius-Levlin K. MILOX pulping and bleaching. In: Young RA, Akhtar M, editors. *Environmentally Friendly Technologies for the Pulp and Paper Industry*. New York: Wiley; 1998. p. 157-190

[57] Rousu PP, Rousu P, Rousu E. Process for producing pulp with a mixture of formic acid and acetic acid as cooking chemical. Pat. US 6562191. 2003

[58] Lam HQ, Le Bigot Y, Denis G, Thao VH, Delmas M. Location and composition of silicon derivatives in rice straw pulp obtained by organic acid pulping. *Appita J.* 2005;58(3):214-217

[59] Cruz J, Fangueiro R. Surface modification of natural fibers: a review. *Procedia Eng.* 2016;155:285-288. DOI: 10.1016/j.proeng.2016.08.030

[60] Sacui IA, Nieuwendaal RC, Burnett DJ, Stranick SJ, et al. Comparison of the properties of cellulose nanocrystals and cellulose nanofibrils isolated from bacteria, tunicate, and wood processed using acid, enzymatic, mechanical, and oxidative methods. *ACS Appl Mater Interfaces.* 2014;6(9):6127-6138. DOI: 10.1021/am500359f. Epub 2014 Apr 18

[61] Zhou Y, Shuji S, Saito T, Isogai A. Characterization of Concentration-Dependent Gelation Behavior of Aqueous TEMPO-Cellulose Nanocrystal Dispersions Using Dynamic Light Scattering. *Biomacromolecules.* 2018; DOI: 10.1021/acs.biomac.8b01689

[62] Fang Z, Zhu H, Preston C, Hu L. Development, application and commercialization of transparent paper *Transl. Mater. Res.* 2014;1:015004. DOI: 10.1088/2053-1613/1/1/015004

[63] Spence KL, Venditti RA, Rojas OJ, Habibi Y and Pawlak J J. A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods. *Cellulose.* 2011;18(4):1097-1111. DOI: 10.1007/s10570-011-9533-z

[64] Siro I, Plackett D. Microfibrillated cellulose and new nanocomposite materials: review. *Cellulose.* 2010;17:291-294. DOI: 10.1007/s10570-010-9405-y

[65] Um BH, Karim MN, Henk LL. Effect of Sulfuric and Phosphoric Acid Pretreatments on Enzymatic Hydrolysis of Corn Stover. *Applied Biochemistry and Biotechnology.* 2003;105-108(1-3):115-25. DOI: 10.1385/ABAB:105:1-3:115

[66] Mahmud MM, Asma M, Asma P, Perveen A, Jahan RA, Arafat MT. Preparation of different polymorphs of cellulose from different acid hydrolysis medium. *International Journal of*

Biological Macromolecules. 2019;130. DOI: 10.1016/j.ijbiomac.2019.03.027

[67] Yan CF, Yu HY, Yao JM. One-step extraction and functionalization of cellulose nanospheres from lyocell fibers with cellulose II crystal structure. *Cellulose*. 2015;22:3773-3788. DOI: 10.1007/s10570-015-0761-5

[68] Biana H, Gaoa Y, Yanga Y, Fang G, Daia H. Improving cellulose nanofibrillation of waste wheat straw using the combined methods of prewashing, p-toluenesulfonic acid hydrolysis, disk grinding, and endoglucanase post-treatment. *Bioresource Technology*. 2018;256:321-327. DOI: 10.1016/j.biortech.2018.02.038.

