



Research Article

Preparation and application of nanocellulose from *Miscanthus × giganteus* to improve the quality of paper for bags

V. A. Barbash¹  · O. V. Yashchenko¹  · O. A. Vasylieva¹ 

Received: 15 December 2019 / Accepted: 14 March 2020 / Published online: 20 March 2020
© Springer Nature Switzerland AG 2020

Abstract

We present the study of the preparation of pulp and nanocellulose from *Miscanthus × giganteus* to improve the quality of the paper for bags. The organosolv miscanthus pulp (OMP) was prepared by the environmentally friendly organosolv method—cooking in a solution of peracetic acid at the first stage and the alkaline treatment at the second stage. Nanocellulose was obtained by hydrolysis of never-dried OMP and subsequent ultrasonic treatment. Structural changes and crystallinity index of OMP and nanocellulose were studied by SEM and FTIR methods. X-ray diffraction analysis confirmed an increase in the crystallinity of OMP and nanocellulose as a result of thermochemical treatment. The nanocellulose had a density of up to 1.6 g/cm³, transparency up to 82%, a crystallinity index of 76.5%, and tensile strength up to 195 MPa. The AFM showed that the particles of nanocellulose have a diameter in the range from 10 to 20 nm. A TGA analysis confirmed that nanocellulose films have a denser structure and lower mass loss in the temperature range 320–440 °C compared to OMP. We established the positive effect of nanocellulose application on the physical and mechanical properties of paper for bags. The application of nanocellulose allows replacing synthetic reinforcing materials and more expensive sulfate unbleached pulp with waste paper in the production of paper and cardboard.

Keywords *Miscanthus × giganteus* · Organosolv pulp · Nanocellulose · Paper

1 Introduction

In recent years, there has been growing interest in the development of biodegradable plant-derived materials. They are able to replace materials made from exhaustible natural resources—oil, gas, coal. The processing products of such renewable plant materials are widely used in the chemical, pharmaceutical, paper, textile and electronic industries [37, 40]. Biodegradable materials based on annually renewable plant raw materials can become the basis for the production of environmentally friendly products and can compete with products made from petroleum materials. The development of technologies of processing renewable plant sources contribute to the sustainable development of society, solving environmental

and economic problems in the production of consumer goods [1, 22].

The main component of all plants is cellulose, which is the most abundant renewable biopolymer on the Earth. Cellulose is a structural component of the cell walls of all plants. Its industrial use is mainly for the manufacture of paper and cardboard, but recently it has also attracted considerable interest as a source of nanocellulose. Nanocellulose has of nanosized particles and unique properties: high elasticity and a specific surface, high transparency and chemical resistance, biodegradability and biocompatibility, a low production cost in comparison with synthetic polymers and has lightweight [31].

Nanocellulose is added to polymer matrices to produce reinforced composites from tenfold to hundredfold

✉ V. A. Barbash, v.barbash@kpi.ua | ¹Department of Ecology and Technology of Plant Polymers, National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”, Kyiv, Ukraine.



mechanical strength and to improve barrier properties [26]. Nano-sized cellulose fibers are considered as promising candidates for the production of nanocomposites, such as filter materials, rheology modifiers for food and cosmetics and additives to enhance the mechanical properties of paper and cardboard by applying nano-coatings [13]. In recent years, worldwide demand for packaging materials from paper and cardboard has grown as an alternative to plastic materials that have a long biodegradation period [29]. In the production of packaging materials, in particular paper for bags, synthetic reinforcing additives are used that adversely affect the environment. All this contributes to extensive research on the replacement of synthetic reinforcing materials with natural substances, particularly the use of nanocellulose [23, 28].

Nanocellulose is obtained by chemical, mechanical, oxidative and enzymatic treatments of cellulose fibers [15, 38]. The most common technique for obtaining of nanocellulose is hydrolysis of cellulosic materials. The main raw material used to produce cellulose on a worldwide scale is wood. As world wood reserves are steadily declining, the urgent problem is the production of pulp from non-wood plants. Non-wood materials include various types of cereal and industrial plants. *Miscanthus* stalks are a good alternative source of fibers for the production of pulp.

Miscanthus × giganteus is widely cultivated in Europe and the USA, is a fast-growing and quite resistant to diseases perennial grass, quite unpretentious and inexpensive to grow [33]. The yield of miscanthus can reach 10–35 dry tons per hectare, and after a single planting culture can be collected annually for 15–20 years [10]. Compared to wood, which requires about 10–12 years to fully mature, miscanthus requires a maximum of 3 years after planting to reach its peak dry biomass production which further showcases its potential as a viable source of raw materials. It is also one of the few plant species being dedicated to biomass cropping and is currently farmed primarily for use in electricity and heat generation (by combustion) as well as feedstock for biofuels. More recently, miscanthus has been expanded into other markets such as advanced materials and biobased products [16].

In the world practice of pulp and paper industry, the dominant technologies of pulp production are the sulfate and sulfite methods, which lead to the environmental pollution. Environmental requirements for the quality of wastewater and gas emissions discharged by industrial enterprises stimulate the development of new technologies for processing plant materials using organic solvents [14]. For example, peracetic acid is a strong oxidizing agent with excellent bleaching properties. This acid is an environmentally friendly alternative to bleaching because it is a totally chlorine-free process resulting in less damage to the fiber [32]. Organosolv methods for the production of

cellulose from *Miscanthus* are discussed in the works [11, 27, 42, 43]. We also studied the obtaining of cellulose from non-wood plant materials in both peracetic and performic acids [2, 7, 8] and in cooking solutions of ethanol, methanol, and isobutanol alcohols [3–5]. As the research results show, in order to obtain cellulose suitable for chemical treatment from non-wood plant materials, in particular, to produce nanocellulose, thermochemical treatment of raw materials in two stages is necessary to remove residual lignin, hemicellulose and minerals, which impair the quality of nanocellulose [7, 9].

The goal of the study was to obtain organosolv pulp from *Miscanthus × giganteus* by cooking in solution of peracetic acid and alkaline treatment and nanocellulose by acid hydrolysis, as well as to investigate the application of nanocellulose to improve the properties of one of the mass production types of the paper industry—paper for bags.

2 Experimental section

2.1 Materials

Stalks of *Miscanthus × giganteus* of a harvest of 2017 from the Kyiv region were used for pulp production. *Miscanthus* stalks were cleaned of leaves and nodes, crushed into particles of 5–7 mm in size and placed in a desiccator to maintain constant moisture and chemical composition. As shown in the article [17], nodes of miscanthus contain less cellulose (28.4%) and more ash (1.6%) than de-pithed internodes and pith. Pith, which is 5–6% of the mass of the stalks and slightly inferior to the de-pithed internodes in terms of the content of the main components, was not separated from the stalks to study the chemical composition and obtain cellulose from miscanthus. The chemical composition of miscanthus was determined according to TAPPI standards [39] namely: T 222 for lignin; T 204 for substances extracted with alcohol-benzene solution for determinate content of resins, fats, waxes; T 211 to determine ash content and cellulose by the Kurschner-Hoffer method. All chemicals, including ice acetic acid, 35% hydrogen peroxide, NaOH and sulfuric acid were used without further purification.

