**WOOD RESEARCH** doi.org/10.37763/wr.1336-4561/67.2.340347
**e-ISSN 2729-8906**
**67(2): 2022 340-347 pp.**

*SHORT NOTES*

# METHODS OF PREPARATION OF NANOFIBRILLATED CELLULOSE FOR SPECIAL FILTER PAPERS WITH EFFECTIVE AIR FILTRATION

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(RECEIVED NOVEMBER 2021)

## ABSTRACT

Nanofibrillated cellulose was prepared from distillery refuse based on maize starch using the extraction with NaOH and HCl involving centrifugation. SEM images of bleached kraft pulp with/without the addition of nanofibrillated cellulose were compared. The results showed that the application of nanofibrillated cellulose caused a visible reduction in the surface porosity. Conversely, mixing of the pulp with the nanofibrillated cellulose resulted in large pores among the fibres. The effect of the cationic retention aid on porosity was not significant, observed in the fines retention. A minimal difference in porosity was found among of fine and coarse fibres. When lyophilisation as drying method was used it yielded nanofibrillated cellulose with a size in the range of approximately 100 to 150 nm.

KEYWORDS: Nanofibrillated cellulose, coarse fibres, fine fibres, nanopores, SEM analysis, lyophilisation, distillery refuse, porosity.

## INTRODUCTION

Nanofibrillated cellulose (NFC) had multiple utilization in paper industry. It can be used as strength additive (Zeng et al. 2021), coating agent for food packaging paper (Jin et al 2021) or for reduction of fibre content while delivering the commercially required strength of paper (Zambrano et al. 2020). Nanocellulose can be isolated from a variety of cellulosic sources. It is characterized by a significantly higher specific surface area, covered with a surface charge (Gardner et al. 2008). Its use leads to a significant reduction in the size of pores as well as to an increase in the adhesive forces on the surface, which in turn leads to an increased capture of microdroplets compared to filters made of conventional cellulose fibres.

The disadvantage of the NFC production is the high energy consumption associated with mechanical fibrillation. Sharma et al. (2011) has successfully demonstrated the process steps of utilization of fibre cake as raw material for NFC production resulting from pilot scale ryegrass biorefining trials which includes mechanical shearing, microfluidising and chemical treatment. Zhu et al. (2011) used bleached sulphate pulp as a source of cellulose and used cellulase enzymes for fractionation, which resulted in a highly crystalline cellulose fraction as a source for the production of nanofibrillated cellulose after mechanical treatment. One possibility is to use a simple fractionation associated with centrifugation in order to reduce size distribution of the extracted slurry derived from hardwood pulp (Zhai et al. 2020). A procedure was developed for the isolation of fibrils from bamboo fibre using negatively charged particles with ultrasonic homogenization (Hu et al. 2017), or from oat hull (Paschoal et al. 2015). Another very efficient method of separation is centrifugation, which has been successfully used to separate longer fibres from corn kernels with optimizing centrifugation conditions such as time, temperature, speed and number of cycles, and of course the consistency of the feedstock (Pažitný et al. 2010, 2011, 2012). Drying nanocellulose materials by conventional methods can lead to irreversible particle agglomeration so that they do not redisperse upon rehydration (Sinquefield et al. 2020). Thus, lyophilisation seems to be sensitive method for the preservation of biologically sensitive materials as well as for drying of inorganic nanodispersions.

The aim of the work was to compare bleached kraft pulp without and with the addition of nanofibrillated pulp, obtained from distillery refuse. The effect of the use of fine and coarse fibres on the porosity of the filter paper was also tested.

## MATERIAL AND METHODS

The maize-based distillery refuse was obtained from the company Enviral, JSC, Slovak Republic. Bleached birch kraft pulp with short fibres (Södra Gold) was beated to 27°SR. The cationic coagulant Acefloc C 2008 0.5% w/w solution (Allied Solutions) was used.

The mechanical and absorption properties of the HEPA filter were first determined. Air permeability was measured by the Gurley method according to the standard ISO 5636-5 (2013). Bending stiffness was tested according to the standard ISO 2493 from machine direction (MD) as well as cross direction (CD) of paper. The contact angle the surface wettability of the paper with castor oil was measured using optical tensiometer OCA 35 (Dataphysics Instruments, Germany) and recorded at a rate of 20 images per second in a time from 0.5 ms to 30 min. Static contact angle values at 0.5 ms are marked as $SCA_0$, and dynamic at 5 sec as $DCA_5$. Roughness of paper surface was measured by the photoclinometric method. The optical surface variability defined by a coefficient of variation expressed in percentage ($OVS_{CLINO}$) was determined and used in our previous works (Gigac et al. 2014, 2016, Kasajová and Gigac 2013). The pore size distribution was determined on the outer side of HEPA filter roll using a 3G porometer from Quantachrome Instruments using an inert fluorinated liquid Porofil with a surface tension of 16.000 dyn/cm and a viscosity of 1.500 Pa.s for paper wetting. A distribution curve was obtained, and the minimum, maximum and average pore sizes were subtracted.