[69] Kargarzadeh H, Ioelovich M, Ahmad I, Thomas S, Dufresne A. Methods for Extraction of Nanocellulose from Various Sources. In: Kargarzadeh H, Ahmad I, Thomas S, Dufresne A, editors. *Handbook of Nanocellulose and Cellulose Nanocomposites*, 1st ed. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2017. p. 1-50

[70] Isogai A. Development of completely dispersed cellulose nanofibers. *Proc. Jpn. Acad., Ser. B*. 2018;94:161-178. DOI: 10.2183/pjab.94.012

[71] Madivoli ES, Kareru PG, Gachanja AN, Mugo SM, Sujee DM, Fromm KM. Isolation of Cellulose Nanofibers from *Oryzasativa* Residues via TEMPO Mediated Oxidation. *Journal of Natural Fibers*, 2020. DOI: 10.1080/15440478.2020.1764454

[72] Coseri S. Phthalimide-N-oxyl (PINO) Radical, a Powerful Catalytic Agent: Its Generation and Versatility Towards Various Organic Substrates, *Catalysis Reviews*, 2009;51(2):218 — 292. DOI: 10.1080/01614940902743841

[73] Amezcua-Allieri MA, Durán TS, Aburto J. Study of chemical and enzymatic hydrolysis of cellulosic

material to obtain fermentable sugars. *J Chem* 2017;1-9. DOI: 10.1155/2017/5680105

[74] Long L, Tian D, Hu J, Wang F, Saddler J. A xylanase-aided enzymatic pretreatment facilitates cellulose nanofibrillation. *Bioresour Technol* 2017;243:898-904. DOI: 10.1016/j.biortech.2017.07.037

[75] Zhanga Y, Haoa N, Lina X, Niea S. Emerging challenges in the thermal management of cellulose nanofibrilbased supercapacitors, lithium-ion batteries and solar cells: A review. *Carbohydrate Polymers*. 2020;234:115888. DOI: 10.1016/j.carbpol.2020.115888

[76] Mariano, M., El Kissi, N., and Dufresne, A. Cellulose nanocrystals and related nanocomposites: review of some properties and challenges. *J. Polym. Sci., Part B: Polym. Phys*. 2014;52:791-806. DOI: 10.1002/polb.23490

[77] Davoudpour Y, Hossain S, Abdul Khalil HPS, Mohamad Haafiz MK, Mohd Ishak ZA, Hassan A, Sarker ZI. Optimization of high pressure homogenization parameters for the isolation of cellulosic nanofibers using response surface methodology. *Ind. Crops Prod*. 2015;74:381-387. DOI: 10.1016/j.indcrop.2015.05.029

[78] Peng BL, Dhar N, Liu HL, Tam KC. Chemistry and applications of nanocrystalline cellulose and its derivatives: a nanotechnology perspective. *Can. J. Chem. Eng.*, 2011;89(5):1191-1206. DOI: 10.1002/cjce.20554

[79] Moon, R.J., Schueneman, G.T. & Simonsen, J. Overview of cellulose nanomaterials, their capabilities and applications. *JOM*. 2016;68:2383-2394. DOI:10.1007/s11837-016-2018-7

[80] Henriksson M, Berglund LA, Isaksson P, Lindström T, Nishino T.

Cellulose nanopaper structures of high toughness. *Biomacromolecules*. 2008;9(6):1579-85. DOI: 10.1021/bm800038n

[81] Ioelovich M. Peculiarities of Cellulose Nanoparticles. *Tappi Journal*. 2014;13(5). DOI: 10.32964/TJ13.5.45

[82] Barbash V, Trembus I, Sokolovska N. Performic pulp from wheat straw. *Cellulose Chem. Technol.* 2018;52(7-8):673-680

[83] Barbash V, Trembus I, Alushkin S, Yashchenko O. Comparative pulping of sunflower stalks, *Scientific Journal Science Rise*. 2016;3/2(20):71-78

[84] Barbash VA, Trembus IV, Oksentyuk NN, Primakov SF. Alternative raw materials for the production of organosolvent pulp products. *Ecotechnology and resource conservation*. 2012;1:27-32

[85] Barbash V, Yashchenko O. Obtaining a straw pulp in the isobutanol medium. *Research Bull NTUU "KPI"* 2015;6(104):80-86. Available from: <http://bulletin.kpi.ua/article/view/51145/67710>

