SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: FP1405
STSM title: Printing conductive lines on nanocellulose-based biocomposites for packaging applications
STSM start and end date: 11-02-2018 to 24-02-2018
Grantee name: Stanislava Maronová

PURPOSE OF THE STSM

(max.500 words)

The purpose of the STSM was to establish collaboration between the research group of Ing. Tomáš Syrový, Ph.D, which is focused to research of material printing, and research group of Dr. Gary Chinga Carrasco at RISE PFI AS, which is oriented to research in area of wood fibres, pulp and paper, new biobased materials and sustainable biorefining. In the context to joined research, Stanislava visited RISE PFI in Trondheim, where she spent two weeks under supervision of Dr. Gary Chinga Carrasco in order to discuss her experience with material printing on different type of substrates and to extend her knowledge in the area of printing on nanocellulose films. The experiments (in terms of functional printing) related to given STSM continued at home institution University of Pardubice under supervision of Dr. Tomas Syrovy.

This activity was for the host and myself mutual benefit, and lead to a strengthening of the collaboration between the host and my home institution.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

(max.500 words)

This Short Term Scientific Mission (STSM) was focused on printing of conductive paths/lines on different kind of printing substrates, which were based on nanocellulose. For given experiments were used cellulose nanofibrils (CNF) from agro-industrial residues as substrates for printing of barrier films for packaging.

For testing and printing were applied three different approaches to make films:

a) Self standing nanocellulose films: The films were made from 2 different CNFs, having different morphology. The different morphology is expected to affect the roughness and porosity of the films, and thus the printing behaviour and oxygen barrier properties of substrates. The CNF films were manufactured without and with plasticizers (PEG) to assess their effect on printing and barrier properties.

b) 3D printing of CNF to form films: a 3D printer was used to deposit CNF hydrogels directly on microscope slides to form small-scale films (20 x 45 mm). The films were characterized and tested for printing of conductive lines by pad printing technology.

c) The coating of paper substrates with CNFs by bar coating method (thickness <10 μm). The CNF coatings were characterized and tested for printing of conductive lines by gravure and flexo printing.

For characterization and analysis of nanocellulose films were used laser and mechanical profilometry, scanning electron microscopy, oxygen transmission rate, gravimetric liquid absorption measurements and gloss measurement.

The second part of the STSM consisted of printing on nanocellulose substrates using appropriate printing techniques. Printing on nanocellulose films was performed using screen printing and pad printing. The paper substrates coated with nanocellulose were printed by flexographic and gravure printer.

For characterization and analysis of printed structures and lines were used mechanical profilometry, optical microscopy and electrical characterization.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

(max. 500 words)

We managed to achieve all activities attached to the proposed work plan including creating CNF films, printing conductive structures/sensors on prepared substrates, measurements of several characteristics of substrates and conductive structures. All data were analysed.

The printing of sensors on nanocellulose films was performed with screen printer using graphene nanoplatelet conductive ink. The printing on paper substrates with CNF coatings was realized by flexo printing technique and by gravure printing technique, where silver nanoparticle ink was used. The PET as reference substrate with very smooth surface film was used for comparison purposes. For most printed electronics tasks, the substrate needs to have minimum surface roughness. In order to satisfy this requirement, synthetic polymeric foils are typically employed as the substrates for printed electronics. Nanopaper possesses tunable optical properties, high tensile strength, and relatively low surface roughness, all of which are favorable characteristics for printing electronics. Moreover, when compared to plastic, paper is much easily recyclable and generally biodegradable. Analysis of results obtained from prints on nanocellulose substrates has shown that nanocellulose has significantly improved properties of conductive lines printed on uncoated paper substrates. Results from electrical measurement, gloss measurement and optical microscopy proved, that achieved characteristics of printed lines on CNF coated papers were close to properties that can be achieved by printing on PET film. Results of this work leads to conclusion that further developments in this area could lead to superseding plastic by transparent nanocellulose paper to create greener electronics. Transparent nanocellulose paper has several advantages such as being low-cost, non-toxic, biocompatible for use in implantable biomedical electronic applications, and promising for visible packaging and biomedical sensing.

All the results achieved so far together with a detailed description of the work carried out during STSM, are described in Appendix below.

FUTURE COLLABORATIONS (if applicable)

(max.500 words)

With Dr. Gary Chinga Carrasco and Ing. Tomáš Syrový, Ph.D, we agree that we can continue with our collaboration after the finishing of the STSM. We consider this STSM a very successful and we estimate that the project will take several weeks to be completed. During the collaboration we also started to work on the second project focused on CNF films for wound dressings applications, with added functionality. Since this project is still in early phase, we intend to disseminate our work by preparing scientific publications for international scientific journals, once our project is complete

Appendix

RESULTS AND DISCUSSION

1) Production of CNF films

3D printing of CNF:

For 3D printing were used 4 types of CNF hydrogels based on 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)-mediated oxidation, using 3.8 mmol or 6.0 mmol hypochlorite (9%NaClO) per gram of pulp fibers. Pulp fibers were obtained from the baggase raw material using two fractionation methods – soda and hydrothermal treatment (HT) combinated with soda. The concentration of the dispersion was 2 wt%.

Table 1: Series of the produced CNF samples:

CNF name	***Pulping***	***TEMPO-mediated oxidation (mmol/g)***
BHS_T3.8	HT+soda	3.8
BS_T3.8	soda	3.8
BHS_T6.0	HT+soda	6.0
BS_T6.0	soda	6.0

The nanocellulose gels were used as inks for 3D printing, which was performed with Regemat3D printing unit (version 1.0). The inks were kept at room temperature (23 °C) for 24 h before printing. 4 types of CNF hydrogels were deposited directly on microscope slides to form small-scale films. Shape and parametres of deposited films as dimension and thickness have been setup in software Regemat3D Designer (version 1.8, Regemat3D, Granada, Spain). For each type of nanocellulose were printed 8 rectangle shaped samples with 0.8 mm thickness and size 20 x 45 mm, composed of two layers, using 0.58 mm conical nozzle. Setting of the flow speed (2-2,5 mm/s) and speed of printing (5-7 mm/s) have been changed depending on the type of CNF and its reological behaviour in order to achieve homogenous films with better uniformity.