2.2 Cooking process

Cooking of miscanthus pulp was carried out in the two stages. At the first stage, treatment of *Miscanthus × giganteus* in the mixture of glacial acetic acid and 35% hydrogen peroxide in a volume ratio of 70:30% at the liquid to solid ratio 10:1, at temperature 95 ± 2 °C during 30–240 min was carried out. Such conditions for the cooking process were

determined as optimal on the basis of previous studies [2, 7, 9], when the effect of all the main technological factors, including the concentration of peracetic acid before and after preparation, on the quality of organosolv pulp was studied. At the second stage, the alkaline treatment of obtained organosolv miscanthus pulp (OMP) by solution of NaOH concentration of 7% during 30–240 min, at the liquid to solid ratio 12:1 at temperature 95 ± 2 °C was carried out. The OMP after alkaline treatment was washed with hot distilled water to a neutral pH and was stored in sealed bags in a refrigerator for further research. The second stage of alkaline treatment is necessary to remove the residual content of lignin and minerals in organosolv pulp and to obtain high-quality nanocellulose from it. The quality parameters of the obtained OMP samples we determined according to standard methods [39].

2.3 Preparation of nanocellulose

We used never-dried organosolv pulp obtained from *Miscanthus × giganteus* to make nanocellulose. Never-dried pulp is better than once dried samples, because it is known that the latter irreversibly lose access to the surface during the drying process. Using never-dried pulp does not require consumption of energy for drying and grinding since dried cellulose fibers lose the ability to swell and percolate due to irreversible cornification. Also, the application of wet pulp enables better percolation of acid into cellulose fibers in the process of hydrolysis. Hydrolysis of never-dried organosolv pulp was carried out by solution of sulfuric acid with concentration of 43% and 50%, at the liquid-to-solid ratio of 10:1, at temperature of 40 and 60 °C during 30–90 min for obtaining of nanocellulose. The calculated amount of sulfate acid with the corresponding concentration was slowly added into the flask with the OMP suspension. Upon expiration of the reaction time, the hydrolysis was stopped by tenfold dilution with distilled water and cooling of the suspension to the room temperature. Hydrolyzed cellulose was washed three times with distilled water by centrifugation at 4000 rpm, followed by dialysis to achieve a neutral pH. Dialysis was performed to further purify the colloidal nanocellulose solution from sulfuric acid molecules, which causes the destruction of the nanocellulose. For this purpose, a solution of nanocellulose with a sulfuric acid residue was transferred to a semi-permeable membrane, which was immersed in a vessel with distilled water for 2 days with periodic water replacement. Hydrolyzed cellulose was subjected to ultrasonic treatment on an ultrasonic disintegrator UZDN-A (SELMi, Ukraine) with an operating frequency of 22 kHz and an ultrasonic power of 300 W during 30, 45 or 60 min. The nanocellulose dispersion was placed in an ice bath to prevent overheating during treatment.

Eventually, the suspension took the form of a homogenous gel-like dispersion and was stored in sealed containers for further research to determine the physical and mechanical characteristics of nanocellulose. The prepared suspensions were poured into Petri dishes and dried in the air at a room temperature to obtain nanocellulose films.

2.4 Preparation of handsheets

Standard laboratory handsheets samples of paper for bags were prepared using a Rapid-Kothen machine according to TAPPI T 205 sp-02. The handsheets of paper for bags of 78 ± 3 g/m² were produced from unbleached sulphate pulp and waste paper of used paper for bags. The unbleached sulphate pulp and waste paper were beaten separately in a Valley beater to 35 ± 3 °SR. Cationic starch and alkyl ketene dimer were added to the pulp in an amount of 3% relative to mass of absolutely dry raw material (a.d.r.m.). The handsheets were dried in the air to a dry-air condition. The mixture of nanocellulose suspension with consumption ranging from 1 to 3 g/m² was applied to each side of the samples of paper for bags using a special mechanical device for coating of nanocellulose suspension. The handsheets were dried in the air to a dry-air condition and then on a drying drum. These sheets were conditioned in a chamber at 23 °C and 50% humidity for 24 h prior to determining their physical and mechanical parameters.

2.5 Determination of pulp, nanocellulose and paper properties

The scanning electron microscope (SEM) analysis was made by the PEM-106I (SELMi, Ukraine) microscope to observe the morphology of organosolv pulp, paper for bags with and without nanocellulose. The topographical characterization of nanocellulose samples was investigated with the use of atomic force microscopy (AFM). Measurements were accomplished with Si cantilever, operating in a tapping mode on the device Solver Pro M (NT-MDT, Russia). The scanning speed and area were 0.6 line/s and 2×2 μm², respectively. The transparency of the nanocellulose films was determined by the electron absorption spectra, which were registered in the range of 200–1100 nm. The electron absorption spectra of the nanocellulose films in UV and in visible and near infrared regions were registered on two-beam spectrophotometer 4802 (UNICO, USA) with a resolution of 1 nm.

X-ray diffraction patterns of the different cellulose samples were measured by Ultima IV diffractometer (Rigaku, Japan). Crystallinity index (CI) was used to calculate relative amount of crystalline material in cellulose by Segal method [34]: $CI = [(I_{200} - I_{am})/I_{200}] \times 100\%$, where I_{200} is

an intensity of (200) reflex about 23° and I_{am} intensity of amorphous scattering at 18.5° .

Functional groups of OMP, OMP after alkaline treatment and nanocellulose samples were analyzed using Fourier transform infrared spectrophotometer (FT-IR- Spectrometer "Tensor-37") in the range of $4000\text{--}500\text{ cm}^{-1}$ with resolution of 2 cm^{-1} .

The thermal degradation behavior of organosolv pulps and nanocellulose samples was explored by heating with the use of a Netzsch STA-409 thermoanalyzer. The samples were heated at a rate of $5\text{ }^\circ\text{C}/\text{min}$, from 25 to $450\text{ }^\circ\text{C}$. Based on the changes in the gravimetric and differential curves of thermal analysis, the initial temperature of the mass weight loss of organosolv pulps and nanocellulose samples from various plant materials were determined.

The density of the nanocellulose films was determined in accordance with ISO 534:1988. Tensile strength of the nanocellulose films were measured at controlled temperature $23 \pm 1\text{ }^\circ\text{C}$ and humidity $50 \pm 2\%$ according to ISO 527-1. The physical and mechanical properties of paper for bags were determined in accordance with ISO or TAPPI standards: tensile strength and elongation and breaking force were determined according to ISO 6892-1; water absorption—according to EN ISO535: 2017.

3 Results and discussion

3.1 Chemical composition

Chemical analysis of *Miscanthus × giganteus* showed that it has the following content of components: 49.7% of cellulose; 27.7% of lignin; 1.8% of resins, fats, waxes; 1.1% of mineral substances to of a.d.r.m. Thus, miscanthus stalks contain more cellulose and minerals, with the same lignin content as coniferous wood. The analysis of the content of the main components of miscanthus a priori allows us to conclude that this raw material can be considered both to produce pulp suitable for paper and cardboard, and pulp for chemical processing, in particular for the production

of nanocellulose. The properties of the organosolv miscanthus pulp after cooking and alkaline treatment are shown in Table 1.

