



Preparation and Properties of Nanocellulose from Peracetic Flax Pulp

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Authors' contributions

This work was carried out in collaboration between all authors. Author VB planned the study, interpreted the experimental data and drafted the manuscript. Author OY carried out its hydrolysis, prepared the nanocellulose films and analyzed their physical and mechanical characteristics, investigated TEM, AFM and TGA images. Author AK obtained the organosolv flax pulp and carried out the ultrasound treatment of nanocellulose suspension. All authors read and approved the final manuscript.

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ABSTRACT

The aim of the study was to obtain a pulp by ecology safer method from flax fibers and nanocellulose from organosolvent flax pulp (OFP) by acid hydrolysis and to investigate of its quality indexes. The OFP has been obtained by cooking in solution of peracetic acid. For obtaining of nanocellulose the hydrolysis of OFP by sulfuric acid with concentration of 43%, 50% and 64% at temperature 30 - 60°C during 30 and 90 min was carried out. The hydrolyzed OFP was washed by many times centrifugation at 8000 rev/min with distilled water until reaching neutral pH. Further ultrasonic treatment of the nanocellulose suspension from 30 to 60 minutes facilitated the formation of a nanocellulose gel, which was dried on Petri dishes to obtain transparent films. The optimal parameters of hydrolysis process are: concentration of sulfuric acid – 43%, temperature - 60°C duration 60 min. The obtained peracetic flax nanocellulose had degree of crystallinity – 62%, particles with diameter less than 60 nm, which is confirmed by AFM data; the transparency of received films was determined by electron absorption spectra and is more than 60%; the tensile strength up to 70 MPa and Young's module up to 9,0 GPa. The obtained nanocellulose had highest thermal stability compared to the OFP, which established by TGA. The method of obtaining

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peracetic flax nanocellulose allows obtaining a product with high quality indexes, which can be used in the production of different composite materials and optoelectronics. These predictors, however, need further work to validate reliability.

Keywords: Flax fibre; organosolvent flax pulp; nanocellulose; acid hydrolysis.

1. INTRODUCTION

In recent years, many studies have been conducted on the replacement of synthetic materials with natural substances. It is, in particular, concern to production of nanocellulose and composite materials on its basis [1–3]. Nanocellulose has unique properties such as nanosize, renewable, low toxicity, biocompatibility, bio-degradation, availability and low cost of raw material, which allows it to be used in multitude spheres [4]. Nanocellulose broadly includes cellulose nanofibrils, cellulose nanocrystals and bacterial nanocellulose. They have been incorporated into polymer matrices to produce reinforced composites with several tens to hundreds times higher mechanical strength [5] as well as enhanced optical transparency [6]. Nanocellulose materials are used in optoelectronics, in the production of chemical current of sources, sorbents, for reinforcement and improving the thermal stability of polymeric and paper composites [7–9].

Nanocellulose is prepared by mechanical, chemical, and enzymatic methods. Mechanical methods require significant energy consumption for reducing the size of the natural cellulose fibers to nanoscale. Spence et al. have shown that the homogenization process is the most expensive method for the nanomaterial isolation [10]. Enzymatic methods generate nanocellulose through the biosynthesis from monosaccharides or fermentation of the cellulose fibers. The enzymatic methods are time-consuming and require expensive reagents [11]. Chemical methods are based on the cleavage of $\beta(1\rightarrow4)$ linked D-glucose units of the cellulose and an isolation of the cellulose nanocrystals eliminating the amorphous cellulose part [12]. Therefore, chemical methods for obtaining nanocellulose remain the most common.

In the pulp and paper industry the traditional cellulose production methods are sulfate and sulfite, which remain the main pollutants in the industry. From an environmental point of view, cooking of pulp in different organic solutions is safer. It is the so-called organosolvent methods of delignification. In particular, as the main

delignification reagent of the cooking solution is widely used peracetic acid, which is formed in the process of interaction of hydrogen peroxide and acetic acid [13].

The pulp can be obtained from a broad range of natural cellulose-containing sources including wood and non-wood plant raw materials. The main raw material for the production of cellulose in the world is wood. For countries that do not have large stocks of free wood the search for alternative sources of cellulose, which includes non-wood plant raw materials, remains an urgent problem.