*Isolation of nanofibrillated cellulose*

Nanofibrillated cellulose was obtained from the distillery refuse by extraction with NaOH and HCl. The dry matter of the distillery refuse was determined to be 34.5%. Extraction with NaOH was performed by heating the suspension to 60°C and standing at room temperature for 24 hours. The feed of NaOH was 30% (pH = 13) on the oven-dry distillery refuse average, dry matter was 3.5%. The mixture was washed with hot water to neutral pH, the excess water was centrifuged, and the dry matter was determined. The first step was followed by acidification, where pH was adjusted to 1.5 with HCl at a concentration of 1 $mol.L^{-1}$. Reaction conditions included a dry matter of 3.5%, heating to 60°C, standing for 24 h at room temperature. The mixture was washed with hot water to neutral pH, the excess water was centrifuged and the dry matter was determined. The obtained fibres were sorted on a Somerwille classifier. The lower sediment layer with coarse fibres was filtered through and set aside. The wet fibres from the top layer were collected in beakers and the excess water was evaporated. The nanofibrillated cellulose after evaporation of 80% water was frozen at -20°C and subsequently, the sample was lyophilized at -50°C.

*Samples preparation*

The bleached birch kraft pulp Södra Gold was beated and filtered through a Büchner funnel under pressure resulting in formation of filter cake. Obtained cellulose fibres are introduced as Experiment No. 1. A layer of nanofibrillated cellulose was applied to the surface of the filter cake without lyophilisation (Experiment No. 2). A layer of nanofibrillated cellulose was applied together with the addition of Acefloc C 2008 (Experiment No. 3). Södra Gold birch kraft pulp was beated and blended with nanofibrillated cellulose obtained without lyophilisation (Experiment No. 4) and with nanofibrillated cellulose with the addition of Acefloc C 2008 (Experiment No. 5). The nanofibrillated cellulose obtained without lyophilisation and without filtration was dried on Petri dishes in a laboratory oven (Experiment No. 6). The nanofibrillated cellulose obtained without lyophilisation was firstly filtered through a Büchner funnel and dried (Experiment No. 7). The lyophilized nanofibrillated cellulose was dried (Experiment No. 8).

*Isolation of nanofibrillated cellulose for application on HEPA filter*

The distillery refuse was diluted with water in ratio 1 : 2. The top layer fine fibres was removed, 10% w/w water was added and the pH was adjusted to 1.3 with HCl. Subsequently, after 24 h, the pH was adjusted to 13 with NaOH and after 24 h the pH was adjusted to 7 with NaOH. Suspension was filtered through a sieve and the fine and coarse fibres were separated. Fibres were separated and dried in a laboratory oven without lyophilisation.

*Application of fine and coarse fibres on HEPA filter substrate*

Nanofibrillated cellulose was applied to HEPA filters using a static sheet former. A commercial HEPA filter (EKO-ŠIMKO s.r.o.) was placed in a static pulp sheet former and a bleached birch kraft pulp suspension was applied. Subsequently, the suspension was evacuated and the filter with the applied cellulose was inserted between two PTFE foils, and placed in a press at a temperature of 110°C and a pressure of up to 5 bar for 10 min. The filter was dried in

a laboratory oven at 105°C for 2 hours. The nanofibrillated cellulose suspension was then applied on the pre-treated filter in the same way.

*SEM analysis*

SEM analysis of lyophilized nanofibrillated cellulose was performed by high resolution scanning electron microscopy using a SEM JSM-7600F (EOL Ltd., Japan). Samples were prepared by cutting of the sample and their adhesion to a double-sided conductive tape, and then the surface was vapour-deposited with silver to prevent the surface from drifting over the drifting image during scanning. The accelerating voltage was 10 kV.