As shown data Table 1, an increase in the cooking time from 30 to 240 min naturally leads to a decrease in the yield, the content of residual lignin and mineral substances. The mineral content in the OMP after 90 min of cooking does not significantly decrease and remains in the range of 0.84–0.94% to a.d.r.m.. Therefore, after 90 min of cooking, cellulose was used for its subsequent alkaline treatment in order to reduce the content of minerals and lignin in it. Table 1 shows that increasing the duration of the alkaline treatment from 30 to 240 min reduces the pulp yield and the content of residual lignin. Subsequent alkaline treatment does not contribute to the extraction of minerals, but rather, the polysaccharides dissolve, the yield of pulp decreases, and, therefore, the percentage of ash increases. Therefore, to prepare nanocellulose from OMP, we used 90-min cooking and alkaline treatment for 60 min with a lignin content of 0.08% and mineral substances of 0.037% to a.d.r.m. Previous studies have shown that the hydrolysis of cellulose with a residual lignin content of more than 1% and mineral substances of more than 0.5% leads to the formation of turbid solutions of nanocellulose, from which opaque breaking films with low physical and mechanical properties are obtained. Thus, carrying out peroxide cooking and alkaline treatment at low temperature $96 \pm 1\text{ }^\circ\text{C}$ allows to obtain cellulose with a high degree of whiteness up to 85% and low emissions of harmful substances into the environment. The obtained OMP have a minimum content of non-cellulosic components and are suitable for chemical processing and for the production of nanocellulose.

3.2 Morphology

The morphology structure of the samples of the miscanthus, organosolv miscanthus pulp before and after alkaline treatment is shown in Fig. 1. The main components of the miscanthus stalks are xylem cells and phloem,

Table 1 The properties of the organosolv miscanthus pulp after stages of its processing

Cooking time (min)	Pulp after the I stage of processing			Pulp after the II stage of processing		
	Yield (%)	Residual lignin (%)	Ash (%)	Yield* (%)	Residual lignin (%)	Ash (%)
30	54.3 ± 1.1	0.5 ± 0.02	1.08 ± 0.04	39.25 ± 1.1	0.13 ± 0.05	0.12 ± 0.02
60	53.0 ± 1.0	0.36 ± 0.05	1.0 ± 0.06	35.7 ± 1.1	0.08 ± 0.01	0.037 ± 0.04
90	52.2 ± 0.9	0.27 ± 0.03	0.94 ± 0.01	32.9 ± 1.3	0.065 ± 0.05	0.041 ± 0.01
120	50.7 ± 1.2	0.22 ± 0.02	0.89 ± 0.01	28.1 ± 1.2	0.042 ± 0.01	0.057 ± 0.01
180	45.2 ± 1.5	0.15 ± 0.04	0.83 ± 0.02	24.7 ± 1.0	0.034 ± 0.02	0.054 ± 0.02
240	43.7 ± 1.4	0.1 ± 0.01	0.84 ± 0.01	22.3 ± 1.1	0.012 ± 0.03	0.054 ± 0.03

*Regarding to the starting raw material

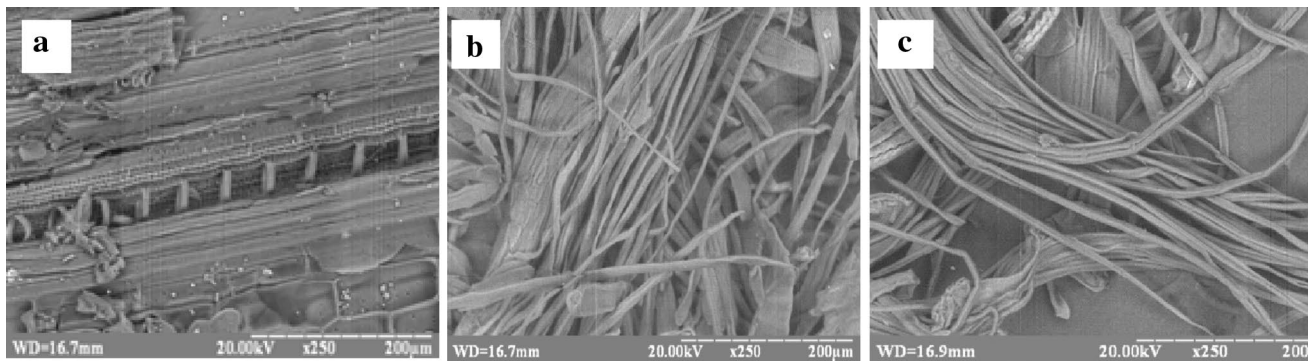


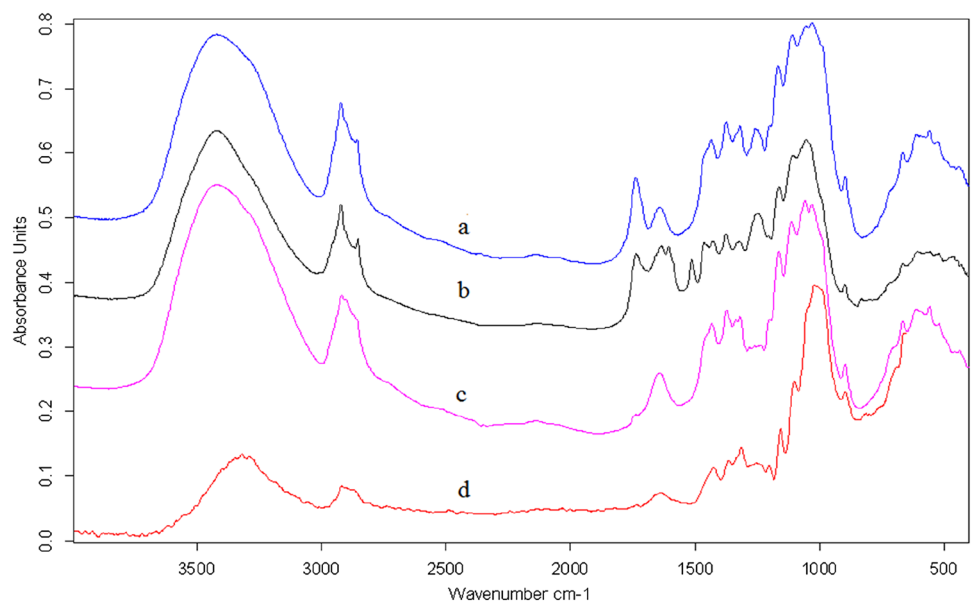
Fig. 1 Scanning electron microscopy images of samples of the miscanthus stalks (a), organosolv miscanthus pulp before (b) and after alkaline treatment (c)

which perform the conductive, mechanical and storage functions. These include cells of tracheids, vessels, libriform, and parenchymal cells (Fig. 1a). The presence of such cells is typical for different representatives of non-wood plant materials. The walls of miscanthus stalks consist of a network of longitudinal oval capillaries that provide access to the cooking solution to the cells. As a result of cooking, the miscanthus is exposed to thermochemical effects and the stalks are folded into separate short and wide fragments (Fig. 1b). According to the SEM, the bulk of pulp from miscanthus is made up of thin, ribbon fibers of different widths and lengths, and can be single and joined to several pieces. The photographs confirm that in the process of thermochemical processing of plant materials, the size of the fibers decreases, primarily their width due to the removal of non-cellulose plant components from them. Moreover, as can be seen from Fig. 1c, the fiber after intensive alkaline treatment has a smooth

surface, which indicates the relative chemical purity of the cellulose fibers.

