Cellulose nanopapers as tight aqueous ultra-filtration membranes

Andreas Mautner^{1*}, Koon-Yang Lee², Tekla Tammelin³, Aji P. Mathew⁴, Alisyn J. Nedoma⁵, Kang Li⁵ and Alexander Bismarck^{1,6,*}

¹ *Polymer & Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, South Kensington Campus, SW7 2AZ London, United Kingdom*

² *Department of Chemical Engineering, University College London, Torrington Place, WC1E 7JE London, United Kingdom*

³ *VTT Technical Research Centre of Finland, Biologinkuja 7, FI-02044 Espoo, Finland*

⁴ *Division of Materials Science, Department of Engineering Sciences and Mathematics, Luleå University of Technology, 97187 Luleå, Sweden*

⁵ *Department of Chemical Engineering, Imperial College London, South Kensington Campus, SW7 2AZ London United Kingdom*

⁶ *Institute for Materials Chemistry & Research, Polymer & Composite Engineering (PaCE) Group, Faculty of Chemistry, University of Vienna, Währingerstr. 42, A-1090 Vienna, Austria*

* Corresponding authors: e-mail: a.mautner@imperial.ac.uk, alexander.bismarck@univie.ac.at

Abstract: Recently, we have demonstrated the use of wood-derived nanocellulose papers, herein termed nanopapers, for organic solvent nanofiltration applications. In this study, we extend the use of these nanopapers to tight ultrafiltration (UF) membranes. The feasibility of such nanopaper-based UF membranes intended for use in water purification is shown. Four types of nanocelluloses, namely bacterial cellulose, wood-derived nanocellulose, TEMPO-oxidized cellulose nanofibrils and cellulose nanocrystals, were used as raw materials for the production of these nanopaper-based membranes. The resulting nanopapers exhibit a transmembrane permeance in the range of commercially available tight UF membranes with molecular weight cut-offs ranging from 6 to 25 kDa, which depends on the type of nanocellulose used. These molecular weight cut-offs correspond to average pore sizes of a few nanometres. The rejection performance of the nanopapers is on the border of nanofiltration and UF. We demonstrate that the pore size of the nanopapers can be controlled by using different types of nanocellulose fibrils.

Keywords: Bacterial Cellulose; Nanocellulose; Nanofiltration; Membrane

1 Introduction

Clean water nowadays is commonplace only in some parts of the world. The struggle for potable water is an all-day problem in many areas of our planet and with the number of people living in these regions still increasing, this problem is increasing [1]. Membrane technologies, such as nanofiltration (NF) or tight ultrafiltration (UF), are key for decentralizing industrial and domestic water treatment aiming at the removal of various contaminants, which are vital for providing clean water [2, 3]. Commercially available membranes used for this purpose are usually produced from polymers derived from fossil resources [4]. Moreover, membrane production processes require huge quantities of solvents, chemicals and energy [5]. Alternatively, renewable materials useful for the fabrication of NF or UF membranes have to be modified or dissolved beforehand (e.g. cellulose acetate or regenerated cellulose) and this also requires significant amounts of solvents and energy [6, 7]. Our vision is to provide a simpler, cleaner and faster production process for renewable UF and NF-membranes, reducing the environmental burden throughout their production and end-of-life. Cellulose fibres having a long tradition as filter materials dating back to ancient times [8], are a potential candidate to achieve this vision. Many of our everyday life and laboratory operations depend on filtration processes that are performed with cellulose-based filter papers. However, there are limitations when it comes to the removal of small molecular weight (M_w) compounds using filter papers.

Nanocellulose (NFC) has gained considerable attention in recent years due to its outstanding mechanical and chemical properties [9, 10], especially when used in composites [11, 12]. Nanocellulose used in paper form, herein termed nanopapers, possesses excellent mechanical properties, low thermal expansion coefficients, high optical transparency and good gas barrier properties [13-20]. Nanopapers possessing pores in the nanometer range could potentially be used in separation applications [21, 22]. Recently, we have demonstrated that nanopapers are a suitable candidate for the fabrication of organic solvent nanofiltration [23] membranes [22]. In addition to organic solvent nanofiltration membranes, such nanopapers are anticipated to serve as alternative for conventional polymer tight ultrafiltration membranes for water purification.