## RESULTS AND DISCUSSION

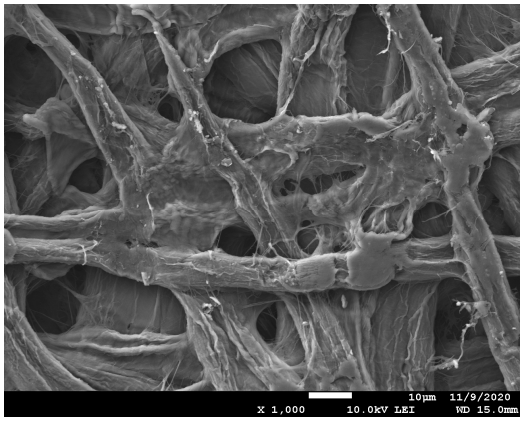
In Tab. 1 the measured mechanical and surface properties of the HEPA filter substrate are illustrated. The very low air permeability 0.4 $s^{-1}$ was measured by the Gurley method. A higher resistance to bending in the machine direction (MD) compared to the inner side of the roll appeared on the outer side of filter, similar in the CD direction. The wettability of the surface with an inert liquid (castor oil) of the outer and the inner sides of the roll did not differ. The outer side of the roll had a lower surface roughness, which was later chosen as the side more suitable for nanofibrillated cellulose application.

*Tab.1: Mechanical and surface properties of HEPA filter substrate.*

| | Outer side of the roll | Inner side of the roll |
|---|---|---|
| Basic weigh ($g.m^{-2}$) | 72.0 | 72.0 |
| Air permeability Gurley ($s^{-1}$) | 0.4 | 0.4 |
| OVS MD (%) | 18.52 | 21.29 |
| OVS CD (%) | 21.19 | 21.35 |
| OVS aver. (%) | 19.90 | 21.32 |
| $SCA_0$ $^{castor}$ (°) | 121 | 121 |
| $DCA_5$ $^{castor}$ (°) | 119 | 121 |
| Bending stiffness MD (mNm) | 199 | 193 |
| Bending stiffness CD (mNm) | 123 | 106 |
| Maximum pore (μm) | 11.22 | 11.22 |
| Minimum pore (μm) | 6.24 | 6.24 |
| Average pore (μm) | 8.28 | 8.28 |
| Air flow rate ($m.s^{-1}$) | 0.667 | 0.667 |

* Three parallel measurements were made for the each measurement.

The experiments with nanofibrillated cellulose, prepared by the procedure No. 1 as well as with bleached birch kraft pulp itself, were observed using of SEM analysis. In case of conventional pulp (Fig. 1a), the pore size is around of few μm (according to the scale, the diameter of the largest pore exceeds 10 μm). As it is visible in Fig. 1b, compared to the original birch pulp, the pores are completely blinded and the bleached birch kraft pulp fibres are only rarely visible. Similar to Fig. 2a, the pores are also completely blinded and the birch pulp fibres are only rarely visible. The surface is visually smoother; probably the cationization caused more cohesion of the fibres.

a) 

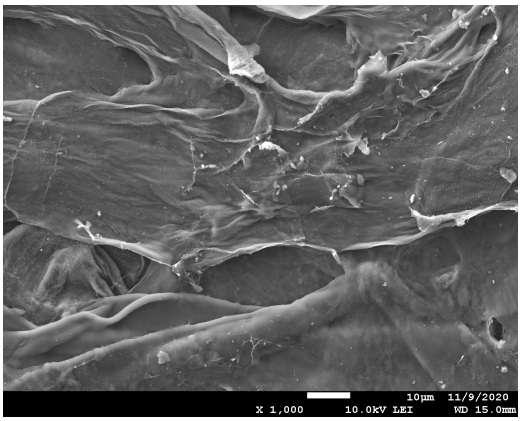
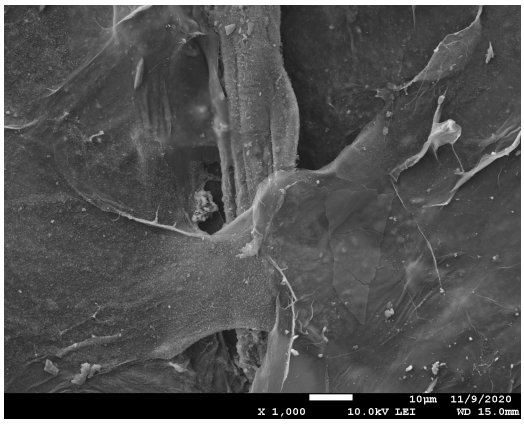
b) 


*Fig. 1: SEM analysis at 1000x magnification of: a) bleached birch kraft pulp surface (Experiment No. 1), b) the surface with applied non-lyophilized nanofibrillated cellulose (Experiment No. 2).*

a) 