[86] Barbash VA, Yaschenko OV, Kovalchuk VO. Optically transparent nanocellulose films from wheat straw. In: *International research and practice conference "Nanotechnology and Nanomaterials" (NANO-2017)*; 23-26 August 2017; Chernivtsi, 2017; p. 543

[87] Barbash VA, Yashchenko O, Kedrovskaya A. Preparation and properties of nanocellulose from peracetic flax pulp. *Journal of Scientific Research and Reports*. 2017;16(1):1-10. DOI: 10.9734/JSRR/2017/36571

[88] Barbash VA, Yashchenko OV, Opolsky VO. Effect of Hydrolysis Conditions of Organosolv Pulp from Kenaf Fibers on the Physicochemical Properties of the Obtained

Nanocellulose. *Theor Exp Chem*. 2018;54(3):193-198. DOI: 10.1007/s11237-018-9561-y

[89] Barbash VA, Yashchenko OV, Vasylieva OV. Preparation and properties of nanocellulose from *Miscanthus x giganteus*. *Hindawi Journal of Nanomaterials*. 2019, Article ID 3241968, 8 p. DOI: 10.1155/2019/3241968

[90] Paschoal G, Muller CM, Carvalho GM, Tischer CA, Mali S. Isolation and characterization of nanofibrillated cellulose from oat hulls. *Quim Nova*. 2015;38(4):478-482. DOI: 10.5935/0100-4042.20150029

[91] Barbash VA, Yaschenko OV, Alushkin SV, Kondratyuk AS, Posudievsky OYu, Koshechko VG. The Effect of Mechanochemical treatment of cellulose on characteristics of nanocellulose films. *Nanoscale Research Letters*. 2016;11:410. DOI: 10.1186/s11671-016-1632-1

[92] Ioelovich M. Superposition of Acid Concentration and Temperature at Production of Nanocrystalline Cellulose Particles. *J. Chem. Edu. Res. Prac.* 2017;1:1-7

[93] Lin N and Dufresne A. Surface chemistry, morphological analysis and properties of cellulose nanocrystals with gradiented sulfation degrees. *Nanoscale*, 2014;6:5384-5393. DOI: 10.1039/C3NR06761K

[94] Barbash VA, Yaschenko OV, Shniruk OM. Preparation and Properties of Nanocellulose from Organosolv Straw Pulp. *Nanoscale Research Letters*, 2017;12:241. DOI: 10.1186/s11671-017-2001-4

[95] Nogi M, Iwamoto S, Nakagaito AN, Yono H. Optically transparent nanofiber paper. *Adv Mater*. 2009;20:1-4. DOI: 10.1002/adma.200803174

[96] Josset S, Orsolini P, Siqueira G, Tejado A, Tingaut P, Zimmermann T.

Energy consumption of the nano-fibrillation of bleached pulp, wheat straw and recycled newspaper through a grinding process. *Nordic Pulp Paper Res J.* 2014;29(1):167-75. DOI: 10.5281/zenodo.32932

[97] Correia VC, dos Santos V, Sain M, Santos SF, Leão AL, Savastano JH. Grinding process for the production of nanofibrillated cellulose based on unbleached and bleached bamboo organosolv pulp. *Cellulose.* 2016;23:2971-2987. DOI: 10.1186/s11671-017-2001-4

[98] Paschoal G, Muller CM, Carvalho GM, Tischer CA, Mali S. Isolation and characterization of nanofibrillated cellulose from oat hulls. *Quim Nova.* 2015;38(4):478-482. DOI: 10.5935/0100-4042.20150029

[99] Sánchez R, Espinosaa E, Domínguez-Roblesa J, Mauricio Loaiza J, Rodríguez A. Isolation and characterization of lignocellulose nanofibers from different wheat straw pulps. *Int J of Biological Macromolecules.* 2016;92:1025-1033. DOI: 10.1016/j.ijbiomac.2016.08.019