The method of nanocellulose obtaining from cotton [14], kenaf [15], rice husk [16], wheat straw [17], flax stalks [18] by the acid hydrolysis are known. Flax fibers can be used as an alternative to cotton and wood cellulose. Therefore, the purpose of this study is to obtain organosolvent pulp and nanocelulose from flax fiber and investigation their properties.

2. MATERIALS AND METHODS

The flax fiber harvested in 2016 from the Chernigov's region (Ukraine) was investigated. Before research, the raw material was ground to 5–7 mm and stored in desiccator for maintenance of constant humidity and chemical composition. The chemical composition of flax fibers was determined according to TAPPI standards [19]: cellulose – 78,1%; lignin – 12,5%; resins, fats, waxes - 3,5%; pentosans – 2,9%; ash – 3,1% from absolutely dry raw materials (a.d.r.m.)

Cooking of flax pulp was carried out in two stages. At the first stage, treatment of flax fiber 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 $95 \pm 2^\circ\text{C}$ during 60 - 240 min was carried out. This cooking regime was determined optimally based on previous studies [13].

At the second stage, the alkaline treatment of flax pulp by solution of NaOH concentration of 20% during 60 min at the liquid to solid ratio 12:1

was carried out. The organosolvent flax pulp (OFP) was washed with hot distilled water to a neutral pH. The quality parameters of the obtained OFP samples are determined according to standard methods [19].

Hydrolysis of the never-dried OFP was carried out by solution of sulfuric acid with concentration of 43, 50 and 64%, at the liquid to solid ratio 10:1, at temperature 30 and 60°C during 30 – 90 min to obtain of nanocellulose. The calculated amount of sulfuric acid with the corresponding concentration was slowly added into the flask with the cellulose suspension, and the required volume of the acid with concentration above 50% was added drop-wise. The temperature of the reaction was maintained in the range from 20 ± 1 to $60 \pm 3^\circ\text{C}$. 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 hydrolyzed cellulose was rinsed with distilled water three times by means of centrifugation at 8000 rev/min and subsequent dialysis until reaching neutral pH. Ultrasound treatment of hydrolyzed cellulose with concentration 0,5% was performed using ultrasound disintegrator UZDN-A (SELMI, Ukraine) with 22 kGz for 30 to 60 min. The cellulose 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 next instrumental methods of analysis of plant raw material, OFP and nanocellulose have been used. The decrease of the cellulose particles size and the increase of its dispersity were assessed by measuring the changes in the degree of polymerization. It was determined according to ISO 5351 by the viscosity of the samples dissolved in copper ethylene-diamine solution.

Scanning electron microscope (SEM) analysis was performed with PEM-106I (SELMI, Ukraine) microscope to observe the morphology of OFP and nanocellulose films. 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 $2 \times 2 \mu\text{m}^2$, respectively. Before AFM investigation, dilute nanocellulose suspensions with the 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 and in visible and near infrared regions were registered on two-beam spectrophotometer 4802 (UNICO, USA) with resolution of 1 nm.

X-ray diffraction patterns of different cellulose samples were obtained by Ultima IV diffractometer (Rigaku, Japan). The method proposed in [20] was used to determine the crystallinity degree (CD) of the samples, in terms of which $CD = [(I_{200} - I_{am})/I_{200}] \cdot 100\%$, where I_{200} is an intensity of (200) reflex about 22.5° ; and I_{am} is an intensity of amorphous scattering at 18.5° .

The thermal degradation behavior of OFP and nanocellulose samples was explored by heating using Netzsch STA-409 thermoanalyzer. The samples were heated at a rate of $5^\circ\text{C}/\text{min}$, from 25 to 450°C . The thickness and density of nanocellulose films were determined according to the ISO 534:1988.

Tensile properties of the nanocellulose films were measured at controlled temperature ($23 \pm 1^\circ\text{C}$) and humidity ($50 \pm 2\%$) according to ISO 527-1. Tension tests were performed at a crosshead speed of 0.5 mm/min on the TIRAtest-2151 (Germany) instrument equipment with a 2-N load stress. For testing, test strips with 10 ± 2 mm width and 25 ± 5 mm long were used. The data reported are tensile strength and Young's modulus. Each composition was tested with a minimum of five specimens to extract an average and standard deviation for each property.