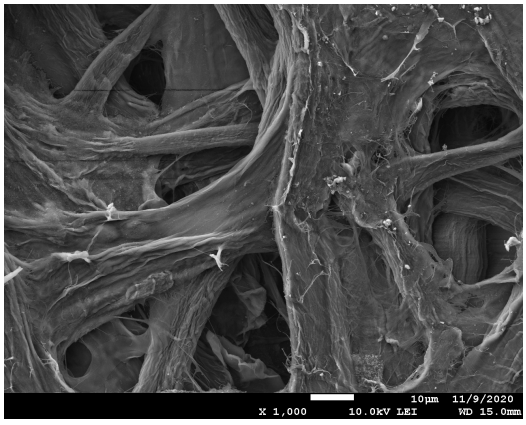
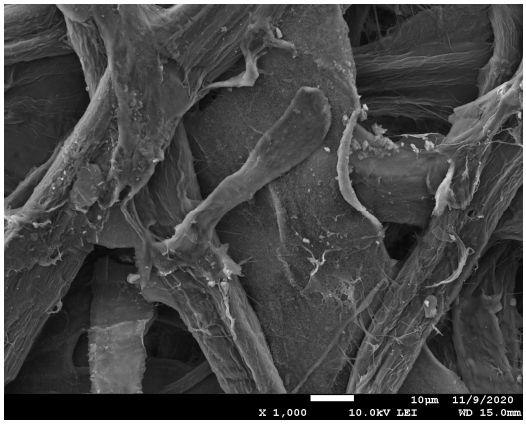
b) 


*Fig. 2: SEM analysis at 1000x magnification of: a) bleached kraft birch pulp surface with deposited non-lyophilized nanofibrillated cellulose with addition of cationic agent (Experiment No.3), b) birch pulp, which was mixed with non-lyophilized nanofibrillated cellulose (Experiment No. 4).*

The process of mixing the nanofibres with the pulp resulted in formation of a microstructure (Fig. 2b) which is very similar to the surface of the birch pulp itself (Fig. 1a). Some places were clogged with nanofibrillated cellulose. Similarly, the surface image of bleached kraft pulp that was mixed with non-lyophilized nanofibrillated cellulose with the addition of a cationic agent shows that some pores were clogged with nanofibres (Fig. 3a). In case of non-lyophilized nanofibres without filtration (Experiment No. 6, Fig. 3b), the surface of these fibres was completely continuous and the pores were present in a minimal amount.

Fig. 4a shows SEM images of the surface of non-lyophilized nanofibrillated cellulose, where the surface is smooth, when impurities were removed during filtration. Fine fibres after defibrillation can be seen at a magnification of 2500 times (red arrow). In Fig. 4b are SEM images of the surface of lyophilized nanofibrillated cellulose that has not been filtered, and cracks are visible; the arrow points to nanopores on the nanofibrillated cellulose. The size of the pores (cracks) was within the range of 100 - 150 nm.

a) 

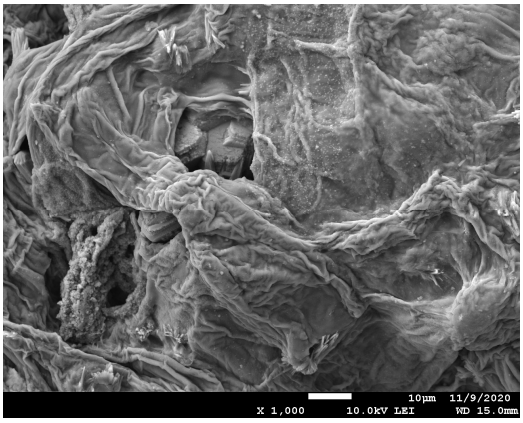
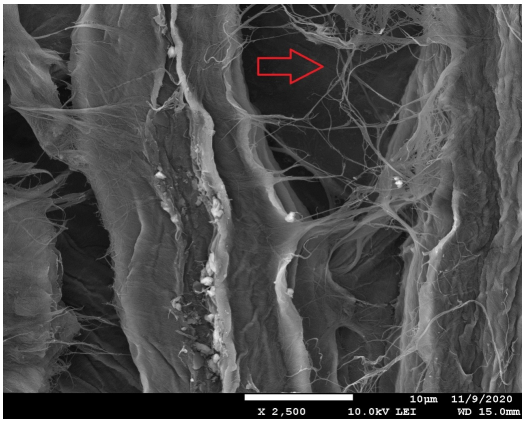
b) 