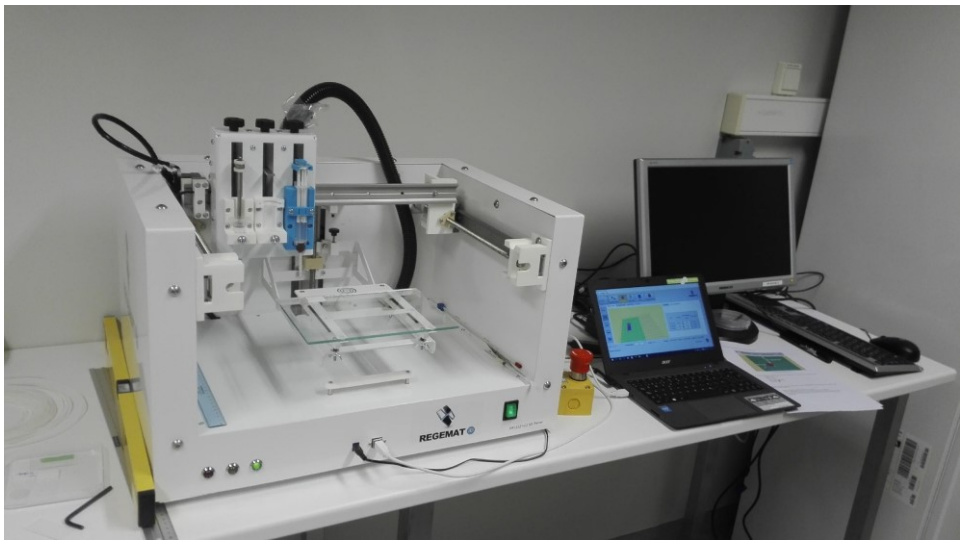

Figure 1: 3D bioprinter

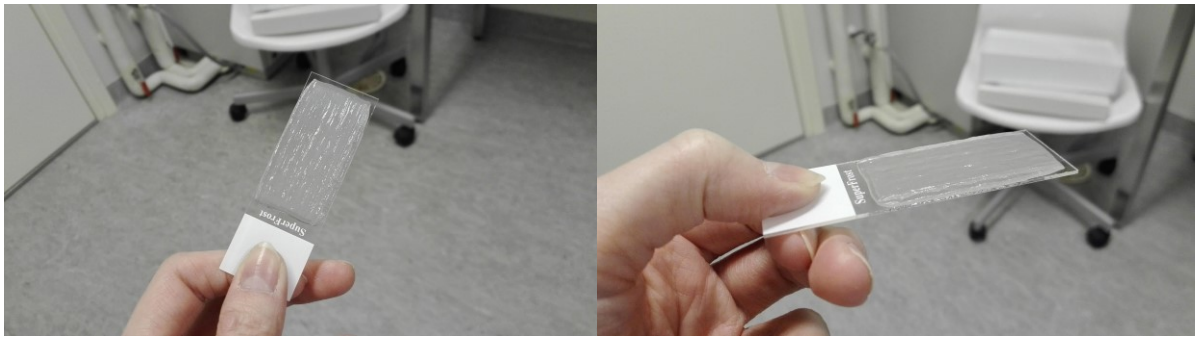

Figure 2: Fresh-printed sample on microscope slide

<u>Self standing films:</u>

The films were made by suspension casting (20 g/m^2), using a 0,2 wt% concentration of CNF-dispersion. The diameter of the of Petri dish was 55 mm. The films were allowed to dry 1 week at room temperature (23 ^{o}C).

Table 2: Films of the produced CNF samples:

Films	***Gel***	***PEG (%)***
FHS_T3.8	BHS_T3.8	-
FS_T3.8	BS_T3.8	-
FHS_T6.0	BHS_T6.0	-
FS_T6.0	BS_T6.0	-
FHS_T3.8_P40	BHS_T3.8	40
FS_T3.8_P40	BS_T3.8	40
FHS_T6.0_P40	BHS_T6.0	40
FS_T6.0_P40	BS_T6.0	40

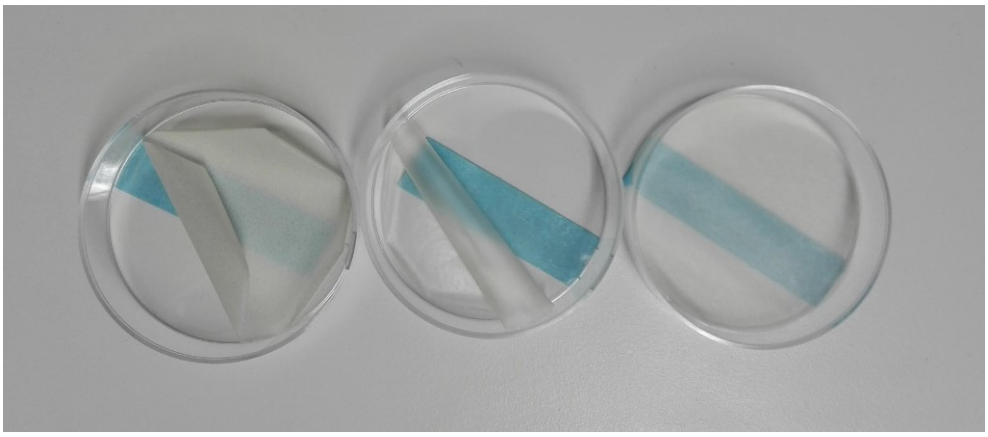

Figure 3:Self standing nanocellulose films

The coating of paper substrates with CNF:

The nanocellulose used for application to paper substrates was produced from never-dried kraft pulp fibers. The fibers were TEMPO mediated oxidized using 3.8 mmol/g NaClO. The fibers (1 wt%) were homogenized using 1000 bar pressure and the nanocellulose was collected after 3 passes through the homogenizer.

The coating of offset uncoated paper substrates (250 g/m^2) with CNF was performed by the TQC Motorised Automatic film applicator with 50 µm wire bar. Nanocellulose gel was homogenized before its application on paper substrates. In this experiment, substrates with single layer, two layers and three layers of CNF, were created. The CNF coatings were characterized and tested for printing of conductive lines by gravure and flexo printing technique.

2) Analysis of nanucellulose films:

Laser profilometry:

Laser profilometry was used to quantify the roughness of the top side of the films and relate the roughness to the achieved print quality. Film samples of each type of nanocellulose of approximately 2 x 1 cm were cut and fixed to microscope slides with double sided adhesive tape. The „transparent“ samples were gold-coated previous to the Laser profilometry analysis by Agar Auto Sputter Coater to prevent and reduce internal reflections and the occurrence of error heights in laser profilometry surface representations. Samples were sputtered with a thin layer of gold for 120 sec. 20 images were acquired from the top side of the film samples with a Lehmann laser profilometer (“LLP”, IVT-Lehmann Messtechnik AG). The lateral and z-resolution of the LP system was 1 µm and 10 nm, respectively. The size of the local areas was 1 mm x 1 mm. The root-mean-square (Sq) was quantified on the LP images. The topography images were processed with the SurfCharJ plugin for ImageJ software. Film surface characteristic details like roughness values, facet orientation and surface pore volume were

quantified. Results (Table 3) showed that the the top side of the films with PEG has rougher surface.