The extraction of non-cellulosic components from OMP in the process of its thermochemical treatment was confirmed by infrared spectroscopy. Figure 2 shows the Fourier IR spectra of the miscanthus stalks, organosolv miscanthus pulp before and after alkaline treatment, nanocellulose after hydrolysis. All spectra are characterized by a wide bandwidth in the region of $3000\text{--}3800\text{ cm}^{-1}$, which corresponds to stretching vibrations of hydroxyl groups included in intramolecular and intermolecular hydrogen bonds. Spectra of miscanthus stalks, organosolv miscanthus pulp before and after alkaline treatment has characteristic high-frequency bands, indicating the formation of intermolecular bonds. The band of nanocellulose in this region is characterized by low intensity, which indicates the formation of strong intermolecular bonds between the

Fig. 2 FTIR spectra of different samples: of miscanthus stalks (a), organosolv miscanthus pulp before (b) and after alkaline treatment (c), nanocellulose film (d)



hydroxyl groups of the macromolecules of nanocellulose. The bands in the area of 3000–2800 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the methylene groups of the cellulose. Bands of stretching vibrations of double bonds lie in the region of 1500–1800 cm^{-1} . Vibration bands in the 1740 cm^{-1} region indicate the presence of a carbonyl group characteristic of hemicelluloses. As can be seen from Fig. 2c, organosolv cooking and subsequent alkaline treatment removes hemicelluloses from the cellulose composition. A decrease in the intensity of vibrations in the region of 1600 cm^{-1} , which is characteristic of aromatic compounds—residual lignin, indicates an almost complete removal of lignin from plant materials and cellulose during their thermochemical treatments. The bands in the region of 1370 and 1430 cm^{-1} are due to the deformation vibrations of the CH_2 groups, the band at 1160 cm^{-1} is due to the asymmetric vibrations of the C–O bonds, while the band at 1060 cm^{-1} corresponds to the vibrations of the C–O–C bridge of the glucopyranose ring of cellulose [20]. The increase of the intensity of the bands in the region of 1050, 1400, 3400 cm^{-1} demonstrates the efficiency of removal of lignin and noncellulose components from the plant feedstock in the investigated sequence of thermochemical treatments.

3.3 Hydrolysis

We show the dependencies of the density, tensile strength and transparency of nanocellulose films on the main technological parameters of the process for obtaining nanocellulose from organosolv miscanthus pulp (Table 2).

As can be seen from the data in Table 2, the hydrolysis of OMP with sulfuric acid solutions of various concentrations leads to the formation of nanocellulose films of different quality. The quality of nanocellulose films improves with increasing sulfuric acid concentration, temperature and duration of hydrolysis. An increase in the duration of ultrasonic treatment of a suspension of nanocellulose obtained during one hydrolysis time from 30 to 60 min increases the strength and transparency of nanocellulose films. The highest values of quality indicators are the samples obtained at the maximum values of the studied technological parameters. The values of transparency of the films prepared in this study is higher than the transparency of the cellulose nanofiber films (40–65%) obtained from bleached kraft eucalyptus, acacia, and pine pulps reported previously [18].

Nanocellulose after hydrolysis and ultrasound treatment of OMP had homogeneous and stable nanocellulose suspension. The nature of stabilization of the colloidal suspension is explained by the presence of charged

Table 2 Dependences of the parameters of nanocellulose films on the main technological parameters of the process of obtaining nanocellulose from organosolv miscanthus pulp

Concent-ration H_2SO_4 (%)	Duration of hydrolysis (min)	Duration of ultrasonic treatment (min)	Quality of received films		
			Density (g/cm^3)	Tensile strength (MPa)	Transparency (%)
Temperature 40 °C					
43/50	30	30	0.87/1.00	56.0/44.2	25.8/57.0
		45	1.04/1.08	58.3/54.1	40.6/64.2
		60	1.05/1.12	80.0/66.7	41.8/67.0
	60	30	1.04/1.12	54.5/50.0	30.3/51.1
		45	1.08/1.15	59.3/66.1	43.3/67.0
		60	1.16/1.22	77.7/83.3	52.7/69.7
	90	30	1.09/1.15	70.7/77.5	42.7/59.9
		45	1.11/1.18	83.3/105.0	54.5/64.3
		60	1.18/1.23	124.0/127.0	55.6/69.3
Temperature 60 °C					
43/50	30	30	1.12/1.1	43.3/66.7	44.3/65.7
		45	1.22/1.23	57.5/70.7	52.0/75.6
		60	1.26/1.28	60.4/75.0	70.7/76.3
	60	30	1.15/1.33	55.5/78.0	68.6/68.7
		45	1.23/1.37	60.0/80.6	65.3/70.9
		60	1.32/1.42	62.0/88.0	74.4/80.8
	90	30	1.04/1.45	44.4/115.0	38.5/75.7
		45	1.18/1.55	40.0/123.0	68.2/78.0
		60	1.25/1.60	41.0/195.0	72.3/82.6

groups on the surface of nanocellulose, which are formed by the interaction of cellulose with sulfuric acid due to the esterification reaction. The stability of nanocellulose suspensions is supported by images immediately after the preparation and after a prolonged storage time. There was no sedimentation of nanocellulose particles when stored at room temperature for extended period of time (after 5 months of storage). Such stabilization of the nanocellulose suspension leads to the formation of films with a transparency of more than 80% in the visible spectral range, which is confirmed by the data of the article [35] and characteristic of nanocellulose from other plant raw materials [6–9].

The results of hydrolysis process showed that the treatment of OMP with sulfuric acid at concentration of 43%, at 60 °C for 90 min allow to obtain nanocellulose with high physical and mechanical properties. The yield of nanocellulose is higher than when using sulfate acid 50% or 63%. Such conditions are in good agreement with the data obtained by loelovich [21] and are more economically favorable than traditional conditions for the hydrolysis of cellulose with 60–65% sulfuric acid at 40–50 °C for 1–2 h [25].

The change in the ratio of amorphous and crystalline parts of OMP during its thermo-chemical and physical treatment was investigated by XRD method. The analysis of X-ray diffraction patterns of miscanthus stalks (Fig. 3a), OMP before (Fig. 3b) and after alkaline treatment (Fig. 3c), and nanocellulose after hydrolysis and sonication (Fig. 3d) were carried out. The crystallinity index of miscanthus stalks was 65.8%, organosolv pulp—72.3%, OMP after alkaline treatment—71.9% and nanocellulose after hydrolysis

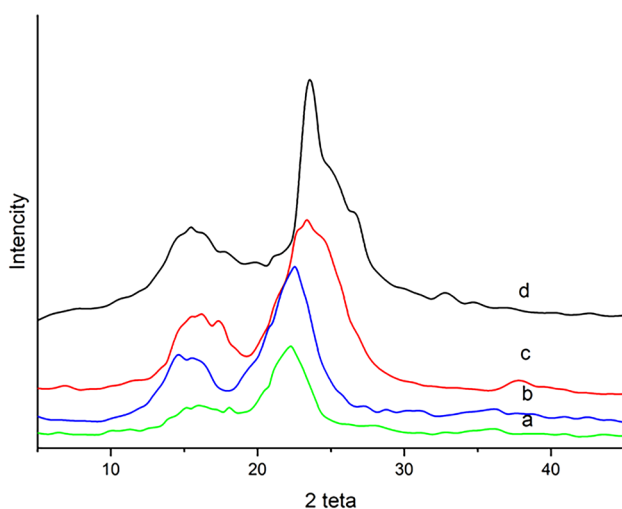


Fig. 3 X-ray diffraction patterns of different cellulose samples: **a** miscanthus stalks, **b** organosolv pulp, **c** OMP after alkaline treatment and **d** nanocellulose after hydrolysis and sonication

and sonication—76.7%. The crystallinity of nanocelluloses is higher than that of the initial organosolv pulps, which is explained by an increase in the crystalline part of cellulose due to a decrease in the amorphous part during its hydrolysis. The dissolution of the amorphous part of the organosolv pulps leads to the formation of nanocellulose films with higher values of density, transparency and tensile strength. Thus, the results of X-ray diffraction analysis indicate an increase in the sample crystallinity in the process of their thermochemical and physical processing. This dependence is observed for cellulose from other representatives of non-wood and woody plant raw materials [6–9, 32].