[100] Kang YJ, Chun SJ, Lee SS, Kim BY, Kim JH, Chung H, Kim W. All-solid-state flexible supercapacitors fabricated with bacterial nanocellulose papers, carbon nanotubes, and triblock-copolymer ion gels. *ACS Nano.* 2012;6(7): 6400-6406. DOI: 10.1021/n301971r. Epub 2012 Jun 25

[101] Bacakova L, Pajorova J, Bacakova M, et al. Versatile Application of Nanocellulose: From Industry to Skin Tissue Engineering and Wound Healing. *Nanomaterials.* 2019;9(2):164. DOI: 10.3390/nano9020164

[102] Johnson DA, Paradis MA, Bilodeau M, Crossley B, Foulger M, Gélinas P. Effects of cellulosic nanofibrils on papermaking properties of fine papers. *Tappi J.* 2016;15:395-402

[103] Lin N, Dufresne A. Nanocellulose in biomedicine: Current status and future prospect. *European Polymer Journal.* 2014;59:302-325. DOI: 10.1016/j.eurpolymj.2014.07.025

[104] Ahmat HO, Wilson W, Sorelli L, et al. Nanocellulose for improved concrete performance: A macro-to-micro investigation for disclosing the effects of cellulose filaments on strength of cement systems. *Construction and Building Materials.* 2019;206:84-96. DOI: 10.1016/j.conbuildmat.2019.02.042

[105] Zhu H, Luo W, Ciesielski PN, Fang Z, Zhu JY, Henriksson G, Himmel ME, Hu L. Wood-derived materials for green electronics, biological devices, and energy applications. *Chem. Rev.* 2016;116(16): 9305-9374. DOI: 10.1021/acs.chemrev.6b00225

[106] Zhang Y, Park S-J. Flexible organic thermoelectric materials and devices for wearable green energy harvesting. 909-1-909-18. *Polymers.* 2019;11(5). DOI: 10.3390/polym11050909

[107] Irimia-Vladu M, Głowacki ED, Voss G, Bauer S, Sariciftci NS. Green and biodegradable electronics. *Mater. Today.* 2012;15(7-8):340-346. DOI: 10.1016/s1369-7021(12)70139-6

[108] Tan MJ, Owh C, Chee PL, Kyaw AKK, Kai D, Loh XJ. Biodegradable electronics: cornerstone for sustainable electronics and transient applications. *J. Mater. Chem. C.* 2016;4(24):5531-5558. DOI: 10.1039/c6tc00678g

[109] Cai J, Niu H, Li Z, Du Y, Cizek P, Xie Z, Xiong H, Lin T. High-Performance Supercapacitor Electrode Materials from Cellulose-Derived Carbon Nanofibers. *ACS Appl. Mater. Interfaces* 2015; 7(27): 14946-14953. DOI: 10.1021/acsami.5b03757

[110] Zhao Z, Hao S, Hao P, Sang Yu, Manivannan A, Wu N, Liu H.