Figure 3: Agar Auto Sputter Coater

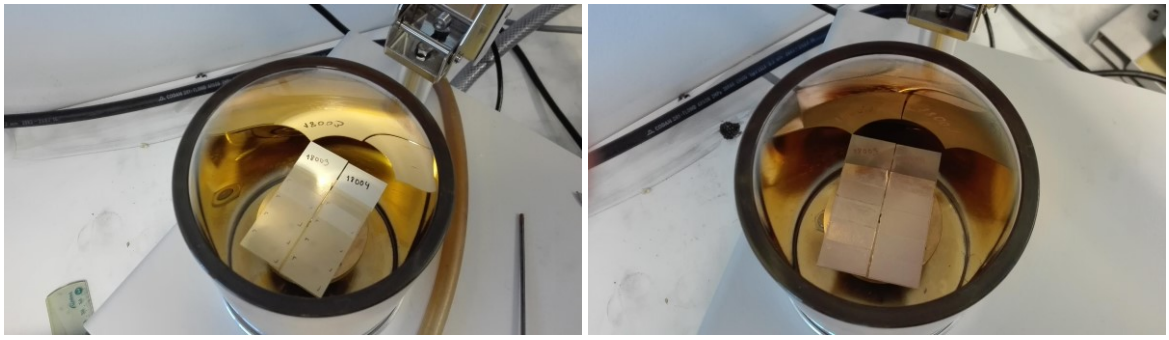

Figure 4: Samples before and after coating with gold

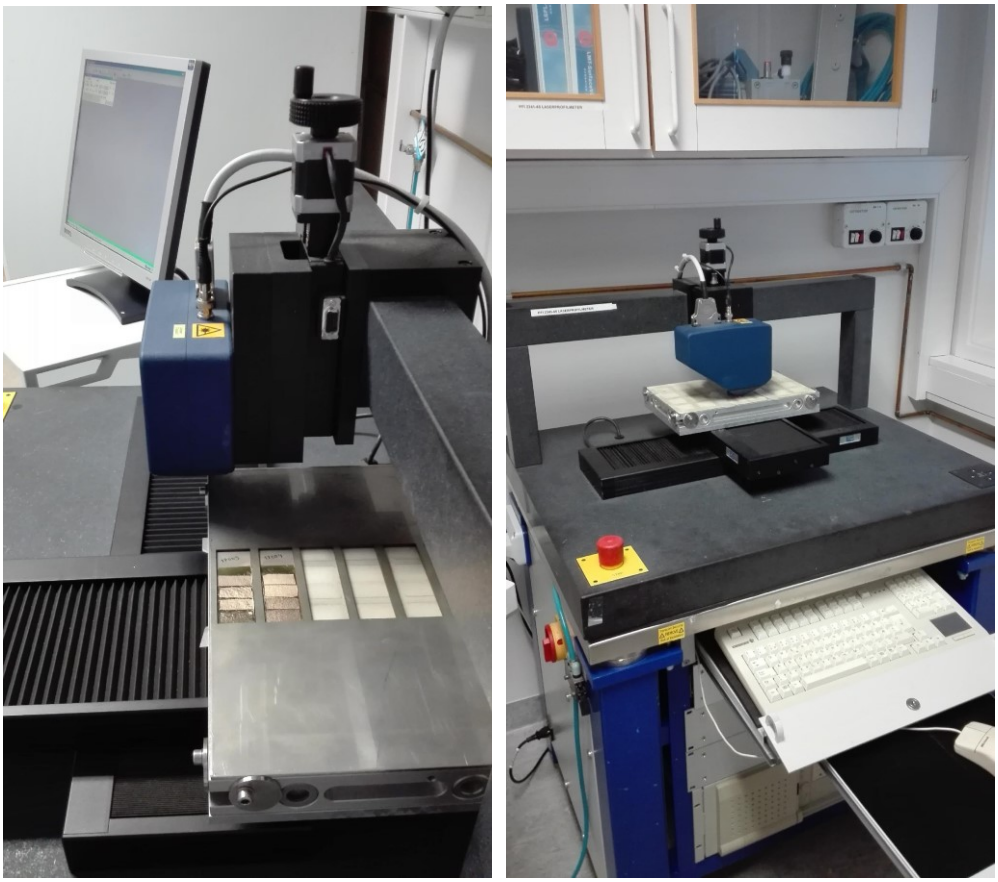

Figure 5: Lehmann laser profilometer

Table 3: Measured roughness values [µm] from laser profilometry

Series	***With 40% PEG***	***Without PEG***
FHS_T38	3.30 ± 0.27	2.66 ± 0.16
FHS_T60	2.46 ± 0.34	0.87 ± 0.15
FS_T38	3.10 ± 0.37	2.04 ± 0.21
FS_T60	2.58 ± 0.20	0.99 ± 0.07

Scanner analysis:

To assess the morphology of nanocellulose films were used scanner analysis. For scanner analysis were cut film samples of approximetly 2 x 1,5 cm. The samples were placed in a special holder between two microscope slides using a tweezers. Optical images from the films were acquired with an Epson Perfection scanner (version V750 PRO) in transmission mode, using 4800 dots per inch resolution, 8 bits per channel (RGB mode). . ImageJ (version 1.50i) was used for computerized image processing and analysis.

The measurement results are shown in Table 4. Image of each sample was cut to 2 x 2 mm (see Figure 6) and subsequently analyzed by histograms (see Figure 7).

Table 4: Measurement results

Sample	*Name of the film*	*Mean*	*StdDev*	*Mode*	*Min*	*Max*	*Median*	*Skew*	*Kurt*
1	FHS_T3.8	152.4	13.2	147	96	215	151	0.7	0.7
2	FS_T3.8	203.5	8.7	207	99	226	205	-1.1	3.5
3	FHS_T6.0	225.5	18688	227	121	232	226	-4.9	86.5
4	FS_T6.0	222.1	4.3	224	134	231	223	-3.6	34.6
5	FHS_T3.8_P40	138.4	11.7	133	87	211	136	1	1.4
6	FS_T3.8_P40	199.6	10.2	204	108	226	201	-0.7	0.4
7	FHS_T6.0_P40	218.7	43440	222	148	231	220	-1.5	5.8
8	FS_T6.0_P40	223.2	4.5	226	116	233	224	-2.9	21.1