The higher density of nanocellulose films in comparison with the density of OMP explains their higher thermal stability, which is confirmed by the thermogravimetric analysis (Fig. 4). As is shown in Fig. 4, in the temperature range from 50 to 90 °C, the maximum weight loss (up to 12%) is observed for OMP, which is due to the evaporation of residual moisture from its fibers. When heating nanocellulose films to 240 °C, and samples of OMP and OMP after alkaline treatment to 260 °C, a slight (up to 3%) loss in mass is observed. In the process of further heating of the OMP and OMP samples after alkaline treatment to 340 °C, up to 70% of their bulk is lost. Samples have final degradation temperature of about 440 °C for OMP and 500 °C for OMP after alkaline treatment. For nanocellulose films, a smooth mass loss is observed in the temperature range 240–500 °C, and the final decomposition is observed at a temperature of 540 °C. It can be explained by the fact that during the chemical treatment and ultrasonic homogenization a dense structure between pulp molecules is formed. The degradation behavior of the cellulose that underwent sulfuric acid hydrolysis was different from that of the initial cellulose and showed higher degradation temperature. The higher degradation temperature of the nanocellulose was due to the formation of a dense crystalline structure of the cellulose. These end chains started to decompose at the lower temperatures, as have been previously shown [19]. Our data also support previous findings that the sulfate groups, introduced during hydrolysis, can work as a flame retardant in such a way they cause an increase in the char fraction [36].

Topographical characterization of organosolv miscanthus nanocellulose by AFM and its 3D projection with definition of sample height is shown in Fig. 5. Figure 5a shows lateral section of the miscanthus nanocellulose nanofibers, which form aggregates. The diameter of separate nanofibers is within the range from 10 to 20 nm and possibly much less, since the image is obtained from fibers of nanocellulose located not in one layer. Therefore, we propose, that nanocellulose forms a film on the surface of the silicon substrate due to bonds between the molecules.

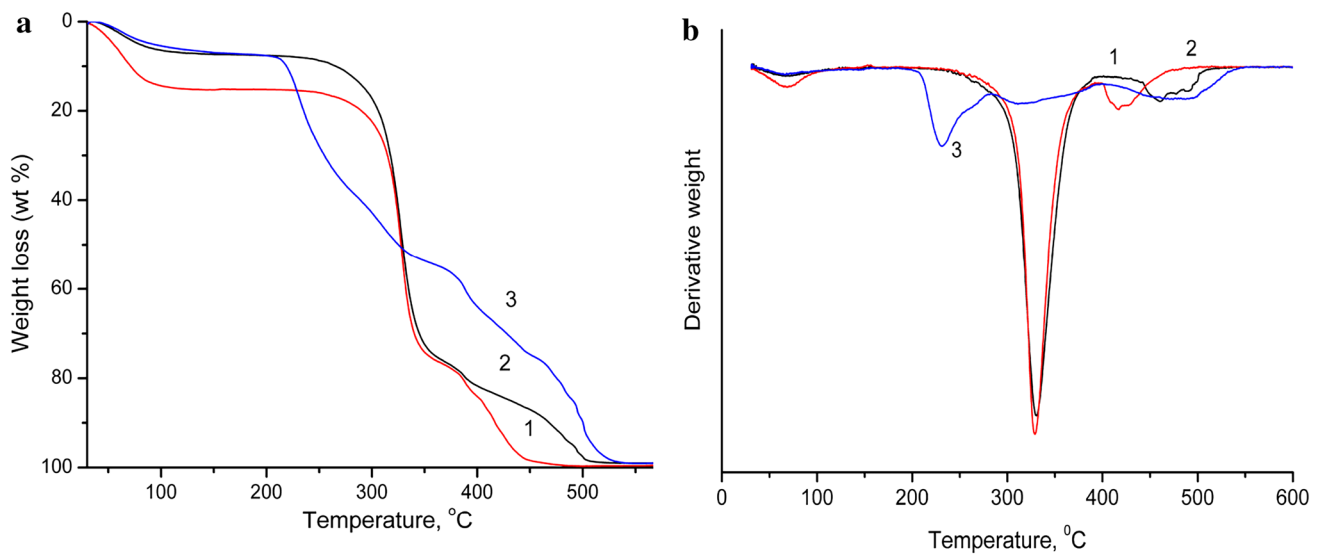


Fig. 4 Gravimetric (a) and differential (b) curves of thermal analysis: (1) OMP; (2) OMP after alkaline treatment and (3) nanocellulose film

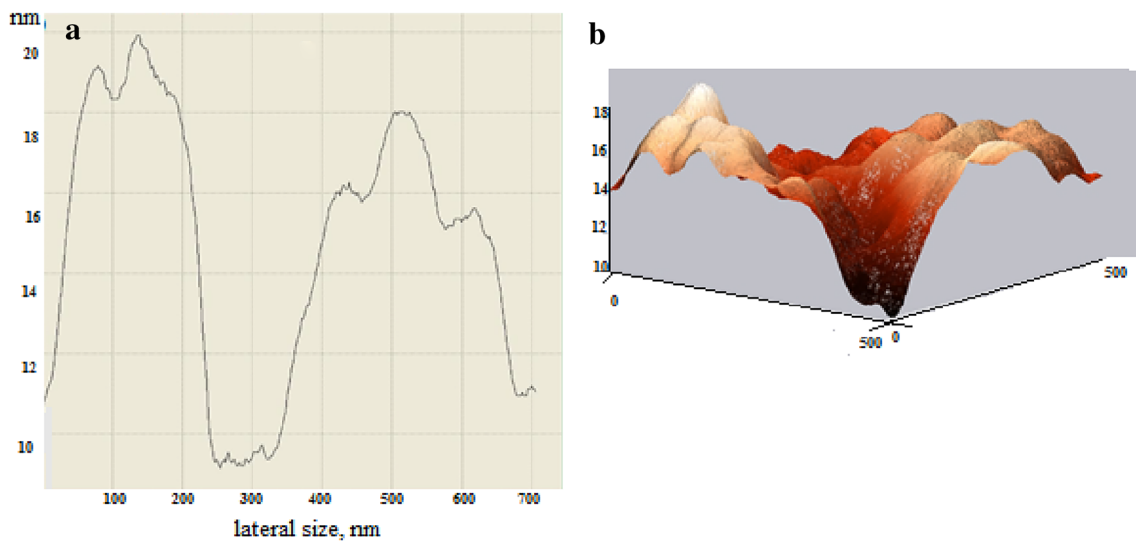


Fig. 5 a The AFM images of lateral size of nanocellulose surface, b 3D projection with definition of sample height tapping mode

The obtained nanocelluloses have high physical, optical and mechanical properties and can therefore be used for making various consumer goods, particularly as a reinforcing additive in the production of paper and cardboard. In this article, we explore the use of nanocellulose extracted from *Miscanthus × giganteus* to improve the qualitative indicators of such mass types of products as paper for bags.