- Lignosulphonate-cellulose derived porous activated carbon for supercapacitor electrode. *J. Mater. Chem. A*, 2015;3:15049-15056. DOI:10.1039/C5TA02770E
- [111] Liua C, Xiaochen W, Haolin Z, Yiwei L, Lin S, Minghua T, Shia J, Shia Z. Cellulose-derived carbon-based electrodes with high capacitance for advanced asymmetric supercapacitors. *J. of Power sources* 2020;457:228056. DOI: 10.1016/j.jpowsour.2020.228056
- [112] Kim I, Jeon H, Kim D, You J, Kim D. All-in-one cellulose based triboelectric nanogenerator for electronic paper using simple filtration process. *Nano Energy* 2018;53:975-981. DOI:10.1016/j.nanoen.2018.09.060
- [113] Kim HJ, Yim EC, Kim JH, Kim SJ, Park JY, Oh IK. Bacterial Nano-Cellulose Triboelectric Nanogenerator. *Nano Energy* 2017;33:130-137. DOI: 10.1016/j.nanoen.2017.01.035
- [114] Zhang L, Liao Y, Wang YC, Zhang S, Yang W, Pan X, Wang ZL. Cellulose II Aerogel-Based Triboelectric Nanogenerator. *Advanced Functional Materials* 2020;2001763. DOI:10.1002/adfm.202001763
- [115] Klochko NP, Barbash VA, Klepikova KS, Kopach VR, Tyukhov II, Yashchenko OV, Zhadan DO, Petrushenko SI, Dukarov SV, Lyubov VM, Khrypunova AL. Use of biomass for a development of nanocellulose-based biodegradable flexible thin film thermoelectric material. *Solar Energy*. 2020;201:21-27. DOI: 10.1016/j.solener.2020.02.091
- [116] Jung M, Kim K, Kim B, Lee K-J, Kang J-W, Jeon S. Vertically stacked nanocellulose tactile sensor. *Nanoscale*. 2017;9(44):17212-17219. DOI: 10.1039/c7nr03685j
- [117] Zhao X, Han W, Jiang Y, Zhao C, Ji X, Kong F, Xu W, Zhang X. Honeycomb-like paper-based thermoelectric generator based on Bi₂Te₃/bacterial cellulose nanofiber coating. *Nanoscale*. 2019;11:17725-17735. DOI: 10.1039/c9nr06197e
- [118] Abol-Fotouh D, Dörfling B, Zapata-Arteaga O, Rodríguez-Martínez X, Gómez A, Reparaz JS, Laromaine A, Roig A, Campoy-Quiles M. Farming thermoelectric paper. *Energy Environ. Sci.* 2019;12:716-725. DOI: 10.1039/c8ee03112f
- [119] Luzi F, Torre L, Kenny LM, Puglia D. Bio- and fossil-based polymeric blends and nanocomposites for packaging: structure-property relationship. *Materials*. 2019;12(3):471. DOI: 10.3390/ma12030471
- [120] Balea A, Merayo N, Fuente E, et al. Cellulose nanofibers from residues to improve linting and mechanical properties of recycled paper. *Cellulose*. 2018;25:1339-1351. DOI: 10.1007/s10570-017-1618-x
- [121] Kim KM, Lee JY, Jo HM, Kim SH. Cellulose nanofibril grades' effect on the strength and drainability of security paper, *BioRes*, 2019;14(4):8364-8375
- [122] Barbash VA, Yashchenko OV. Preparation and application of nanocellulose from non-wood plants to improve the quality of paper and cardboard. *Applied Nanoscience*. 2020. DOI: 10.1007/s13204-019-01242-8
- [123] Barbash VA, Yashchenko OV, Vasyliova OA. Preparation and application of nanocellulose from *Miscanthus x giganteus* to improve the quality of paper for bags. *SN Applied Sciences* 2020;2:727. DOI:10.1007/s42452-020-2529-2
- [124] Miao C, Du H, Parit M, et al. Superior crack initiation and growth characteristics of cellulose nanopapers. *Cellulose*. 2020;27:3181-3195. DOI: 10.1007/s10570-020-03015-x