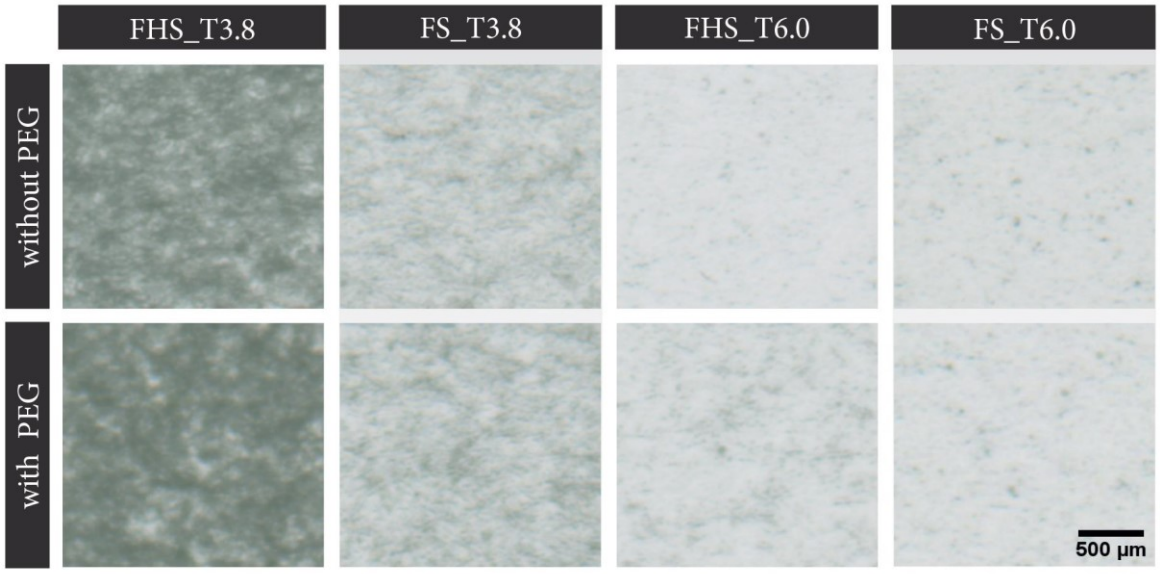

Figure 6: Optical images of individual sample cuts

The nanofibrillation degree can be assesed by quantifying the transluency of the nanocellulose films. The higher transluency is, the higher the nanofibrillation. Figure 7 shows the distribution of pixels as a function of tonal variation. A larger tonal variation of the samples means a lower trancluency value. Samples FHS_T6.0 and FS_T6.0 have higher transluency value (better fibrillated samples), however samples with polyethylene glycol seems to have a little bit worse transluency value than samples without PEG. This is also confirmed by the skewness value of the transluency distrubution and by the rougness assesed by laser profilometry, because the rougness at the assessed scale is affected by residual fibres. The lesser the fraction of residual fibers, the higher the nanofibrils, and the smoother films. This is also confirmedby the SEM images (Figure 10). The FS series shows signifcantly larger amount of particles, which are presumptively silica particles from baggase parenchyma cells. [2]

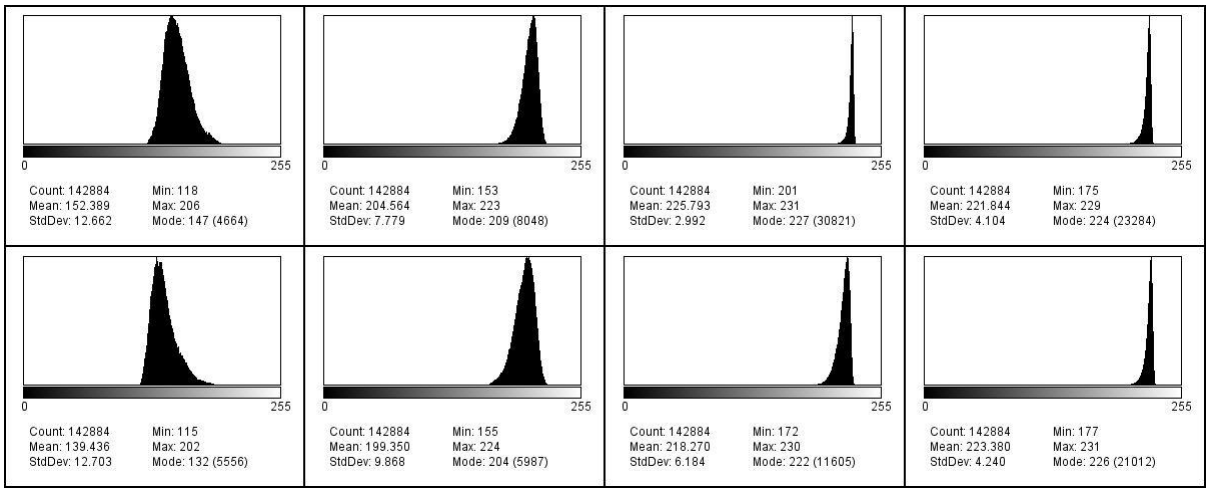

Figure 7: Histograms of individual sample cuts

<u>Gravimetric liquid absorption measurements:</u>

Two sets of film samples were created. One set for gravimetric water absorption (samples of approximately 2 x 2 cm), the other set for gravimetric PBS absorption (sample of approximately 2 x 1.5 cm). Samples were dried for 1 hour at 105 ° C before testing. Dry samples were weighed, followed by gravimetric testing, where the samples were immersed in water/PBS for 5, 15, 30, 60 minutes and 2, 24 hours, then slightly dried with laboratory wipes and weighted on analytical balance Mettler AT201. For handling with samples was used tweezer.

Most of samples were damaged /dissolved in the gravimetric water absorption test. The most problematic were samples with plasticisers (sample 5 – 8). Three samples of 8 (1, 2 and 4) passed the test. In the gravimetric PBS absorption test all samples more or less passed the test. Manual drying of the film samples with laboratory wipes could caused that one sample was dried more than other, which significantly reflected on the weight of the samples. Sometimes the sample exhibited a lower weight (smaller volume of absorbed liquid) after a longer period of time in the liquid, which is clear evidence of a measurement error. Sample handling was very difficult, and since only one piece of sample was available for each type of film, informative value of this test is not high.

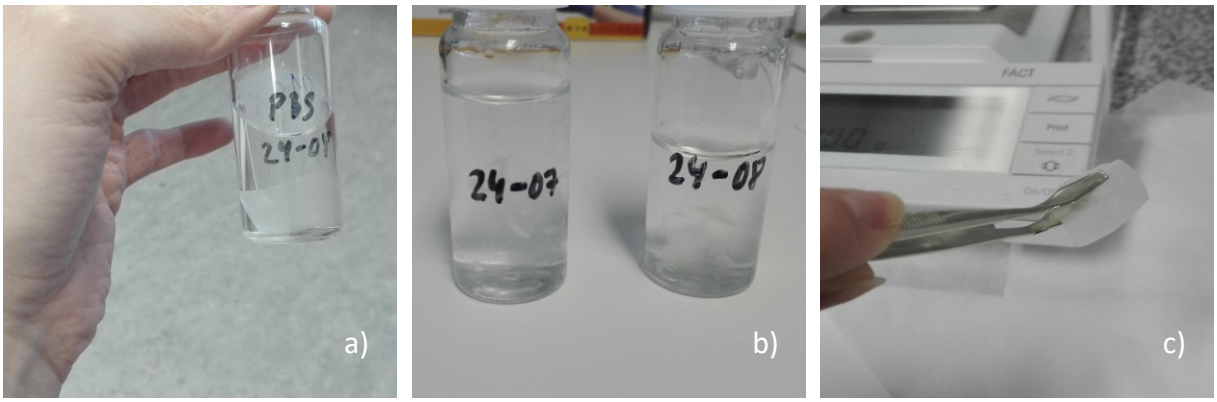

Figure 8: a) Sample immersed in PBS b) Dissolved samples c) Sample handling with tweezer

SEM Analysis:

Film samples of each type of nanocellulose of approximately 1 x 1 cm were cut and sputtered with a thin layer of gold (Agar Auto Sputter Coater). Scanning electron microscopy (SEM) was performed with a Hitachi SU3500 microscope, in secondary electron imaging (SEI) mode. Images were acquired with 100x magnification, using 5kV acceleration voltage. The size of acquired images was 5120 x 3840 pixels, having a resolution of 1024 pixels/inch. ImageJ was used for computerized image processing and analysis.