3. RESULTS AND DISCUSSION

In results of peracetic cooking was found, that the main part of non-cellulosic components is removed from flax fibers during the first hour of the delignification process. In this case, the content of ash and lignin in the resulting OFP decreases by 90%. Further cooking does not contribute to the removal of minerals and lignin, on the contrary, their percentage content is increased due to the hydrolysis and dissolution of the carbohydrates in the acidic medium, which is confirmed by the OFP degree of polymerization.

Increasing the cooking time leads to the destruction of cellulose fibers and the reduction of their length. Thus, the OFP degree of polymerization is linearly reduced from 670 to 340 at 1 and 4 hours of cooking, respectively. To reduce the content of residual lignin and other non-cellulosic components, alkaline treatment of OFP was carried out at 60 min. Studies have shown that additional alkaline treatment helps to remove mineral substances and lignin from OFP. Thus, the treatment of OFP with a solution of NaOH at a concentration of 20% for 60 min reduces the content of lignin to 0.015%, and the residual content of mineral substances to 0.04% from mass a.d.r.m. This OFP was used for obtaining nanocellulose.

Previous studies have shown the efficiency of using of sulfate acid at a concentration of 43% for the production of organosolvent straw nanocellulose [17]. Therefore, under these conditions, further studies on the production of nanocellulose from OFP have been carried out. In this case, the effect of the hydrolysis temperature is from 30 to 60°C, the duration from 30 to 90 min. and the duration of ultrasonic treatment from 30 to 60 min on the quality indices nanocellulose was determined. Results of hydrolysis of the OFP are presented in Table 1.

The investigations of the influence of the hydrolysis temperature have shown that the optimum conditions for obtaining nanocellulose are at temperature of 60°C. The destruction of cellulose fibers with increasing of hydrolysis duration from 30 to 90 minutes, leads to the production of films with lower strength and density (Table 1).

In addition, studies on the effect of the duration of ultrasonic treatment showed that the formation of a homogeneous nanocellulose suspension at a concentration of 0.5% occurs in 30 minutes. A further increase in the duration of ultrasound action contributes to increasing the transparency of the nanocellulose suspension and reducing viscosity, indicating a decrease in the size of cellulose fibers. Therefore, increasing the duration of ultrasonic treatment improves the quality of nanocellulose films: the tensile strength increases from 50 to 70 MPa, Young's module from 6,3 to 9,0 GPa, the density - from 1,2 to 1,37 g/cm³, and transparency - from 40 to 60% (Fig. 1).

The samples of nanocellulose obtained by hydrolysis of 50 % H₂SO₄ have lower indexes of quality in comparison with the samples after hydrolysis with 43% acid. Increasing of the duration of ultrasonic treatment for a suspension of nanocellulose after 90 minutes of hydrolysis is not indicative of the possibility of forming films, since they are cracked on individual crystals. The tensile strength and Young's modulus of these films are reduced to 30 MPa and 3.8 GPa, respectively.

It was observed, that the hydrolysis of OFP at high concentration of sulfate acid of 64% at a temperature of 30 - 60°C for duration of 30 - 60 min, leads to the complete destruction of cellulose, because the acid actively reacts with cellulose and dissolves it to monosaccharides, the solution becomes brown color. The obtained nanocellulose films from OFP have a density up to 1.3 g/cm³, a tensile strength = 70 MPa, and a transparency of up to 60% in the visible region of the spectrum.