In this work we demonstrate the feasibility of such nanopapers for pressurized tight UF filtration for water purification. These nanopapers are produced using a papermaking process utilizing aqueous nanocellulose suspensions. This avoids the use of vast amounts of organic solvents commonly needed for the production of conventional tight UF polymer membranes [24]. Within nanopapers the nanofibrils are packed densely to form a network with pore-dimensions in the range of the diameter of the cellulose nanofibrils. This concept was mathematically proven by Zhang [25]. Thus, by utilizing different types of nanocelluloses and fibril diameters it should be possible to control the pore size and accordingly the permeance and molecular weight cut-off of the resulting membranes.

2 Experimental

2.1 Materials

Calcium sulfate dehydrate for testing the ion rejection and aluminum chloride hexahydrate (purity $\geq 97\%$) used as multivalent ions to coagulate the nanofibrillated cellulose in water suspension were purchased from BDH (Poole, UK) and used as multivalent ions to coagulate the nanofibrillated cellulose in water suspension. Poly(ethylene glycol) (PEG) standards (1, 4, 10, 20, 35, 50, 93 kDa) were purchased from Polymer Labs (Shropshire, UK) and used to quantify the molecular weight cut-offs of the nanopapers. Four different types of nanocellulose were studied in this work, namely bacterial cellulose, wood-based nanofibrillated cellulose, TEMPO-oxidized nanocellulose and cellulose nanocrystals. Commercial available bacterial cellulose (BC) was kindly supplied by *fzmb* GmbH (Bad Langensalza, Germany) in the form of wet pellicles containing 94 wt.-% water. The diameter of BC was found to be approximately 50 nm with fibril lengths of up to several micrometres [26]. Nanofibrillated cellulose was prepared by the mechanical grinding (MKZA10-15J Supermasscolloider, Masuko Sangyo Co., Kawaguchi, Japan) of chlorine free never-dried bleached birch kraft pulp (UPM-Kymmene Corporation, Pietarsaari, Finland) [19]. Herein, we termed this nanofibrillated cellulose as NFC-K. The pulp was passed through the grinder seven times and the final consistency of the aqueous gel-like NFC-K was 1.8 wt.-%. NFC-K fibrils possess a fibrous structure with diameters of

approximately 50 nm and lengths of up to several micrometres [19]. The carbohydrate composition of the pulp and the NFC produced from it are similar, consisting of 73 % glucose, 26 % xylose and 1 % mannose, respectively [27]. In addition to this, the pulp also contains 0.2 % of residual lignin and 0.09 % residual extractives [28]. The charge of the pulp, measured using the standard titration method (SCAN CM 65:02), was found to be approximately 0.04 mmol g⁻¹. (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (TEMPO) oxidized cellulose nanofibril grade (herein termed NFC-O) under the trade name of UPM Biofibrils was kindly supplied by UPM-Kymmene Corporation (Helsinki, Finland) as 2.5 wt.-% aqueous dispersion. Prior to mechanical disintegration, the never-dried bleached birch kraft pulp with similar chemical composition as the aforementioned NFC-K was TEMPO-oxidized [29]. The charge of the oxidized pulp, determined via conductometric titration (reported by the supplier), was found to be 1.03 mmol g⁻¹. The fibril diameter distribution varied within 5-25 nm, with 55 % of the nanofibrils possess a fibre diameter of 10-15 nm as reported by the supplier. Cellulose nanocrystals (CNC) were produced following a protocol as reported by Mathews et al. [30]. Briefly, debarked Norway spruce (*Picea abies*) wood chips with a dry matter content of 50–55 % were treated in a continuous mode of sulphur dioxide in a pressurized reactor at 200 °C. The slurry was then diluted with water and the residual solids were then separated from the liquid using a membrane filter press. The solid matter was then purified by Soxhlet extraction using toluene/acetone (2:1), followed by bleaching, washing and centrifugation. The purified cellulose was diluted to 2 wt.-% and passed through an APV 2000 high-pressure homogenizer (SPX, Soeborg, Denmark) 10 times at a pressure of 500 bars. The consistency of the obtained aqueous gel-like CNC, with diameters ranging from 5 to 15 nm, was 1.4 wt.-%.