3.4 Paper for bags

The properties of paper for bags with different nanocellulose consumption on its surface are shown in Fig. 6.

We present in Fig. 6 how the application of nanocellulose from OMP on the surface paper coating improves its quality parameters. As can be seen from the data in Fig. 6, the main factor influencing the physical and mechanical properties of the paper for bags is the kind of pulp. Primary and secondary fibers differ significantly in their paper-forming properties. Samples of paper made from primary fiber—unbleached pulp, have significantly better quality indicators, and paper samples made from waste paper do not meet the requirements of the standard for any indicator. Paper made from unbleached pulp without the surface application of nanocellulose has high values that are close to the

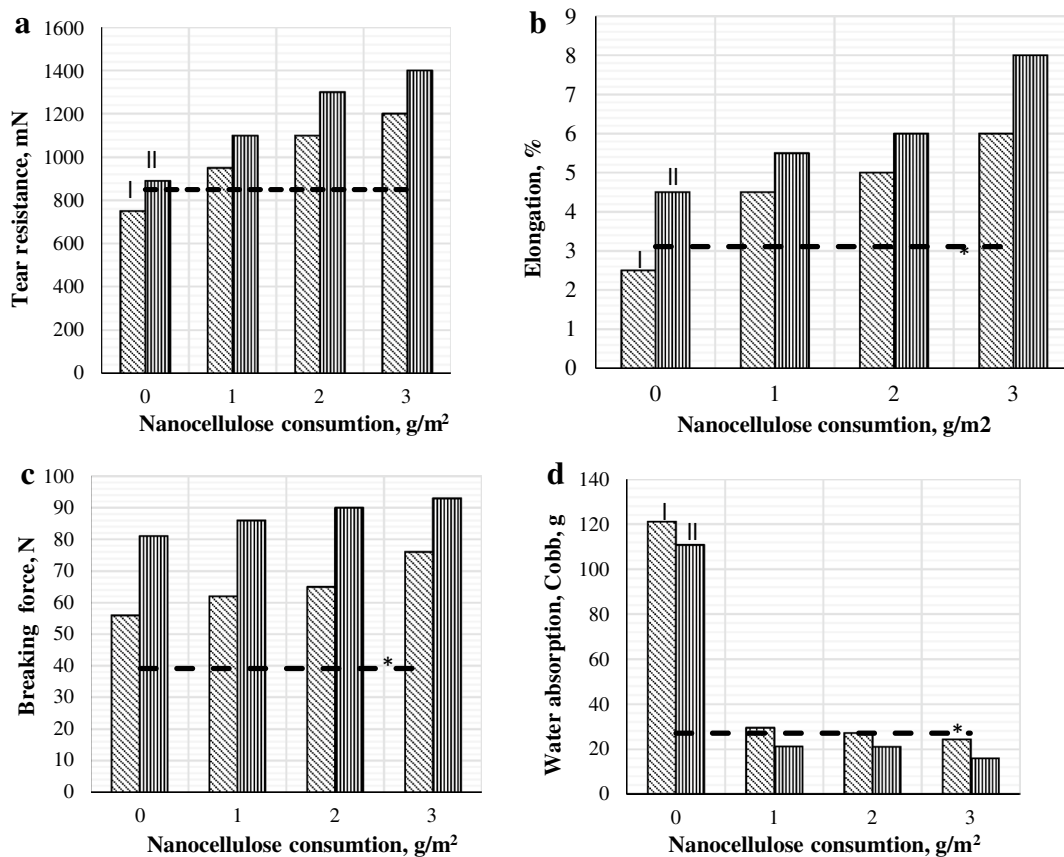


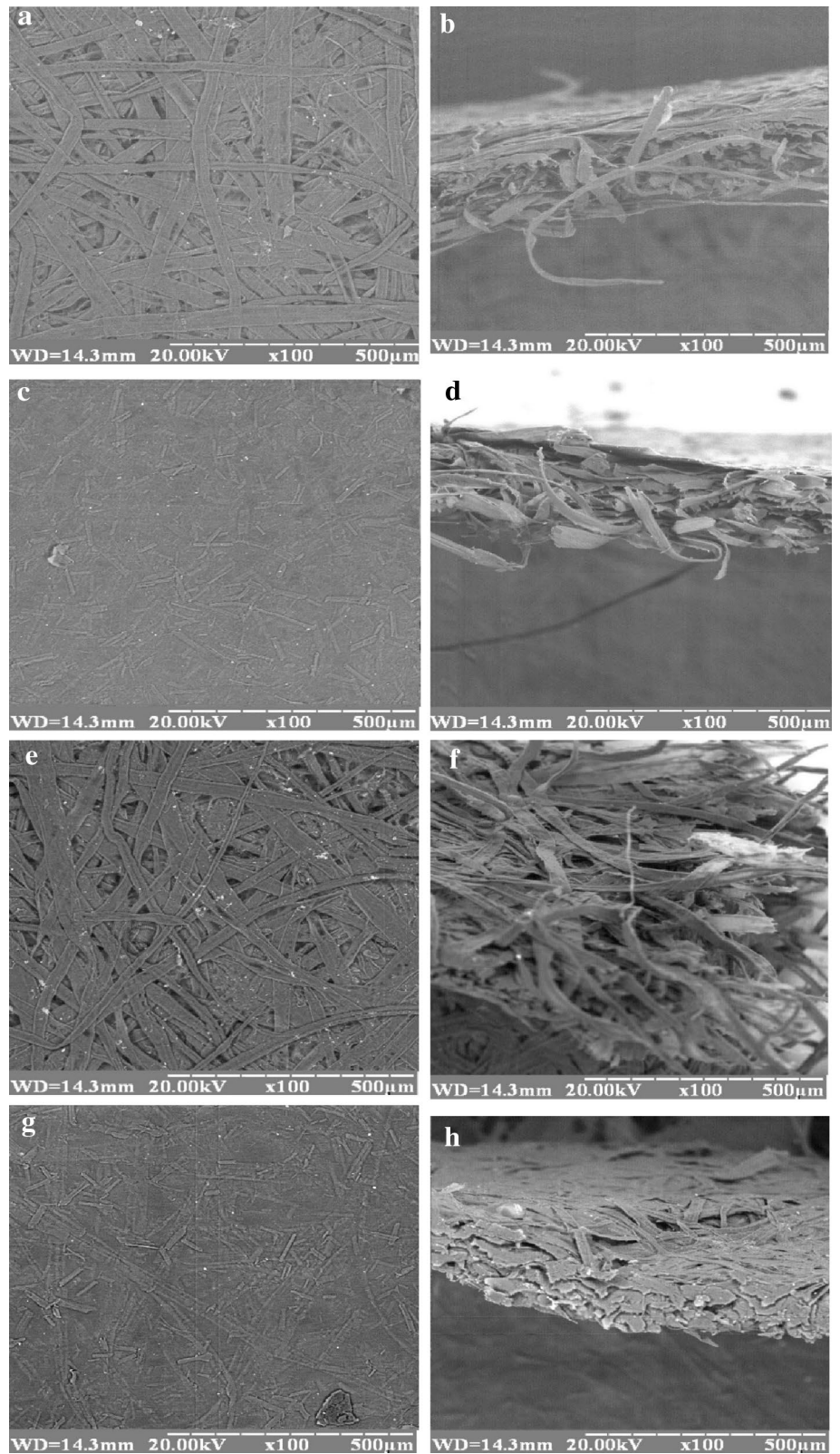
Fig. 6 a–d Dependences of the properties of paper from waste paper (I) and unbleached pulp (II) on the consumption of nanocellulose a Tear resistance, b Elongation, c Breaking force, d Water absorption, Cobb30, *line of standard requirements

requirements of the standard. However, even a small amount of nanocellulose (1 g/m²) makes it possible to achieve values of paper for bags that meet the standards. The application of nanocellulose to the surface of the paper with a consumption of 3 g/m² increases the tear resistance by 57% and 60% for papers made from unbleached pulp and waste paper, respectively. At the same time, the elongation for paper from unbleached pulp and waste paper is increased by 78% and 140% and breaking strength—36% and 10%, respectively. The application of nanocellulose to the surface reduces the water absorption of paper made from unbleached pulp and waste paper by approximately the same values—by 88% and 80%, respectively.