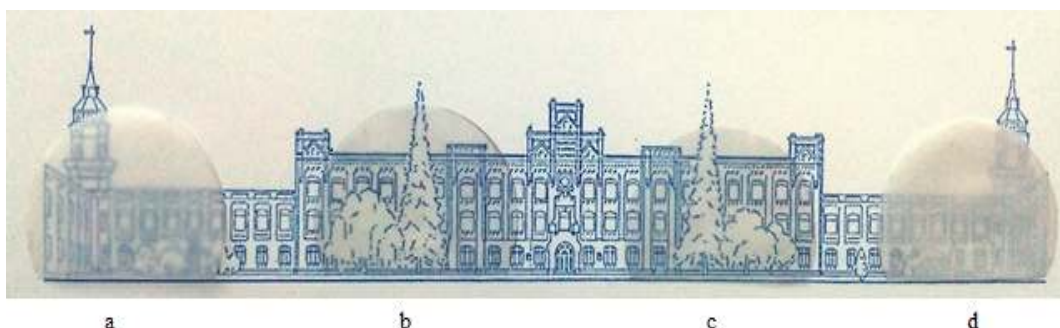


Fig. 1 Comparison of transparent nanocellulose samples made from OFP after hydrolysis by sulfate acid of concentration 43% at temperature 60 °C and ultrasound treatment 30 (a), 45 (b), 60 (c) min and after hydrolysis by sulfate acid of concentration 50 % at temperature 30 °C and ultrasound treatment 45 min (d).

Table 1. Indexes of quality of nanocellulose films

Temperature, °C	Duration of hydrolysis, min	Duration of ultrasound treatment, min	Indexes of quality of nanocellulose films				
			Thick-ness, µm	Density, g/cm ³	Tensile strength, MPa	Young's module, GPa	Transparency, %
H₂SO₄ concentration – 43 %							
60	30	30	35	1,20±0,040	50±0,43	6,4±0,031	40
		45	30	1,20±0,036	57±0,36	7,3±0,045	45
		60	30	1,37±0,042	70±0,50	9,0±0,059	57
	90	30	20	1,15±0,051	50±0,40	6,4±0,067	42
		45	25	1,20±0,064	60±0,38	7,7±0,084	51
		60	25	1,20±0,045	65±0,29	8,4±0,097	60
H₂SO₄ concentration – 50 %							
30	30	30	20	1,10±0,043	45±0,49	5,9±0,058	-
		45	15	1,20±0,045	53±0,50	6,8±0,073	-
		60	15	1,30±0,051	59±0,46	7,6±0,042	-
	90	30	20	1,00±0,039	30±0,38	3,8±0,041	-
		45	20	1,10±0,041	-	-	-
		60	20	1,10±0,047	-	-	-

Changing the structure of the raw material in process of chemical-thermal treatment is investigated by scanning electron microscopy; the results are shown in Fig. 2.

As shown Fig. 2 the flax fibers have a fibrous structure, fibers are homogeneous, long, and the surface is smooth. During the cooking process, the fibers are shortened and their cross-sectional dimensions reduced, due to the removal of lignin, mineral and extractive substances from plant raw materials. The widths of flax fibers are more than 20 microns and after peracetic cooking and alkaline treatment are 20 and 10 microns, respectively (Fig. 2b). The length of flax fibers varies and reaches several millimeters. With subsequent alkaline treatment there is a deep removal of non-cellulosic fiber constituents, they have a uniform size and width, up to 10 microns (Fig. 2c). Nanocellulose film has a homogeneous structure with undifferentiated fiber sizes (Fig. 2d).

Topographical characterization of AFM of organosolvent flax nanocellulose and its 3D projection with definition of sample height are presented Figs. 3a and 3b respectively. In Fig. 3a shows a network of cellulose nanofibers of flax forming aggregates. The diameter and length of the nanocellulose fibers are less than 60 nm. The diameter of separate nanofibers is within the range to 60 nm and possibly much less, since the image is obtained from fibers of nanocellulose located not in one layer. This is explained by the fact that nanocellulose forms a dense film due to the bonds between its molecules on the surface of the silicon substrate.

