Chapter 19
Preparation, Properties and Application of Miscanthus Nanocellulose as Coating Layer

V. A. Barbash, O. V. Yashchenko and O. A. Vasylieva

Abstract The data on the preparation of nanocellulose from organosolvent miscanthus pulp and its application as coating layer in the production of bag paper are reported. The influence of technological factors on the properties of nanocellulose films was determined. The obtained nanocellulose films had density up to 1.46 g/cm^3, transparency up to 80%, crystallinity degree up to 77% and tensile strength up to 70 MPa. The properties of nanocellulose films studied by means of electron absorption spectra, XRD and AFM methods. The bag paper with consumption of nanocellulose of 5 g/m^2 has mechanical properties of 12–68% higher and the elongation increases 2.9 times than paper without the use of surface treatment. The using of obtained nanocellulose as a coating layer exhibit great potential its application for improving fiber-based mechanical and barrier properties of paper and cardboard.

19.1 Background

In recent years, many studies have been conducted on the replacement of synthetic materials with natural substances. It is, in particular, concern to the production of nanocellulose and composite materials on its basis. Cellulose, as one of the most common natural polymers on Earth, is widely used for the production of bio-based nanoparticles. Nanocellulose has unique properties such as nanosized, renewable, low toxicity, biocompatibility, biodegradation, availability and low cost of raw material, which allows it to be used in multitude spheres [1, 2]. Nanocellulose is used in optoelectronics, in the production of chemical current of sources, sorbents, for reinforcement and improving the thermal stability of polymeric and paper composites [3, 4]. Nanocellulose has been incorporated into polymer matrices to produce reinforced composites with several tens to hundreds folds higher mechanical strength [5] as well

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A. D. Pogrebnjak and O. Bondar (eds.), *Microstructure and Properties of Micro- and Nanoscale Materials, Films, and Coatings (NAP 2019)*,
Springer Proceedings in Physics 240, https://doi.org/10.1007/978-981-15-1742-6_19

as enhanced optical transparency [6]. These specific characteristics of nanocellulose use to improve the mechanical or barrier properties of nanocomposites [7].

Nanocellulose usually are obtained by acid hydrolysis of pulp from wood and non-wood plants. The main raw material for the production of pulp in the world is wood. For countries that do not have large stocks of free wood, the development of alternative sources of pulp remains an urgent problem. Such sources of raw materials include various types of non-wood plant materials, in particular, Miscanthus x giganteus. The high yield of Miscanthus x giganteus makes it a promising crop for the production of bioenergy and biomaterials, including non-wood pulp [8].

There are few methods to make pulp from wood and non-wood plant materials with different environmental effects [9]. Organosolvent delignification has been suggested as an environmentally friendly process and an alternative method for pulp obtaining. Among organic solvents, acetic acid and hydrogen peroxide should be considered as potential agents for the delignification of plant raw materials. The cooking process, in this case, is carried out at a low temperature and in a relatively short time, which reduces energy costs [10].

Therefore, the purpose of this study is to obtain organosolvent pulp and nanocellulose from Miscanthus x giganteus, investigation their properties and application of nanocellulose as a coating layer for improving mechanical and barrier properties of paper and cardboard.

19.2 Methods

We have used the second year Miscanthus x giganteus biomass as starting. Before research, the miscanthus stalks were ground to 5–7 mm and stored in desiccator for maintenance of constant humidity and chemical composition. The chemical composition of miscanthus chips was determined according to TAPPI standards [11]: cellulose—49.7%; lignin—27.7%, resins, fats, waxes—1.8%; holocellulose—61.9%; ash—1.1% from mass of absolutely dry raw materials (a.d.m.).

The glacial acetic acid, hydrogen peroxide, sulfate acid, NaOH were purchased from Khimlaborreaktiv Ltd. (Ukraine). The reagents were chemically pure.

The preparation of nanocellulose from miscanthus was carried out in 3 stages. At the first stage, cooking was done. To this end, crushed miscanthus chips are loaded into a glass-flask, a cooking solution is added at a liquid to solid ratio of 10:1 containing glacial acetic acid and hydrogen peroxide at a concentration of 35% and a volume ratio of 70:30%, at a temperature of 95 ± 2 °C during 90 min. This cooking regime was determined optimally on the basis of previous studies [12]. In the second stage, the alkaline treatment of miscanthus pulp by the solution of NaOH concentration of 7% during 15–240 min, at the liquid to solid ratio 12:1 at temperature 95 ± 2 °C was carried out. The organosolvent miscanthus pulp (OMP) was washed with hot distilled water to a neutral pH. The quality parameters of the obtained OMP samples are determined according to standard methods [11].