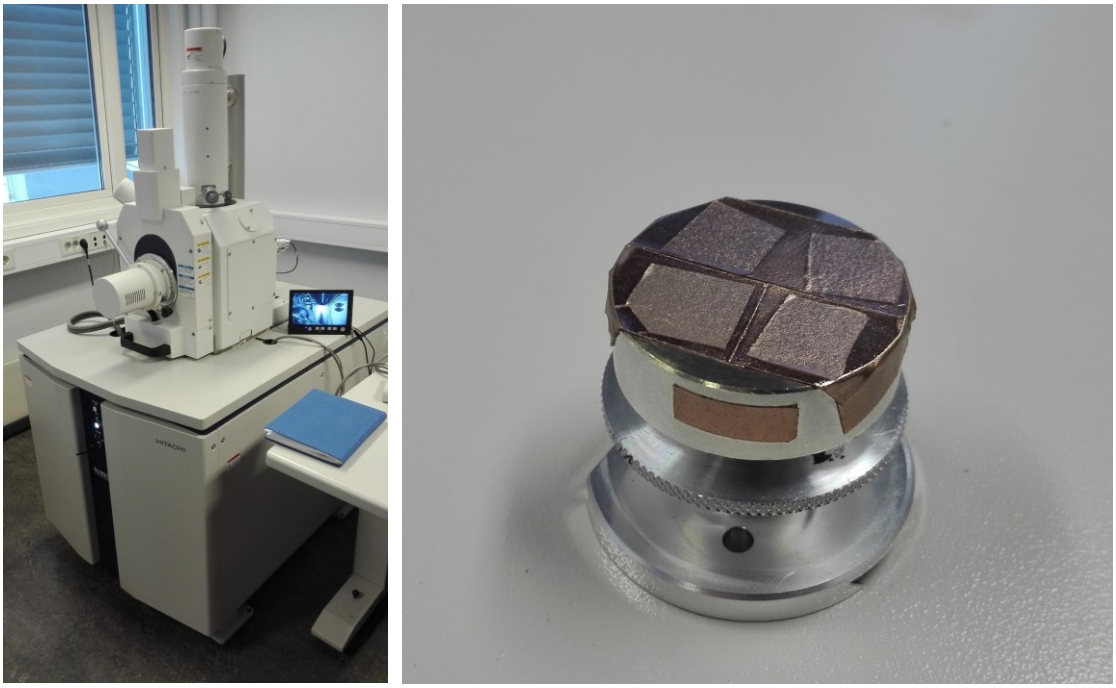

Figure 9: Hitachi SU3500 microscope and samples prepared for SEM analysis

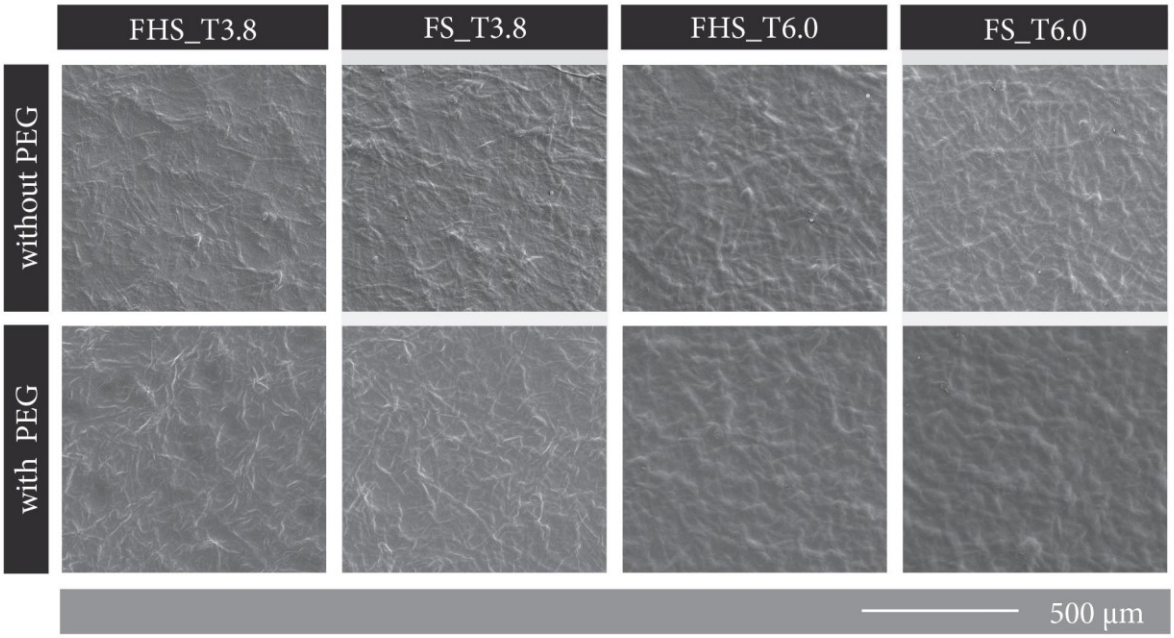

Figure 10: SEM images of nanocellulose films

Oxygen transmission rate measurements:

To assess the oxygen barrier properties of selected films were used Oxygen transmission rate (OTR). OTR was measured with a Mocon OX-TRAN® 1/ 50 test system (Mocon, Minneapolis, MN, USA) at 50% relative humidity and 23°C. The samples were placed in a test cell divided into two chambers separated by the sample material. The upper chamber was filled with Nitrogen and the lower chamber with test gas (Oxygen). Measured values from OTR are shown in Table 5. OTR values lower than 20 mL m^{-2} day^{-1} have been recommended for packaging applications [1]. Results showed that for packaging applications are appropriate samples without PEG: FS_T3.8, FHS_T6.0 and FS_T6.0.

Figure 11: Mocon OX-TRAN® 1/ 50

Table 5: Measured values from OTR

Sample	***cc/m²/day***
FHS_T3.8	384.3
FS_T3.8	3.87
FHS_T6.0	3.65
FS_T6.0	3.88
FHS_T3.8 + PEG	Could not be measured
FS_T3.8 + PEG	146.5
FHS_T6.0 + PEG	156.6
FS_T6.0 + PEG	150.2

Mechanical profilometry:

The Dektak XT stylus profiler was used to measure the surface roughness of nanocellulose films with measurement range of 524 µm, length of 6000 µm, duration of 60 sec and stylus force of 3 mg.