The use of nanocellulose makes paper stronger because the nanocellulose particles fill the empty space between fibers, thereby increasing the number of fiber–fiber bonds and, as a result, boost the hydrogen bonds during consolidation and drying of the fiber network [12, 30]. These conclusions are confirmed by SEM images of the surface and cross-section of paper samples made from unbleached pulp and from waste paper with and without the application of nanocellulose on its surface (Fig. 7).

The data in Fig. 7a shows that the surface of the paper without applying of nanocellulose has a porous structure, the fibers are long and clearly expressed. The surface coating by nanocellulose suspension (Fig. 7c) contributes to a reduction of porosity of paper. In this case, the surface becomes more uniform and smooth. There is a decrease in the number of pores between layers and an increase in the density of paper. As seen in the cross-sectional view of paper (Fig. 7b), spun fibers are placed in paper layers with a loose structure and cavities between them. When a nanocellulose suspension is applied to the surface (Fig. 7c, d), the density of the surface layer of paper increases. This a priori indicates an improvement in the physical–mechanical and barrier properties of this nanocomposite material. Thus, the use of nanocellulose with a consumption of 3 g/m² allows to obtain samples of paper with indicators that meet the requirements of the standard (Fig. 6). A similar pattern is observed when nanocellulose is applied to the surface of waste paper castings (Fig. 7e, f). Figure 7 shows that the sulfate cellulose fibers have a smoother surface and a more uniform length unlike waste paper. On the surface of the waste paper castings with nanocellulose application and without other inclusions (fillers, minerals) can

Fig. 7 CEM images of the surface (left side) and cross-section (right side) of paper samples made from unbleached pulp (**a–d**) and from waste paper (**e–h**) with a surface coating of nanocellulose (**c, d, g, h**) and uncoated (**a, b, e, f**)



be observed. They prevent the formation of more dense packing of fibers. Waste castings are also characterized by impregnation of nanocellulose into the mass and bonding of fibers.

Nanocellulose particles are located in the space between the fibers in the surface layer of paper for bags, act as a binding agent, thereby increasing the number of fiber–fiber bonds through a complex network, increasing the strength of the hydrogen bonds and making the paper more durable. Authors of a number of articles [24, 41] also note an improvement in the strength and barrier properties of paper using nanocellulose due to the formation of additional hydrogen bonds.

We can argue that the use of nanocellulose allows the use of waste paper as a raw material for the manufacture of paper for bags. Thus, nanocellulose improves quality indicators of paper and exhibits properties not only as a reinforcing additive, but also as a hydrophobic substance. This will replace the more expensive sulphate unbleached pulp and reduce the cost of production.

4 Conclusion

The organosolv pulp from *Miscanthus × giganteus* was prepared by the environmentally safer organosolv method—cooking in a solution of peracetic acid and alkaline treatment at low temperature 96 ± 1 °C. The organosolv miscanthus pulp (OMP) had a high degree of whiteness up to 85%, traces of non-cellulosic substances and was used to prepare nanocellulose. The results of hydrolysis of never dried cellulose with a solution of sulfuric acid with a concentration of 43 and 50% followed by ultrasonic treatment of nanocellulose, are presented. The structural changes and crystallinity of OMP and nanocellulose were studied by SEM and FTIR techniques. XRD analysis confirmed the increase of crystallinity of the OMP and nanocellulose as a result of thermochemical treatment. We report that nanocellulose has a density up to 1.6 g/cm^3 , transparency up to 82%, crystallinity up to 76.5% and tensile strength up to 195 MPa. Using AFM microscopy, it was found that nanocellulose has a particle diameter in the range from 10 to 20 nm. Thermogravimetric analysis confirmed that nanocellulose films have a more dense structure and smaller mass loss in the temperature range 320–440 °C compared with OMP. Samples have final degradation temperature of about 440 °C for OMP and 500 °C for OMP after alkaline treatment, but for nanocellulose films the final decomposition is observed at a temperature of 540 °C. We established the positive effect of nanocellulose application on the physical and mechanical properties of paper for bags. The application of nanocellulose from *Miscanthus × giganteus* allows replacing synthetic reinforcing materials and

more expensive sulfate unbleached pulp with waste paper in the production of paper and cardboard.

Acknowledgements This work was funded by Ministry of Education and Science of Ukraine, under project no. 2002.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Abdul Khalil HPS, Bhat AH, Ireana Yusra AF (2012) Green composites from sustainable cellulose nanofibrils: a review. *Carbohydr Polym* 87:963–979. <https://doi.org/10.1016/j.carbpol.2011.08.078>
2. Barbash V, Poyda V, Deykun I (2011) Peracetic acid pulp from annual plants. *Cellul Chem Technol* 45(9–10):613–618. [http://www.cellulosechemtechnol.ro/pdf/CCT45_9-10\(2011\)/p.613-618.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT45_9-10(2011)/p.613-618.pdf)
3. Barbash V, Trembus I, Nagorna J (2012) Pulp obtaining from corn stalks. *Chem @ Chem Technol* 6(1):83–87. http://science2016.lp.edu.ua/sites/default/files/Full_text_of_%20papers/full_text_439.pdf
4. Barbash V, Trembus I, Shevchenko V (2014) Ammonia-sulfite-ethanol pulp from wheat straw. *Cellul Chem Technol* 48(3–4):345–353. [http://www.cellulosechemtechnol.ro/pdf/CCT3-4\(2014\)/p.345-353.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT3-4(2014)/p.345-353.pdf)
5. Barbash VA, Yaschenko OV (2015) Obtaining of straw pulp in isobutanol medium. *Naukovi Visti NTUU KPI* 6:80–86. <http://bulletin.kpi.ua/article/view/51145/67710>
6. Barbash VA, Yaschenko OV, Alushkin SV, Kondratyuk AS, Posudievsky OY, Koshechko VG (2016) The effect of mechanochemical treatment of cellulose on characteristics of nanocellulose films. *Nanoscale Res Lett* 11:410. <https://doi.org/10.1186/s11671-016-1632-1>
7. Barbash V, Yashchenko O, Kedrovskaya A (2017) Preparation and properties of nanocellulose from peracetic flax pulp. *JSRR* 16(1):1–10. <https://doi.org/10.9734/JSRR/2017/36571>
8. Barbash V, Trembus I, Sokolovska N. (2018a) Performic pulp from wheat straw. *Cellul Chem Technol* 52 (7–8):673–680. [http://www.cellulosechemtechnol.ro/pdf/CCT7-8\(2018\)/p.673-680.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT7-8(2018)/p.673-680.pdf)
9. Barbash VA, Yashchenko OV, Opolsky VO (2018) Effect of hydrolysis conditions of organosolv pulp from kenaf fibers on the physicochemical properties of the obtained nanocellulose. *Theor Exp Chem* 54:193–198. <https://doi.org/10.1007/s11237-018-9561-y>
10. Brosse N, Dufour A, Meng X, Sun Q, Ragauskas A (2012) *Miscanthus*: a fast-growing crop for biofuel and chemicals production. *Biofuels Bioprod Biorefining* 6(5):580–598. <https://doi.org/10.1002/bbb.1353>
11. Caridad R, Ligeró P, Bao M (2004) Formic acid delignification of *Miscanthus sinensis*. *Cell Chem Technol* 39:235–244
12. Charani PR, Moradian MN (2019) Utilization of cellulose nanofibers and cationic polymers to improve breaking length of paper. *Cellul Chem Technol* 53(7–8):767–774. <https://doi.org/10.35812/CelluloseChemTechnol.2019.53.75>
13. Chattopadhyay DP, Patel BH (2016) Synthesis, characterization and application of nano cellulose for enhanced performance of textiles. *J Text Sci Eng* 6:248. <https://doi.org/10.4172/2165-8064.1000248>