2.2 Manufacturing of nanopapers

To produce BC-based nanopapers, the BC pellicles were first cut into small pieces (with a length of approximately 5 to 10 mm) and blended (Breville VBL065-01, Oldham, UK) for 2 min at a consistency of 0.2 wt.-% in deionized water to produce a homogeneous suspension of the BC-in-water. For CNC, NFC-K and NFC-O-based nanopapers, the nanocellulose-in-water suspension was adjusted from a starting consistency of 1.4, 1.8 or 2.5 wt.-%, respectively, to 0.3 wt.-%

prior to blending. For the case of NFC-O and CNC, 1 mmol L⁻¹ and 2 mmol L⁻¹ of AlCl₃, respectively, were added into the suspensions in order to coagulate the fibrils prior to filtration (see results and discussion later). These nanocellulose-in-water suspensions were then vacuum-filtered onto a cellulose filter paper (VWR 413, 5-13 µm pore size, Lutterworth, UK). The wet filter cake was wet-pressed under a weight of 10 kg between blotting papers (3MM Chr VWR, Lutterworth, UK) for 5 min to further absorb the excess water. These wet filter cakes, which had a measured moisture content of approximately 85 %, were then consolidated and dried in a hot-press (25-12-2H, Carver Inc., Wabash, USA) under a compression weight of 1 t for 1 h at 120 °C by sandwiching the wet filter cakes between fresh blotting papers and metal plates.

2.2.1 Zeta-potential of nanocellulose

The Zeta-potential (ζ-potential) of the nanocellulose was determined using electrophoresis (Brookhaven ZetaPALS analyzer, Holtsville, USA). The ζ-potential was calculated from the measured electrophoretic mobility using the Smoluchowski method. The measurements were conducted in 1 mM KCl supporting electrolyte at a nanocellulose concentration and temperature of 0.25 mg mL⁻¹ and 20 °C, respectively.

2.3 Characterization of nanopapers

2.3.1 Grammage and thickness of nanopapers

The grammage of nanopapers was determined by the ratio between the weight and cross-sectional area of 49 mm diameter (area = 1886 mm²) nanopapers. The thickness of the nanopapers was measured using a digital micrometre (705-1229, RS components, Corby, UK).

2.3.2 Nanopaper membrane performance

The membrane performance of our produced nanopapers was evaluated by measuring the nanopapers' permeance, molecular weight cut-off (*MWCO*) and ion rejection. The nanopapers' permeance were determined in dead-end Sterlitech HP4750 stirred cell (Sterlitech, Kent, USA). Discs of nanopapers with a diameter of 49 mm were cut, soaked in deionized water for at least three days to ensure equilibration, and placed on a sintered ceramic plate. Water was forced through

the nanopapers at 20 °C using nitrogen at a head pressure of 0.2 MPa and 1 MPa for BC, NFC-K and NFC-O nanopapers with grammages < 20 gsm and > 20 gsm, respectively. For CNC-based nanopapers, on the other hand, a head pressure of 0.2 MPa and 0.5 MPa were used for nanopapers possessing grammages < 20 gsm and > 20 gsm, respectively, for CNC papers, also the thicker ones, did not withstand a pressure of 1 MPa. The water permeance [$\text{L m}^{-2} \text{h}^{-1} \text{MPa}^{-1}$] for the active filtration area (1735 mm^2) was obtained by measuring the volume permeated per unit area per unit time.