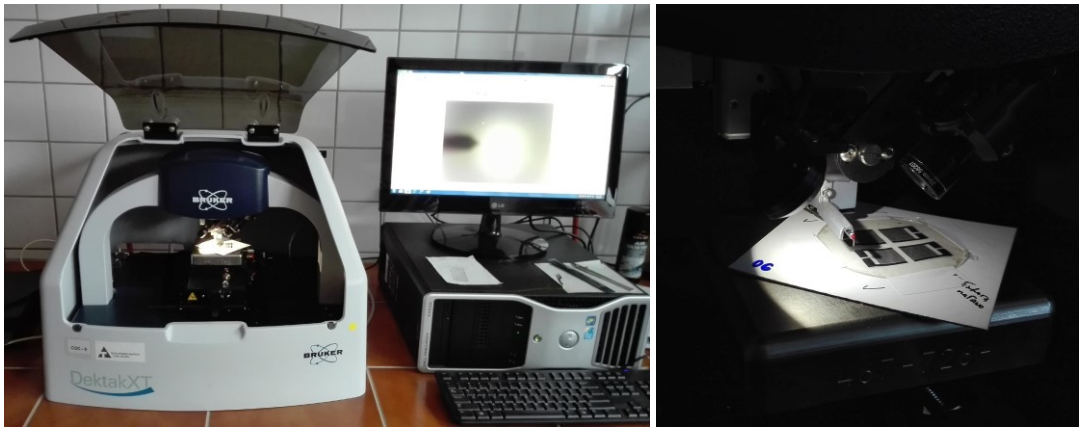

Figure 12: Dektak XT stylus profiler

Table 6: Measured roughness values [µm] from mechanical profilometry

Series	***With 40% PEG***	***Without PEG***
FHS_T38	2,68	1,65
FHS_T60	1,88	1,39
FS_T38	2,06	1,61
FS_T60	2,08	1,54

3) Analysis of coated paper substrates:

Gloss measurement

The gloss measurement of coated papers was performed with glossmeter Micro-TRI-gloss µ at the position 20, 60 and 85°. The results of gloss shown in the Table 7 were measured at 85°

for samples with 0, 1 and 2 layers of CNF and 60 ° for samples with 3 layers of CNF. The angle was selected based on the gloss range. Results of measurement made at 20, 60 and 80° angles are shown in the Figure 13. The surface of paper substrates with 3 layers of CNF is the smoothest, which causes the values of measured GU are highest.

Table 7: The gloss of paper substrates coated with CNF measured under selected angle

Number of CNF layers	***Average of GU***	***Modus of GU***	***Median of GU***
0	6.40	6.20	6.35
1	7.73	8.00	7.80
2	7.95	6.70	7.90
3	11.30	10.30	10.80

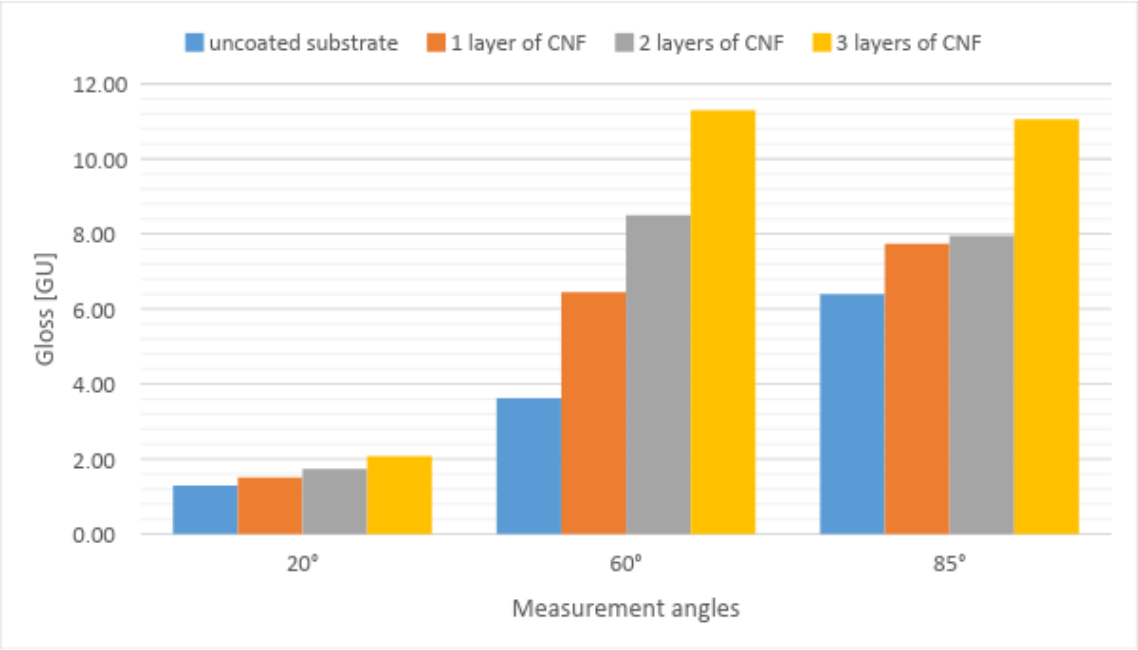

Figure 13: The values of gloss of paper substrates coated with CNF

4) Printing:

The printing on nanocellulose films was performed with Pneumatic flat screen printer Everbright S-200HF. On each type of nanocellulose film were printed 4 sensors using graphene nanoplatelet conductive ink (GVS7).

For printing on paper substrates with CNF coatings was utilized flexo IGT F1C printing press and Caibang CB100-E gravure proofing machine using silver nanoparticle ink (nanoflex AG315). The printing on PET film was also carried out for comparison purposes.