14. Correia VC, dos Santos V, Sain M, Santos SF, Leão AL, Junior HS (2016) Grinding process for the production of nanofibrillated cellulose based on unbleached and bleached bamboo organosolv pulp. *Cellulose* 23:2971–2987. <https://doi.org/10.1007/s10570-016-0996-9>
15. Cruz J, Fangueiro R (2016) Surface modification of natural fibers: a review. *Procedia Eng* 155:285–288
16. Cudjoe E, Hunsen M, Xue Z, Way AE et al (2017) *Miscanthus giganteus*: a commercially viable sustainable source of cellulose nanocrystals. *Carbohydr Polym* 155:230–241
17. Danielewicz D, Dybka-Stepien K, Surma-Slusarska B (2018) Processing of *Miscanthus × giganteus* stalks into various soda and kraft pulps. Part I: chemical composition, types of cells and pulping effects. *Cellulose* 25:6731–6744
18. Fall AB, Burman A, Wagberg L (2014) Cellulosic nanofibrils from eucalyptus, acacia and pine fibers. *Nord Pulp Paper Res J* 29(1):176–184
19. Hashaikeh R, Abushammala H (2011) Acid mediated networked cellulose: preparation and characterization. *Carbohydr Polym* 83:1088–1094
20. Ilyas RA, Sapuan SM, Ishak MR, Zainudin ES (2017) Effect of delignification on the physical, thermal, chemical, and structural properties of sugar palm fibre. *BioResources* 12(4):8734–8754
21. loelovich M (2017) Superposition of acid concentration and temperature at production of nanocrystalline cellulose particles. *J Chem Edu Res Prac* 1(1):1–6. <https://www.researchgate.net/publication/322021487>
22. Jasmani L, Thielemans W (2018) Preparation of nanocellulose and its potential application. *For Res* 7:222. <https://doi.org/10.4172/2168-9776.1000222>
23. Johnson DA, Paradis MA, Bilodeau M, Crossley B, Foulger M, Gélinas P (2016) Effects of cellulosic nanofibrils on papermaking properties of fine papers. *Tappi J* 15:395–402
24. Kumar V (2018) Roll-to-roll processing of nanocellulose into coatings. Dissertation, Åbo Akademi University
25. Lin N, Dufresne A (2014) Nanocellulose in biomedicine: current status and future prospect. *Eur Polym J* 59:302–325. <https://doi.org/10.1016/j.eurpolymj.2014.07.025>
26. Lee K-Y, Aitomaki Y, Berglund LA (2014) On the use of nanocellulose as reinforcement in polymer matrix composites. *Compos Sci Technol* 105:15–27
27. Ligeró P, Vega A, Villaverde JJ (2010) Delignification of *Miscanthus × giganteus* by the Milox process. *Biores Technol* 101(9):3188–3193
28. Luzi F, Torre L, Kenny LM, Puglia D (2019) Bio- and fossil-based polymeric blends and nanocomposites for packaging: structure-property relationship. *Materials* 12(3):471. <https://doi.org/10.3390/ma12030471>
29. McCracken A, Sadeghian P (2018) Corrugated cardboard core sandwich beams with bio-based flax fiber composite skins. *J Build Eng* 20:114–122. <https://doi.org/10.1016/j.jobbe.2018.07.009>
30. Mishra RK, Sabu A, Tiwari SK (2018) Materials chemistry and the futurist eco-friendly applications of nanocellulose: status and prospect. *J Saudi Chem Soc* 22:949–978. <https://doi.org/10.1016/j.jscs.2018.02.005>
31. Mondal S (2016) Preparation, properties and applications of nanocellulosic materials. *Carbohydr Polym*. <https://doi.org/10.1016/j.carbpol.2016.12.050>
32. Paschoal G, Muller CM, Carvalho GM, Tischera CA, Malia S (2015) Isolation and characterization of nanofibrillated cellulose from oat hulls. *Quim Nova* 38(4):478–482. <https://doi.org/10.5935/0100-4042.20150029>
33. Płażek A, Dubert F, Kopeć P, Krępski T (2015) In vitro-propagated *Miscanthus × giganteus* plants can be a source of diversity in terms of their chemical composition. *Biomass Bioenergy* 75:142–149
34. Poletto M, Júnior HLO, Zattera AJ (2014) Native Cellulose: structure, characterization and thermal properties. *Materials* 7:6105–6119. <https://doi.org/10.3390/ma7096105>
35. Reising AB, Moon RJ, Youngblood JP (2012) Effect of particle alignment on mechanical properties of neat cellulose nanocrystal films. *J Sci Technol For Prod Processes* 2(6):32–41
36. Roman M, Winter W (2004) Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules* 5(5):1671–1677
37. Sagar NA, Pareek S, Sharma S, Yahia EM, Lobo MG (2018) Fruit and vegetable waste: bioactive compounds, their extraction, and possible utilization. *Compr Rev Food Sci Food Saf* 17:512–531. <https://doi.org/10.1111/1541-4337.12330>
38. Sacui IA, Nieuwendaal RC, Burnett DJ, Stranick SJ et al (2014) 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* 6(9):6127–6138
39. TAPPI Test Methods (2004) TAPPI Test Methods. Tappi Press, Atlanta
40. Thomas B, Raj MC, Athira KB, Rubiyah MH, Joy J, Moores A, Drisko GL, Sanchez C (2018) Nanocellulose, a versatile green platform: from biosources to materials and their applications. *Chem Rev* 118(24):11575–11625
41. Viana LC, Potulski DC, Muniz GIB, Andrade AS, Silva EL (2018) Nanofibrillated cellulose as an additive for recycled paper. *CERNE* 24(2):140–148. <https://doi.org/10.1590/01047760201824022518>
42. Villaverde JJ, Ligeró P, De Vega A (2010) Formic and acetic acid as agents for a cleaner fractionation of *Miscanthus × giganteus*. *J Clean Prod* 18:395–401
43. Villaverde JJ, Ligeró P, Vega A (2015) Fractionation of *Miscanthus × Giganteus* via modification of the Formacell process. *Ind Crops Prod* 77:275–281

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.