In the third stage, hydrolysis of the obtained OMP was carried out. To obtain nanocellulose, hydrolysis of never dried OMP with a solution of sulfate acid with a concentration of 43 and 50% was carried out, at a liquid to solid ratio of 10:1, at a temperature of 40 and 60 °C for 30–90 min. The calculated amount of sulfuric acid with the corresponding concentration was slowly added into the flask with the cellulose suspension. The hydrolysis was carried out at a temperature of 40, 50 and 60 ± 1 °C. 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. The nanocellulose was rinsed with distilled water three times by means of centrifugation at 4000 rev/min and subsequent dialysis until reaching neutral pH. Ultrasonic processing of nanocellulose was carried out using an ultrasonic disintegrator UZDN-A (SELMI, Ukraine) from 22 kHz for 30, 45 and 60 min. The nanocellulose dispersion was placed in an ice bath to prevent overheating during treatment. Eventually, the suspension had the form of a homogenous gel-like dispersion.

The decrease of the size of the cellulose particles and the increase of its dispersity were assessed by measuring the changes in the dimensions of miscanthus pulp. Topographical characterization of nanocellulose samples was investigated using atomic force microscopy (AFM). The measurements were accomplished with Si cantilever, operating in the tapping mode on the device Solver Pro M (NT-MDT, Russia). The scanning speed and area were 0.6 line/s and $2 \times 2\ \mu m^2$, respectively. Before AFM investigation, dilute nanocellulose suspensions with a concentration of 0.01 wt% were ultrasonically treated for 10 min. Subsequently, one drop of nanocellulose dispersion for sample was injected onto a freshly cleaned glass-ceramic and air-dried at room temperature.

Transparency of the nanocellulose films was determined by electron absorption spectra, which were registered in regions from 200 to 1100 nm. Electron absorption spectra of the nanocellulose films in UV, visible and near-infrared regions were registered on two-beam spectrophotometer 4802 (UNICO, USA) with the resolution of 1 nm.

X-ray diffraction patterns of different cellulose samples were obtained by Ultima IV diffractometer (Rigaku, Japan). The method proposed in [13] was used to determine the crystallinity degree (CD) of the samples, in terms of which $CD = [(I200 - Iam)/I200] \times 100\%$, where I200 is an intensity of (200) reflex about 22.5°, and Iam is an intensity of amorphous scattering at 18.5°.

The mechanical properties of the nanocellulose films were measured at controlled temperature (23 ± 1 °C) and humidity (50 ± 2%) according to ISO 527-1. Breaking strength tests of nanocellulose films were performed at a crosshead speed of 0.5 mm/min on the TIRAtest-2151 (Germany) instrument equipment with 2-N load stress. For testing, test strips with 10 ± 2 mm width and 25 ± 5 mm long were used. Each composition was tested with a minimum of five specimens to extract an average and standard deviation for each property.

A nanocellulose suspension was applied directly to the paper samples using a coating process. Samples of bag paper were made from sulfate unbleached pulp according to standard procedures. A layer of nanocellulose was applied to received samples of paper with the consumption of nanocellulose from 1 to 5 g/m^2 on each side. Each sample of paper was kept at a temperature of 23 °C and relative humidity of 50% for at least 24 h before determining its properties. All characteristics of the paper have been determined in accordance with the standards of TAPPI [11].

19.3 Results and Discussion

The results of the peracetic cooking of miscanthus pulp showed that an increase in the duration of cooking naturally leads to a decrease in the yield of pulp and the residual content of lignin and mineral substances in it. Therefore, to remove lignin and minerals from organosolvent pulp, it was alkaline treated with NaOH solution. For alkaline treatment, pulp from Miscanthus x giganteus was used after cooking for 90 min. Dependences of properties of organosolvent miscanthus pulp on the duration of alkaline treatment are shown in Table 19.1.