MWCO is defined as the molecular weight of a molecule that has been rejected by 90 % [31]. In order to determine the *MWCO* of the nanopapers, the rejections of polymer molecules were quantified as a function of the molecular weights of the polymers. A feed solution consisting of a homologous series of PEG oligomer and polymer standards was used to obtain this rejection curve. The PEG solutions used was at concentration of 1 g L^{-1} . The *MWCO* was determined for nanopapers with 65 gsm. The amount and molecular weight of the filtrate was analysed using gel permeation chromatography (GPC, Viscotek GPCmax VE2001, VE3580 RI detector, Malvern, UK; columns: Agilent PL Aquagel-OH 30, $8\mu\text{m}$ $300 \times 7.5\text{mm}$ plus PL Aquagel-OH, Guard $8\mu\text{m}$ $50 \times 7.5 \text{ mm}$, Wokingham, UK).

The ion rejection of our nanopapers were determined by passing 0.1, 0.5 and 5 mM solutions of Ca^{2+} and SO_4^{2-} ions in deionized water through the nanopapers. The filtrate was analysed using ion chromatography (882 Compact IC plus with 863 Compact Autosampler, Metrohm, Herisau, Switzerland) and gravimetry. One part of the filtrate was analyzed by ion chromatography while the other one dried at 70 °C over night and the mass of solid CaSO_4 determined.

2.3.3 Morphology of the cellulose nanopapers

The morphology of the nanopapers was characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Prior to SEM, the nanopapers were mounted onto aluminium stubs using carbon tabs and gold coated (K550 sputter coater, Emitech Ltd, Kent, UK) for 2 min at 20 mA. SEM was carried out using LEO Gemini 1525 FEG-SEM (Leo Electron Microscopy Ltd, Cambridge, UK) at an accelerating voltage of 5 kV. AFM was conducted on a Bruker diInnova atomic force microscope in tapping mode to obtain height and phase images. Prior to AFM, the nanopapers were cut to size and mounted onto 12

mm magnetic AFM specimen discs using double-sided conductive carbon discs. The raw data were flattened to account for the bowed motion of the scanner.

3 Results and Discussion

3.1 Manufacturing of nanopapers

Our previous study [22] showed that filtering nanocellulose with very small diameters and high surface charge, such as NFC-O, was problematic. We solved this challenge by coagulating those nanofibrils prior to filtration by the addition of multivalent ions. Similarly, CNC proved to be difficult to be processed into nanopapers by vacuum-filtration. To enable efficient filtration and nanopaper production using CNC suspensions, we adapted this approach to flocculate the fibrils by changing the surface charge of CNC. We measured the ζ -potential of NFC-O and CNC, as well as BC and NFC-K (for completeness, as these nanocelluloses do not require flocculation in order to be efficiently filtered) as function of pH in a 1 mM KCl electrolyte (Fig. 1, left).

Fig 1.

For NFC-O and CNC, the negative ζ -potential at high pH and the low isoelectric point (iep), where $\zeta = 0$, is characteristic of an acidic solid surface. Both NFC-O and CNC contain a multitude of carboxylic acid groups [29, 30]. The magnitude of the ζ -potential (-41 mV for NFC-O and -60 mV for CNC, respectively) is determined by the relative pK_a and concentration of acidic surface groups present on the surface. By decreasing the pH the magnitude of the ζ -potential decreases as a result of the protonation of the acidic functional groups. Ultimately, the iep was reached by the further reduction of pH. The iep of NFC-O, NFC-K, CNC and BC were found to be 1.5 (by extrapolation), 2.2, 2.2 and 3.8, respectively. If we were to induce flocculation by changing the pH of both NFC-O and CNC suspensions in order to facilitate filtration, the pH of these suspensions will have to be adjusted to 1.5 and 2.2, respectively. This is rather harsh for most industrial processing equipment and could possibly result in acid hydrolysis of NFC-O [32].