*Fig. 3: SEM analysis at 1000x magnification of: a) the surface of birch pulp, which was mixed with non-lyophilized nanofibrillated cellulose with the addition of cationic agent (Experiment No.5), b) the surface of non-lyophilized nanofibrillated cellulose (without filtration) (Experiment No. 6).*

a) 

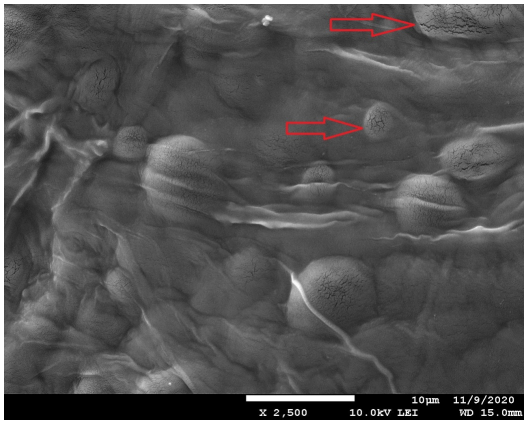
b) 


*Fig. 4: SEM analysis at 2 500x magnification of: a) the surface of non-lyophilized nanofibrillated cellulose (filtered)(Experiment No.7), b) the surface of lyophilized nanofibrillated cellulose (without filtration) (Experiment No. 8).*

The porosity of HEPA filter is higher with an average pore size of 9.28 µm. As in Tab. 2, the application of nanofibrillated fibres significantly reduced the pore size. Already the application of the bleached kraft pulp which contains short fibres resulted in a reduction of the maximum pore size more than threefold and the medium and small pore size by 3.8-times. After applying of nanofibrillated cellulose to a HEPA filter on which bleached kraft pulp was applied before, the porosity was further reduced. When comparing fine fibres with coarse fibres, the same blending of bleached kraft pulp and nanofibrillated cellulose, only a minimal difference was found. The ratio of bleached kraft pulp to nanofibrillated cellulose in this case was approximately 4 : 1. By using of a smaller amount of bleached kraft pulp compared to a 7-fold higher ratio of nanofibrillated cellulose, the maximum pore size (2.48 µm) was higher than in case of using of a larger proportion of pulp. Increasing of the ratio of bleached sulphate pulp and at the same time nanofibrillated fibres reduced the size of all pores.

*Tab. 2: Porosity and permeability of filter paper with applied nanofibrillated cellulose.*

| Sample No.1 | Fibres | $C_{pulp}$ ($g.m^{-2}$) | $C_{nanocel}$ ($g.m^{-2}$) | Maximum pore (μm) | Minimum pore (μm) | Average pore (μm) |
|---|---|---|---|---|---|---|
| 0 | | 0 | 0 | 11.22 | 6.24 | 9.28 |
| 1 | without NFC | 22.8 | 0 | 3.36 | 1.63 | 2.40 |
| 2 | fine | 23.5 | 5.0 | 1.93 | 0.81 | 1.28 |
| 3 | coarse | 23.5 | 5.0 | 1.93 | 0.81 | 1.41 |
| 4 | fine | 45.6 | 10.0 | 1.34 | 0.51 | 1.16 |
| 5 | coarse | 45.6 | 10.0 | 1.26 | 0.56 | 1.19 |
| 6 | coarse | 6.6 | 40.0 | 2.48 | 0.51 | 1.79 |

## CONCLUSIONS

SEM images of bleached kraft pulp with and without the addition of nanofibrillated cellulose were compared, either applied to the surface of the bleached kraft pulp or mixed with the pulp. The results showed that the application of nanofibrillated cellulose caused a visible reduction in the inter-fibre porosity on the surface, and conversely, the mixing of the pulp with the nanofibrillated cellulose resulted in large inter-fibre spaces. The effect of the cationic agent did not appear here. In case of filtered nanofibrillated cellulose which was evaporated in its aqueous phase on Petri dishes and the sample was subsequently lyophilized, nanopores of approximately 100 to 150 nm were obtained.

When the same nanofibrillated cellulose ratio was used and applied on HEPA filter, only a minimal difference in porosity was found between using of fine fibres and coarse fibres which were isolated from the distillery refuse. The use of larger proportion of bleached short-fibres kraft pulp leads to a significant reduction of maximal and minimal pore size as well as medium pore size.

## ACKNOWLEDGEMENT

This work was supported by the Slovak Research and Development Agency under the contract PP-COVID-20-0103.

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