- [125] Hubbe MA, Ferrer A, Tyagi P, Yin Y, Salas C, Pal L, Rojas OJ. Nanocellulose in Thin Films, Coatings, and Plies for Packaging Applications: A Review. *BioResources*. 2017;12(1):2143-2233
- [126] Zheng, G., Cui, Y., Karabulut, E., Wågberg, L., Zhu, H., Hu, L. Nanostructured paper for flexible energy and electronic devices. *MRS Bull.* 2013;38(04):320-325. DOI: 10.1557/mrs.2013.59
- [127] Burrs SL, Bhargava M, Sidhu R, Kiernan-Lewis J, Gomes C, Claussen JC, McLamore ES. A paper based graphene-nanocauliflower hybrid composite for point of care biosensing. *Biosens Bioelectron.* 2016;85:479-487. DOI: 10.1016/j.bios.2016.05.037. Epub 2016 May 11
- [128] Feig VR, Tran H, Bao Z. Biodegradable polymeric materials in degradable electronic devices. *ACS Cent. Sci.* 2018;4(3):337-348. DOI: 10.1021/acscentsci.7b00595
- [129] Hoeng F, Denneulin A, Bras J. Use of nanocellulose in printed electronics: a review. *Nanoscale.* 2016;8 (27):13131-13154. DOI: 10.1039/c6nr03054h
- [130] Huang J, Zhu H, Chen Y, Preston C, Rohrbach K, Cumings J, Hu L, Highly transparent and flexible nanopaper transistors. *ACS Nano.* 2013;7(3): 2106-2113. DOI: 10.1021/nn3044071
- [131] Fang Z, Hou G, Chen C, Hu L. Nanocellulose-based films and their emerging applications. 100764-1-100764-11. *Curr. Opin. Solid State Mater. Sci.* 2019;23. DOI: 10.1016/j.cossms.2019.07.003
- [132] Lee K-Y, Aitomaki Y, Berglund LA On the use of nanocellulose as reinforcement in polymer matrix composites. *Compos Sci Technol.* 2014;105:15-27. DOI: 10.1016/j.compscitech.2014.08.032
- [133] Chattopadhyay DP, Patel BH. Synthesis, characterization and application of nanocellulose for enhanced performance of textiles. *J Text Sci Eng.* 2016;6:248. DOI: 10.4172/2165-8064.1000248
- [134] Dufresne A. Cellulose nanomaterial reinforced polymer nanocomposites. *Current Opinion in Colloid & Interface Science.* 2017;29:1-8. DOI: 10.1016/j.cocis.2017.01.004
- [135] Al-Turaif HA. Relationship between tensile properties and film formation kinetics of epoxy resin reinforced with cellulose. *Prog Org Coat.* 2013 nanofibrillated;76:477-481. DOI: 10.1016/j.porgcoat.2012.11.001
- [136] Chen J, Huang X, Zhu Y, Jiang P. Cellulose nanofiber supported 3D interconnected BN nanosheets for epoxy nanocomposites with ultrahigh thermal management capability. *Advanced Functional Materials.* 2017;27(5):1604754. DOI: 10.1002/adfm.201604754
- [137] Guimarães JrM, Botarob VR, Novackc KM, Teixeirad FG, Tonolie GH. Starch/PVA-based nanocomposites reinforced with bamboo nanofibrils. *Industrial Crops and Products.* 2015;70:72-83. DOI: 10.1016/j.indcrop.2015.03.014
- [138] Flauzino Neto WP, Marianoc M, Vieira da Silvaa IS, Silvério HA, Putauxe JL, Otaguroa H, Pasquini D, Dufresnec A. Mechanical properties of natural rubber nanocomposites reinforced with high aspect ratio cellulose nanocrystals isolated from soy hulls. *Carbohydrate Polymers.* 2016;153:143-152. DOI:10.1016/j.carbpol.2016.07.073
- [139] Sigareva NV, Barbash VA, Yashchenko OV, Shulga SV, Starokadomsky DL, Gorelov BM. Influence of cellulose particles on chemical resistance, mechanical and

thermal properties of epoxy composites.
Biophysical bulletin iss. 2020;43:57-70

[140] Guancha-Chalapud MA,
Gálvez J, Serna-Cock L, Aguilar CN.
Valorization of Colombian fique
(*Furcraea bedinghausii*) for production
of cellulose nanofibers and its
application in hydrogels. Scientific
Reports. 2020;10:11637. DOI: 10.1038/
s41598-020-68368-6

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