The ζ -potential as measure of surface charge is not only dependent on the pH but also on the ionic strength of the supporting electrolyte. The ionic strength is most effectively increased by addition of multivalent ions. Accordingly, the point of zero charge (p.z.c.) was determined by measuring the ζ -potential as a function of AlCl_3 concentration. At the p.z.c., the nanocellulose fibrils have zero net surface charge and consequently, no electrostatic repulsion between the nanofibrils. This causes the whole nanocellulose suspension to form a single gel as the multivalent cations will specifically adsorb on the negatively charged nanocellulose surface, thereby reducing the ζ -potential until the p.z.c., beyond which the charge reverses (Fig. 1, right).

The p.z.c. was reached for NFC-O and CNC upon adjusting the electrolyte concentration of AlCl_3 to 1 mM and 2 mM, respectively. This allowed us to produce filter cakes using vacuum filtration that were subsequently consolidated into nanopapers by hot pressing. The consolidation and hot pressing steps under high compression pressure prevents the shrinkage of nanopapers and increases the (bulk) density of the sheets, resulting in better mechanical properties of the papers [20].

Nanopapers with grammages ranging between 10 and 85 g m^{-2} (gsm) were produced and used as membrane directly for filtration. When plotting the nanopaper grammage (G) as a function of paper thickness (d), a linear relationship was observed (Fig. 2). The slope of these curves corresponds to the bulk density of the nanopapers. These bulk densities were determined to be 1.01 g m^{-3} for BC, 1.05 g m^{-3} for NFC-K and 1.10 g m^{-3} for NFC-O and CNC, respectively. Moreover, this figure also shows that the thickness of the nanopaper membranes can be easily predicted and controlled by adjusting the grammage.

Fig 2

3.2. Nanopaper membrane performance

UF/NF membranes are usually characterized by two parameters: (i) the membrane permeance P and (ii) the rejection. The permeance describes the flux through a membrane (i.e. how much volume of water passes through the membrane per unit time, area and pressure), whilst the rejection is quantified by the molecular weight

cut-off (*MWCO*) [31] or the amount of ions [33], e.g. Ca^{2+} or SO_4^{2-} , retained by the membrane.

3.2.1. Permeance of nanopaper-based membranes

In the beginning of the measurement, the permeance decreased significantly. This is attributed to nanopaper compaction due to the applied pressure [34]. The compaction of the nanopapers is shown exemplarily in Fig. 3 for a 55 gsm CNC nanopaper.

Fig 3

The permeance decreased by a factor of 300 within five hours of operation at an applied driving pressure of 0.5 MPa. The reason for this is the reduction in membrane thickness, which leads to an increase in density and subsequently reduction in pore volume. Therefore, less solvent can be transported through the membrane per unit time interval. After a certain time, the permeance levels off and stays constant. To ensure the equilibrium permeance was reached before any permeance measurements, water was passed through the membranes until the permeance did not change more than 1 % within an hour. Data collection started only after this constant permeance was achieved. The dependence of P on the grammage of the nanopapers is depicted in Fig. 4. The permeance is dependent on the thickness (and thus the grammage) of the nanopapers. The absolute water permeance for nanopaper membranes with a grammage of around 80 gsm was around $1 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ for NFC-O and CNC papers and $5 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ for BC and NFC-K papers. For papers with a grammage of around 20 gsm the results are similar; BC and NFC-K nanopapers possess permeances just below $20 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ and NFC-O and CNC nanopapers of around $4 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$. In the case of very thin BC nanopapers (10 gsm) a permeance of $50 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ was even measured.

Fig 4

Furthermore, the type of nanocellulose also influences the permeance. BC and NFC-K have higher permeance than CNC and NFC-O at all grammages tested.