Further, the change in the ratio of amorphous and crystalline parts of flax fibrils during its chemical and physical treatment was also investigated. These changes in the degree of crystallinity of the obtained cellulose samples were investigated by X-ray diffraction analysis (Fig. 4). Several different crystalline structures of

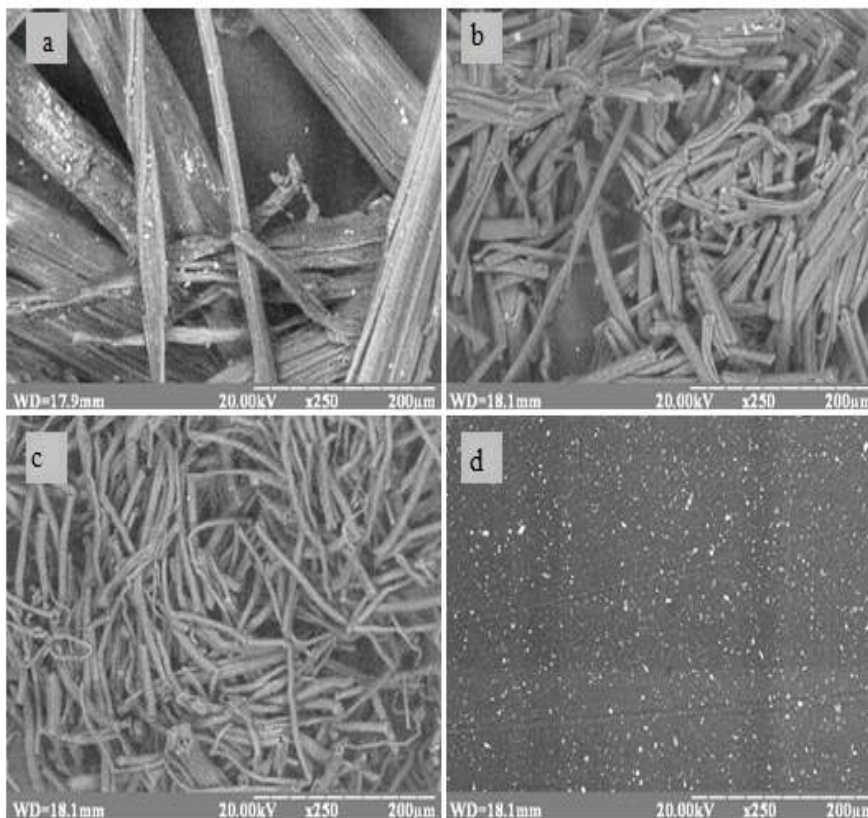


Fig. 2 SEM images of flax fibers (a), pulp after peracetic cooking (b), pulp after additive alkaline treatment (c), nanocellulose film (d)

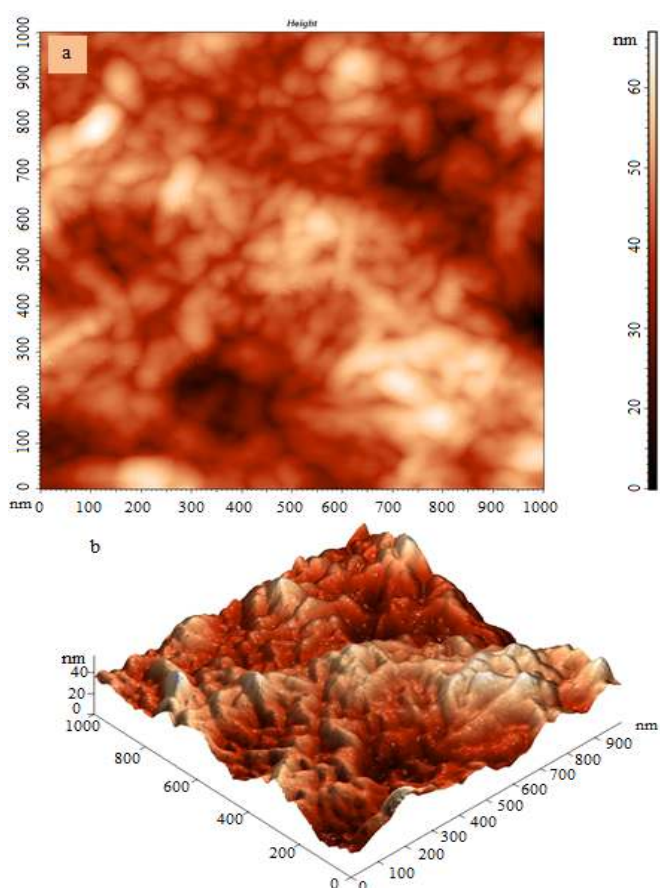


Fig. 3 The AFM images of organosolvent flax nanocellulose film (a) and 3D projection with definition of sample height (b) tapping mode

cellulose are known, corresponding to the location of hydrogen bonds between and within strands. Natural cellulose is cellulose I. Cellulose II is formed from cellulose I during alkaline treatment with high alkaline concentration. The conversion of cellulose I to cellulose II is irreversible, suggesting that cellulose I is metastable and cellulose II is stable. With various chemical treatments it is possible to produce the structures cellulose III and cellulose IV. The transformation of cellulose I into cellulose II can be traced on X-ray diffractograms.