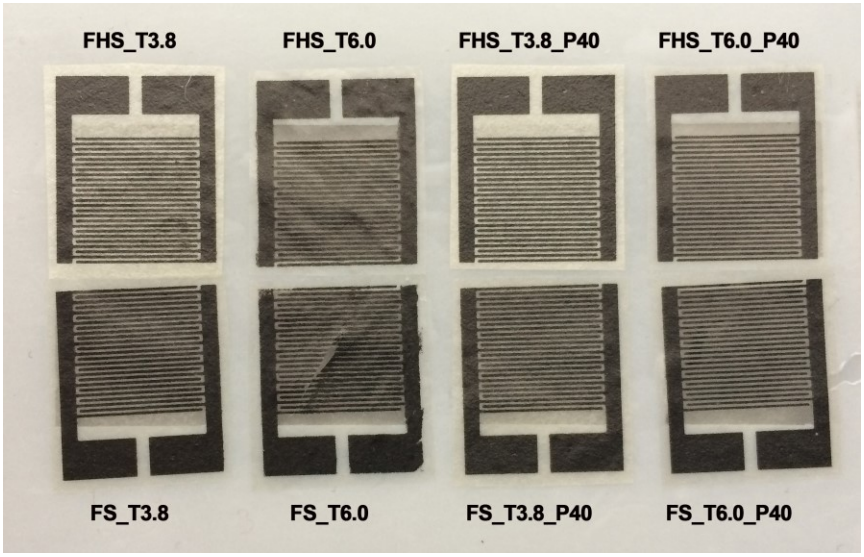

Figure 14: Sensors printed by screen printing technique on nanocellulose films

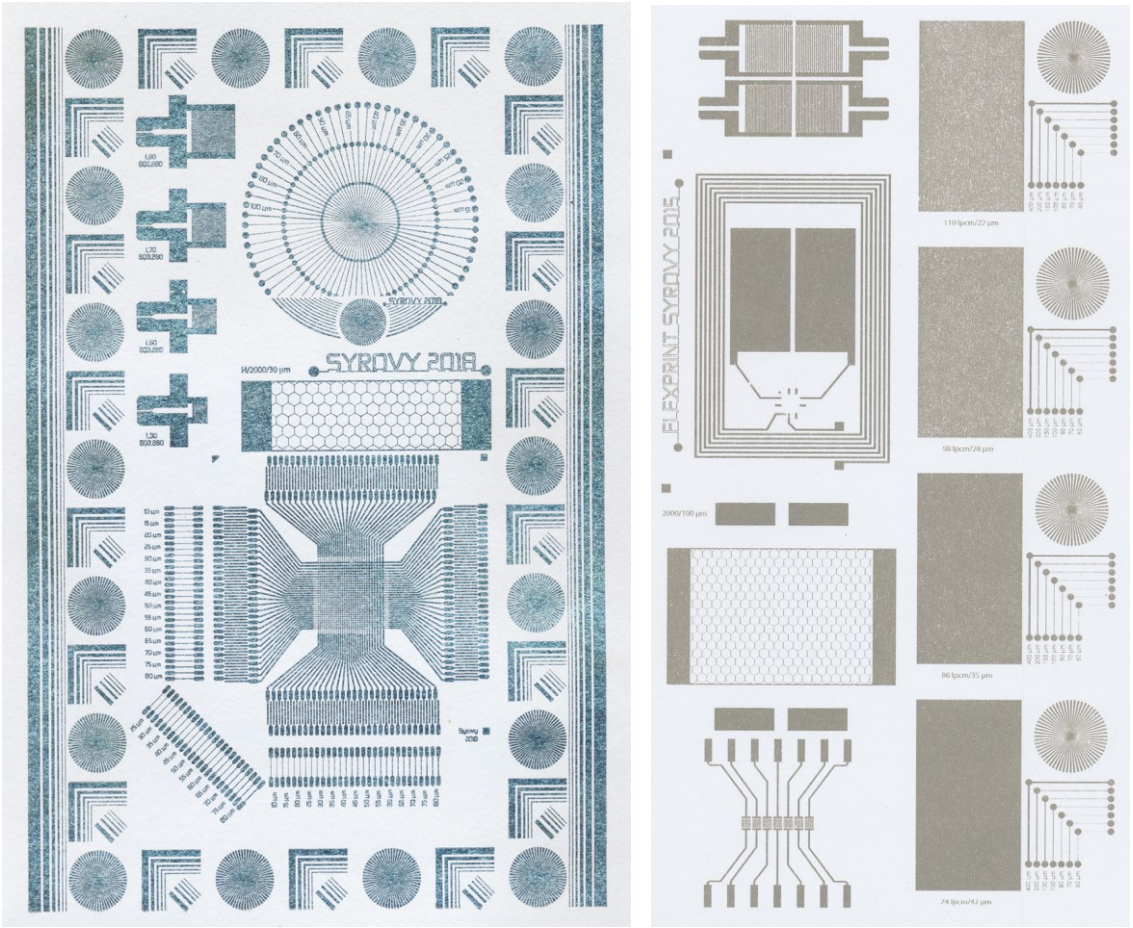

Figure 15: Designed structures printed a) by flexography on paper coated with 3 layers of CNF b) gravure printing on uncoated paper

5) Analysis of printed structures:

Gloss measurement:

The gloss of printed areas by gravure and flexo printing on coated papers were measured with glossmeter VIPTRONIC VIPGLOSS-I (instrument designed for measuring the shine papers,inks and varnishes in printing industry). The measurement results are summarized in Figure 16.

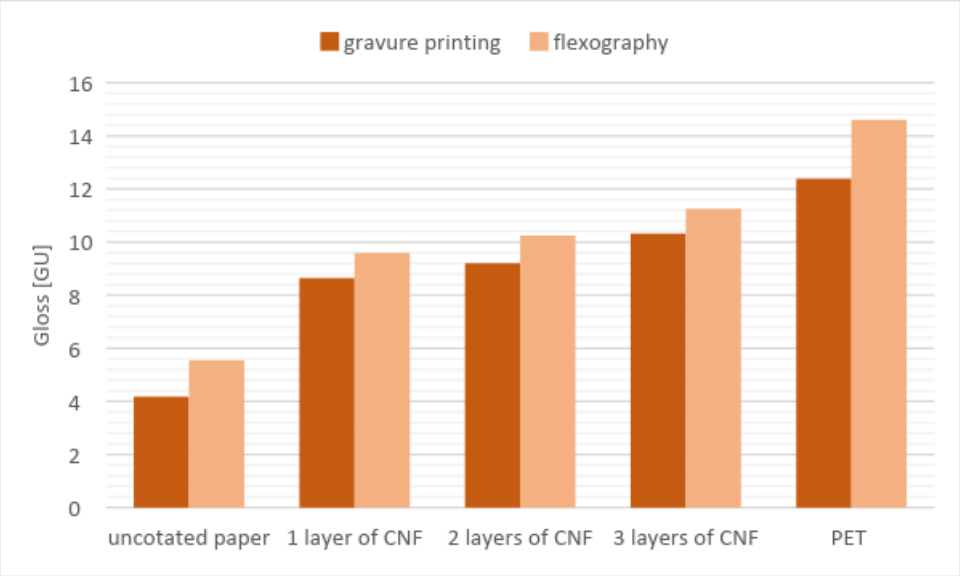

Figure 16: The values of gloss of printed areas by gravure and flexo printing technique

The results showed that gloss of printed areas has a increasing dependence on the number of CNF layers. The gloss of printed areas on paper substrates with 3 layers of CNF are close to the gloss values that can be achieved by printing on PET film.

Electrical measurement:

To evaluate the electrical properties of the structures printed on paper substrates coated with CNF was utilized digital multimeter Rigol DMM 3068 together with four point probe with needle spacing 8 mm. Resistance was measured at three locations of the printed area. Averaged results from four point resistance measurement for gravure printed areas are shown in Figure 17. The measured resistance of printed areas on paper substrates with 3 layers of CNF are close to the resistance values that can be achieved by printing on PET film. Also amount of ink transfer on substrate by using gravure printing is higher than ink transfer in flexo , resulting in achieved lower resistance values (Figure 18).