This is a result of the differences in the nanofibril diameters. BC and NFC-K have larger fibrils diameters compared to NFC-O and CNC (see Fig. 5). Fibrous networks can be seen, however the average fibre diameters as determined from AFM images differ. Those are 13.5 nm for CNC, 18.6 nm for NFC-O, 30.6 nm for NFC-K and 80.1 nm for BC. Thus, these nanopapers should be able to be used for filtration operations just as filter papers with the difference of a much smaller pore sizes of the filters. This is consistent with the observation that varying the aspect ratio of randomly packed high aspect ratio cylinders hardly affects the porosity of a fibre mat [35]. Since the number of fibrils per unit mass within the same volume element is higher for smaller fibrils, this results in a larger number of pores, which are smaller in diameter due to the constant porosity (around 35 %). Therefore, in conjunction with selecting the appropriate nanocellulose fibril, the permeance of the nanopapers can be controlled over a wide range by varying the grammage of the nanopapers.

Fig 5

3.2.2. Rejection performance of nanopaper membranes

The *MWCO* is defined as the molecular weight of which 90 % of a solute is rejected [31]. In our case the solute is PEG dissolved in deionized water with molecular weights between 1 and 93 kDa. The rejection as a function of the molecular weight of PEG standards is shown for BC, NFC-K, NFC-O and CNC nanopapers with 65 gsm in Fig. 6. From the graph, it can be seen that NFC-O exhibits the lowest *MWCO*, followed by NFC-K. For BC and CNC no *MWCO* could be determined within the range of standards tested. The *MWCO* for NFC-O was found to be 6 kDa, corresponding to a hydrodynamic radius of PEG, which represents the pore size, of 2.4 nm [36]. Thus, a *MWCO* close to the range of NF was observed. For NFC-K nanopapers the *MWCO* was 25 kDa, which corresponds to a hydrodynamic radius of 5 nm [36]. It was demonstrated that it is possible to adjust the pore dimensions of the resulting nanopaper membranes by using cellulose nanofibrils of different diameters (see Fig. 5, around 19 nm for NFC-O and 31 nm for NFC-K). As aforementioned, this is a result of a reduced pore size due to the random packing of cylinders with smaller diameters.

Fig 6

In the case of BC, the PEG standard with the highest M_w (93 kDa, corresponding to approximately 10 nm hydrodynamic radius) was rejected only to 75%. To alternatively characterize the pore dimensions, BET measurements were performed. The results from BET, which provided an average pore size of 16 nm, corresponds well with the findings from the rejection experiments. The larger pore size of BC nanopapers is explained by the larger diameter of the BC fibrils [37] thus leading to larger pore sizes as outlined above. For CNC, BET was also performed to have an alternative measure of the pore dimensions, but repeatedly did not give any reliable results. The reason for this is unknown. However, from the results of rejection and permeance, it can be concluded that a similar pore size is to be expected. We hypothesis that the shorter length of the crystals compared to nanofibrils led to the crystals overlap on a shorter scale. As a result, the network formed is inherently weaker due to fewer interactions per crystal, whereby defects such as pinholes that can negatively influence the rejection, are formed more easily. Furthermore, the shorter lengths of the crystals will also lead to a much higher number of crystals, and thus crystals ends, which are inherent defects within the network, whose higher number sacrifices again the retention behavior, taking place in the network-formation.

For NF membranes used for H₂O purification the rejection of ions is more commonly quantified. Therefore, for NFC-O nanopapers, ion rejection experiments were performed to further characterize the filtration performance. From an aqueous solution containing 0.1 mM of Ca²⁺ and SO₄²⁻ ions, 34 % of the ions were rejected. For 0.5 and 5 mM, this value was 22 and 5 %, respectively. Thus, NFC-O membranes were not only to be capable of rejection molecules of 6 kDa, but also rejecting ions to a certain extent. A similar behaviour, of rejecting SO₄²⁻ ions at different concentrations, was reported for conventional polymer NF membranes [33].