As can be seen from Table 19.1, increasing the duration of alkaline treatment leads to a monotonous decrease in the yield of OMP, the residual content of lignin and the ash content. From the obtained results it can be seen that alkaline treatment of more than 60 min does not significantly reduce the content of lignin and ash. Therefore, to obtain nanocellulose, cellulose from miscanthus was used after organosolvent cooking for 90 min and alkaline treatment with a duration of 60 min with minimum content of lignin (0.08%) and mineral substances (0.07%).

In previous studies, the process of hydrolysis of pulp from non-wood plants has been shown that the action of a solution of sulfate acid at a concentration of 64% leads to almost complete dissolution of the nanocellulose from flax fibers [12], wheat straw [14] and kenaf fibers [15]. When the acid acts at a concentration of 50%, a low yield of nanocellulose (about 10%) is observed. In the case of a 43% solution of $H2SO_4$, the yield of nanocellulose was 25–30%. Therefore, under these conditions, further studies on the production of nanocellulose from OMP have been carried out.

In this case, the effect of the hydrolysis by acid at a concentration of 43 and 50%, temperature is from 40 to 60 °C, the duration from 30 to 90 min and the duration of ultrasonic treatment from 30 to 60 min on the quality indexes nanocellulose films was determined. The influence of the duration of the hydrolysis process by acid H2SO4

Table 19.1 Properties of organosolvent miscanthus pulp after alkaline treatment, % from mass of a.d.m

Duration of treatment (min)	Yield OMP	Residual lignin	Ash
15	72.3	0.19	0.13
30	67.0	0.13	0.12
45	64.2	0.10	0.09
60	55.5	0.08	0.07
120	54.7	0.04	0.06
240	51.0	0.01	0.05

concentration 50% at 60 °C and the duration of ultrasonic treatment on the properties of the nanocellulosic films are shown in Fig. 19.1.

From Fig. 19.1 it can be seen that with increasing prolonged hydrolysis and ultrasonic treatment, all the investigated parameters of nanocellulose films are improved. This is due to the fact that in the process of hydrolysis the amorphous part of the macromolecule of the cellulose begins to rise and thereby increases the percentage of the crystalline part. To confirm this, the crystallinity degree (CD) of the miscanthus stems and various samples of organosolvent miscanthus pulp was determined on the basis of the processing of X-ray diffraction patterns (Fig. 19.2).

The analysis of X-ray investigated diffraction patterns showed increasing of crystallinity degree as a result of thermochemical stages of miscanthus stalks treatment.

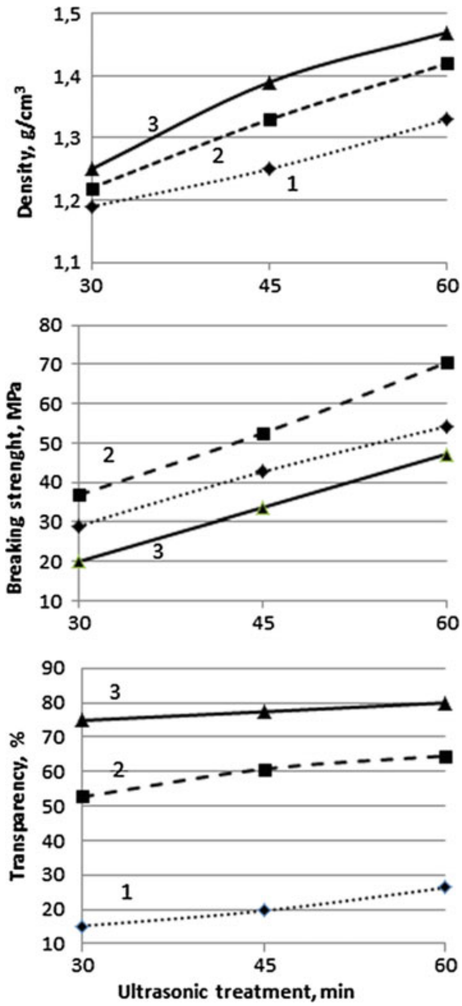
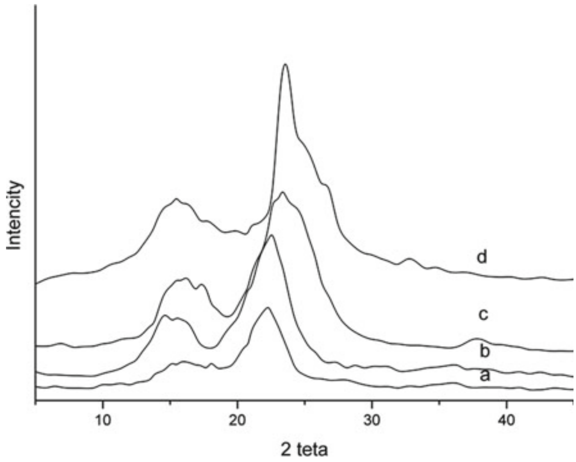