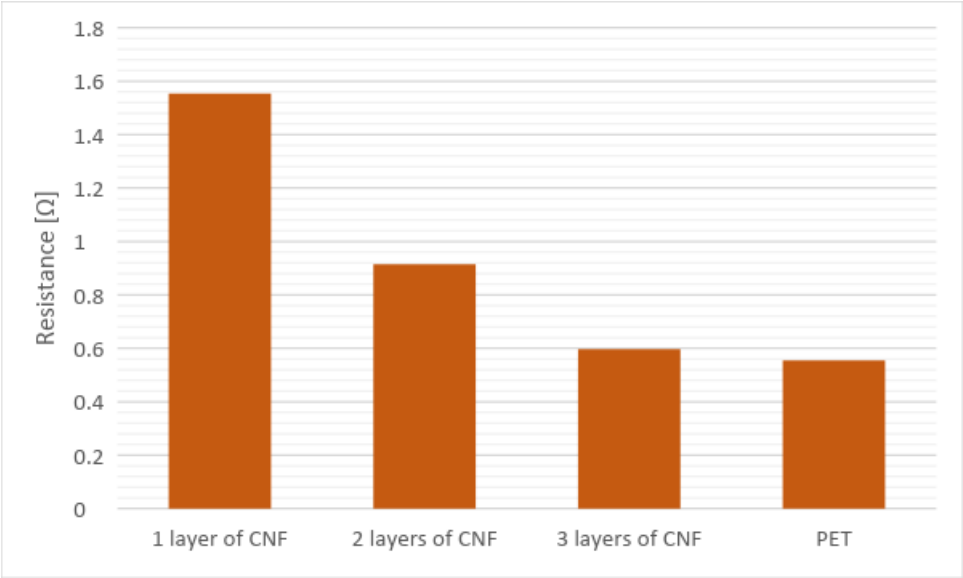

Figure 17: Measured resistance of gravure printed areas on PET and paper substrates coated with CNF

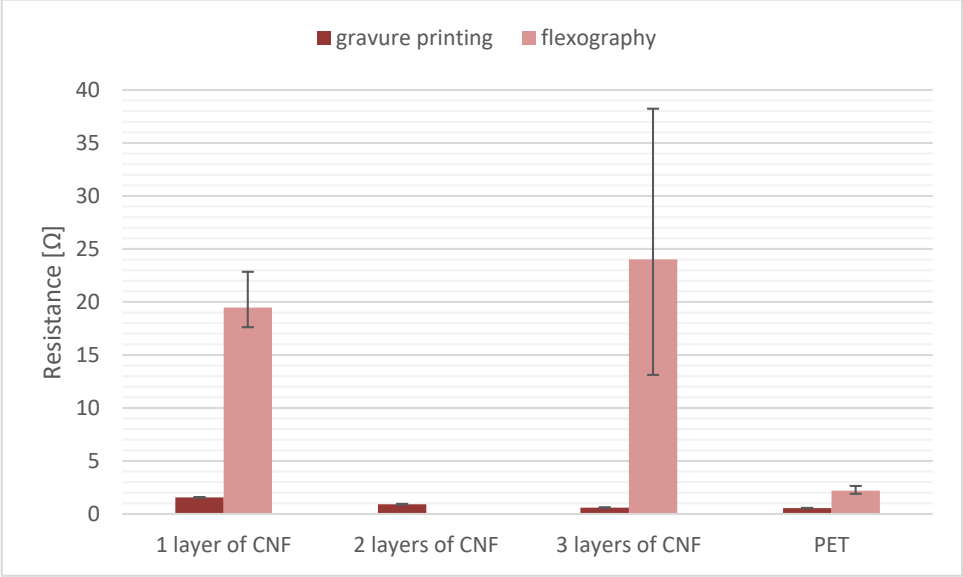

Figure 18: Measured resistance of printed areas by gravure and flexo printing technique

Optical miscrocopy:

The quality of structures printed by flexography and its geometrical properties were analyzed by optical microscopy. The analysis was performed with a Nikon LV microscope. Images of the size 1920 x 1200 pixels, were acquired with 100x magnification.
Images acquired from optical microscopy showed that CNF coating of paper substrates (and the thickness of layer of CNF) significantly affects the print quality. The CNF coating closes the pores of uncoated paper and avoid ink penetration to the paper structure, which improves homogeneity of printed lines and leads to better sharpness of the edges of printed structures.

Table 8: Minimum achieved linewidth of printed lines by flexographic printing technique on individual substrates

Substrate	***Minimum linewidth [µm]***
Uncoated paper	62.6
Paper with 1 layer of CNF	51.12
Paper with 2 layers of CNF	50.08
Paper with 3 layers of CNF	49.04
PET	35.47

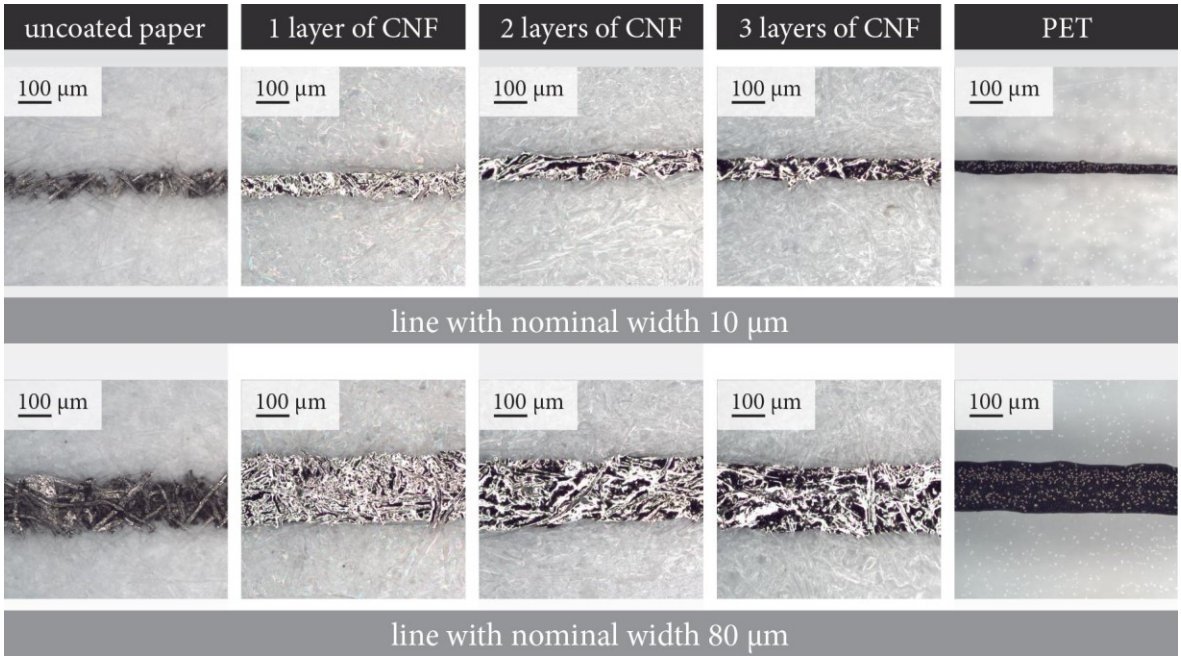

Figure 19: Optical images of flexography *printed lines on different substrates*

References:

[1] Parry RT: Principles and Applications of Modified Atmosphere Packaging of Foods Suffolk: Chapman & Hall; 1993.

[2] Gary CHINGA-CARRASCO, Nanci V. EHMAN, Jennifer PETTERSSON, María E. VALLEJOS, Malin W. BRODIN, Fernando E. FELISSIA, Joakim HÅKANSSON, María C. AREA, *Pulping and Pretreatment Affect the Characteristics of Bagasse Inks for Three-dimensional Printing*, ACS Sustainable Chemistry & Engineering, 2018, 6(3), 4068-4075 [cit. 2018-03-22], ISSN 2168-0485.