The analysis of X-ray diffraction patterns of flax fiber (Fig. 4a), pulp after peracetic cooking (Fig. 4b), pulp after additive alkaline treatment 20% NaOH (Fig. 4c), and nanocellulose film (Fig. 4d), was carried out, and its degree of crystallinity was calculated. The crystallinity degree flax fiber is 64.5%, pulp after peracetic cooking is 68%, and further alkaline treatment increases the crystallinity degree of cellulose to 74.6%. As shown from Fig. 4, X-ray diffraction spectra (a) and (b) correspond to the spectrum of cellulose I

in the form, and alkaline treatment changes the structure of cellulose I into cellulose II indicating a peak mix from the region $15-16^\circ\theta$ to the region $12^\circ\theta$, indicating a high content of alpha-cellulose in organosolvent cellulose. The crystallinity degree of nanocellulose films is 62%. Reduction of crystallinity degree is due to intensive ultrasonic treatment, which results in the destruction of nanocellulose crystals.

To determine the thermal stability of the samples, a thermogravimetric analysis of OFP after peracetic cooking and alkaline treatment (1) and nanocellulose films after hydrolysis with 43% sulphate acid with ultrasonic treatment of 30 minutes (2) was performed (Fig. 5).

Fig. 5 shows that the mass loss of the investigated samples begins at a temperature of 80°C , which is associated with the evaporation of residual moisture from cellulose. The main loss of flaxseed pulp is observed at a temperature of $220-240^\circ\text{C}$, continues to 300°C and ends at 400°C .