Fig. 19.1 The dependences of density (**a**), transparency (**b**) and tensile strength (**c**) of nanocellulose films on the duration of ultrasonic treatment after hydrolysis of OMP for different duration: 30 min (1), 60 min (2) and 90 min (3)

Fig. 19.2 X-ray diffraction patterns of miscanthus stalks (**a**), OMP (**b**), OMP after further alkaline treatment (**c**) and nanocellulose (**d**)



The crystallinity degree of miscanthus stalks was 64.7%, CD of pulp after peracetic cooking was 68.8%, and further alkaline treatment increases the crystallinity degree of OMP to 75.5% and the CD after hydrolysis was up to 77.0%.

From the obtained data (Fig. 19.1) it also follows that an increase in the action of ultrasonic treatment contributes to the grinding of cellulose nanoparticles, which leads to an increase in their density. Ultrasonic treatment also contributes to the process of obtaining a homogeneous suspension of nanocellulose, which increases the transparency and mechanical properties of the obtained particles of nanocellulose from OMP.

Topographical characterization AFM of organosolvent miscanthus nanocellulose and its 3D projection with a definition of sample height are presented in Fig. 19.3. In Fig. 19.3a shows the surface section of layer of forming nanocellulose aggregates. The diameter of separate nanoparticles is within the range to 20 nm and possibly much less since the image is obtained from nanocellulose particles located not in one layer. Therefore, can propose, that nanocellulose forms a film on the surface of the silicon substrate due to bonds between the nanocellulose particles.

In Table 19.2, the properties of bag paper with different nanocellulose consumption are presented. As can be seen from the data in Table 19.2, deposition of the nanocellulose mixture on the paper surface gives an increase in the physic-mechanical parameters of the bag paper. From the data obtained it follows that the application of the nanocellulose layer on the surface of the bag paper naturally increases its mechanical properties. When applied to the surface of the paper 5 g/m^2 of nanocellulose, the tear resistance of the samples increases by 68%, and the elongation increases 2.9 times.

At the same time, the breaking force and burst resistance of bag paper increase by 12% and 14%, respectively. The surface application of nanocellulose leads to a decrease in the surface water absorption (Cobb30) of samples from 136 to 62 g, which indicates the formation of a dense film on the surface of the casting. The

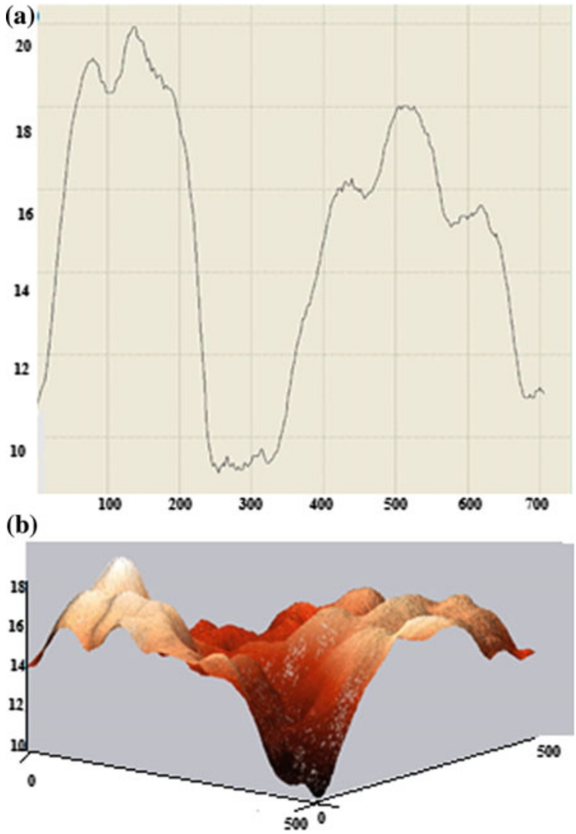


Fig. 19.3 The AFM images of the surface section of a layer of the nanocellulose (**a**) and 3D projection with a definition of sample height (**b**) tapping mode (values are in nm)