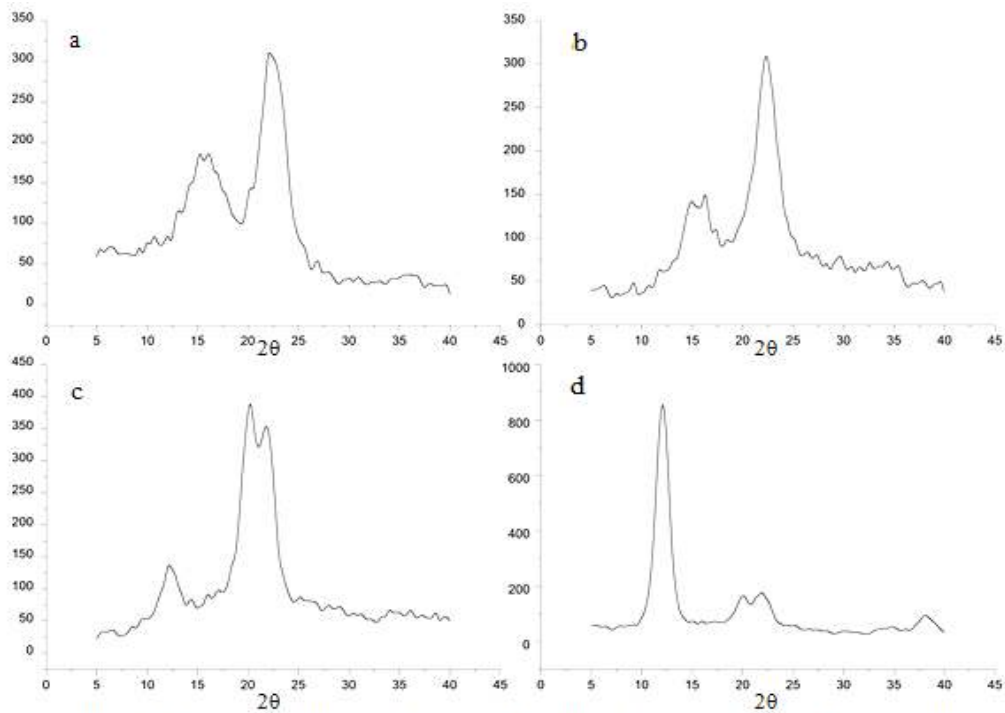


Fig. 4 X-ray diffraction patterns of the flax fiber (a), pulp after peracetic cooking (b), pulp after additive alkaline treatment (c), nanocellulose film (d) after hydrolysis 43% H_2SO_4 , 60 °C, 30 min and ultrasonic treatment 30 min.

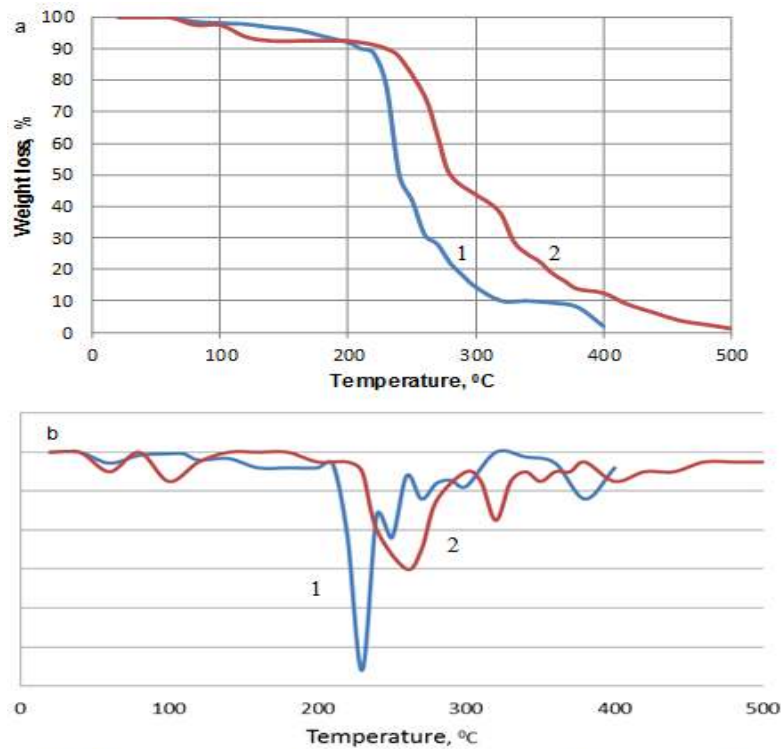


Fig. 5 Gravimetric (a) and differential (b) curves of thermal analysis: organosolvent flax pulp (1) and nanocellulose film (2) after hydrolysis 43% H_2SO_4 , 60 °C, 30 min and ultrasonic treatment 30 min

Destruction of nanocellulose films (curve 2) has a different character. The loss of almost 50% of the mass of nanocellulose films occurs at a temperature of 280°C, which is on 40°C higher than that of the original cellulose. There is a slow sequential destruction with increasing temperature that ends at a temperature of about 500°C, which is higher than that for wheat nanocellulose films [17]. This is due to the fact that in the process of chemical processing and ultrasonic homogenization is the formation of a dense structure between the cellulose molecules.

4. CONCLUSION

1. The organosolvent flax pulp from flax fibers was obtained by ecology safer method - cooking in solution of peracetic acid. Obtained organosolvent flax pulp had ash content of 0.04%, lignin— 0.015%, degree of polymerization—300 and used it for preparation of nanocellulose.
2. The optimal parameters of hydrolysis process of organosolvent flax pulp were investigated: concentration of sulfuric acid – 43%, temperature – 60°C duration 60 min. The obtained flax nanocellulose had degree of crystallinity 62%, particles with diameter less than 60 nm, which is confirmed by AFM data; the transparency of received films is more than 60%, and the tensile strength up to 70 MPa, and higher thermal stability compared to the organosolvent flax pulp.
3. The preliminary studies made it possible to assert that the obtained flax nanocellulose can be used in the production of different composite materials and optoelectronics, the results of which will be reported additionally.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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