Table 19.2 Properties of bag paper with different nanocellulose consumption

Indicators	Nanocellulose Consumption (g/m^2)					
	1	2	3	4	5	6
Tear resistance, MN	890	1050	1200	1300	1400	1500
Burst resistance, MPa	523	533	560	570	580	600
Breaking strength, N	81	82	84	86	88	91
Elongation, %	1.6	2.5	3.2	3.7	4.2	4.6
Water adsorption, Cobb30, g	136	110	97	76	69	62

obtained values of the indicators exceed the requirements of standards for bag paper and confirm the possibility of using nanocellulose to improve the properties of paper and cardboard.

19.4 Conclusions

The organosolvent pulp from Miscanthus x giganteus was obtained in an environmentally safe method—by cooking in a solution of peracetic acid, followed by alkaline treatment. The obtained OMP had a minimum content of lignin (0.08%) and mineral substances (0.07%) and was used to prepare of nanocellulose.

The obtained miscanthus nanocellulose had a degree of crystallinity 77%, particles with diameter less than 20 nm; the transparency of received films is up 80%, and the breaking strength up to 70 MPa. Such indicators of nanocellulose from miscanthus are close to the values of nanocellulose obtained from other kinds of non-wood plant raw materials—wheat straw, flax fibers and kenaf [12, 14, 15].

The obtained miscanthus nanocellulose exhibit great potential its application in the paper industry—it can be used as a coating layer for improving fiber-based mechanical and barrier properties of paper and cardboard.

Acknowledgements The authors wish to thanks the Ministry of Education and Science of Ukraine for the finance support this work.

References

1. B. Deepa, E. Abraham, N. Cordeiro, M. Mozetic, A.P. Mathew, K. Oksman, M. Faria, S. Thomas, L.A. Pothan, Cellulose **22**, 1075 (2015)
2. K. Uetani, T. Okada, H.T. Oyama, J. Mater. Chem. C **4**, 9697 (2016)
3. S. Thiemann, S.J. Sachnov, F. Pettersson, R. Bollström, R. Österbacka, P. Wasserscheid, J. Zaumseil, Adv. Func. Mater. **24**, 625 (2014)
4. A.M. Adel, A.A. El-Gendy, M.A. Diab, R.E. Abou-Zeid, W.K. El-Zawawy, A. Dufresne, Ind. Crops Prod. **93**, 161 (2016)
5. J. Luo, H. Chang, A.A.B. Davijani, H.C. Liu, P.-H. Wang, R.J. Moon, S. Kumar, Cellulose **24**, 1745 (2017)
6. Y. Su, Y. Zhao, H. Zhang, X. Feng, L. Shi, J. Fang, J. Mater. Chem. C **5**, 573 (2017)
7. K.-Y. Lee, Y. Aitomaki, L.A. Berglund, K. Oksman, A. Bismarck, Compos Sci Technol. **105**, 15 (2014)
8. O. Daraban, Ș. Jurcoane, Sci. Pap. Agron. UASVM Iași **58**(2), 185 (2015)
9. X.J. Pan, D. Xie, R.W. Yu, D. Lam, J.N. Saddler, Ind. Eng. Chem. Res. **46**(8), 2609 (2007)
10. A. Ferraz, J. Rodriguez, J. Freer, J. Baeza, J. Chem. Technol. Biotechnol. **75**(12), 1190 (2000)
11. *TAPPI Test Methods* (Tappi Press, Atlanta, Georgia, 2004)
12. V.A. Barbash, O.V. Yashchenko, A.N. Kedrovska, J. Sci. Res. Rep. **16**(1), 1 (2017)
13. L.A. Costa, A.F. Fonseca, F.V. Pereira, J.I. Druzian, Cell Chem Technol. **49**, 127 (2015)
14. V.A. Barbash, O.V. Yaschenko, O.M. Shniruk, Dig. Nanoscale Res. Lett. **12**, 241 (2017)
15. V.A. Barbash, O.V. Yashchenko, V.O. Opolsky, Theor. Exp. Chem. **54**(3), 193 (2018)