4. Conclusions

Nanopapers using four different types of nanocellulose were manufactured and it was demonstrated that these nanopapers are suitable for tight ultrafiltration

operations. It was observed that the permeance of nanopapers was governed by the type of nanocellulose and thus the dimensions of the nanofibrils and the grammage of the produced nanopapers. The *MWCO* was also determined by the dimensions of the nanofibrils, which determine the pore dimensions of the nanopapers. Tailoring the membrane performance by selecting nanofibrils with different diameters and lengths and making nanopapers with different grammages might produce membranes for a wide range of potential applications. By now the rejection performance of nanopaper filters is reduced by the fact that the nanofibrils do not exhibit uniform diameters but rather a quite big size distribution. If NFC with fibrils of evenly distributed diameters eventually could be produced, potentially even thinner active membrane layers could be manufactured. This would lead to a reduced *MWCO* and improved permeance, drastically improving the performance of these types of tight ultrafiltration membranes.

Acknowledgments

The authors greatly acknowledge the funding provided by EU FP7 project NanoSelect (Grant No. 280519). We also would like to express our thanks to fzmb and UPM for providing the base materials and to Konstanze Seidler (TU Vienna) and Dr Ivan Zadrazil (Imperial) for performing the GPC-measurements.

References

- [1] M. Montgomery, M. Elimelech, *Environ. Sci. Technol.*, 4 (2007) 17-24.
- [2] R.J. Petersen, *J. Membr. Sci.*, 83 (1993) 81-150.
- [3] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, *Nature* (London, U. K.), 452 (2008) 301-310.
- [4] K.P. Lee, T.C. Arnot, D. Mattia, *J. Membr. Sci.*, 370 (2011) 1-22.
- [5] K. Li, *Ceramic Membranes for Separation and Reaction*, John Wiley & Sons, Ltd., Chichester, UK, 2007.
- [6] M. Henmi, K. Nakatsuji, T. Ichikawa, H. Tomioka, T. Sakamoto, M. Yoshio, T. Kato, *Adv. Mater. (Weinheim, Ger.)*, 24 (2012) 2238-2241.
- [7] A.A. Mungray, Z.V.P. Murthy, *Ionics*, 18 (2012) 811-816.
- [8] M.N. Baker, *The Quest for Pure Water: the History of Water Purification from the Earliest Records to the Twentieth Century*, American waterworks assoc., Denver, 1948.
- [9] D. Klemm, F. Kramer, S. Moritz, T. Lindstroem, M. Ankerfors, D. Gray, A. Dorris, *Angew. Chem., Int. Ed.*, 50 (2011) 5438-5466.
- [10] P. Chen, S.Y. Cho, H.-J. Jin, *Macromol. Res.*, 18 (2010) 309-320.
- [11] S.J. Eichhorn, A. Dufresne, M. Aranguren, N.E. Marcovich, J.R. Capadona, S.J. Rowan, C. Weder, W. Thielemans, M. Toman, S. Renneckar, W. Gindl, S. Veigel, J. Keckes, H. Yano, K. Abe, M. Nogi, A.N. Nakagaito, A. Mangalam, J. Simonsen, A.S. Benight, A. Bismarck, L.A. Berglund, T. Peijs, *J. Mater. Sci.*, 45 (2010) 1-33.
- [12] J.J. Blaker, K.-Y. Lee, A. Bismarck, *J. Biobased Mater. Bioenergy*, 5 (2011) 1-16.

- [13] S.-J. Chun, S.-Y. Lee, G.-H. Doh, S. Lee, J.H. Kim, *J. Ind. Eng. Chem. (Amsterdam, Neth.)*, 17 (2011) 521-526.
- [14] A. Dufresne, *Nanocellulose: From Nature to High Performance Tailored Materials*, Walter de Gruyter & Co, Berlin/Boston, 2012.
- [15] J. Gutierrez, S.C.M. Fernandes, I. Mondragon, A. Tercjak, *ChemSusChem*, 5 (2012) 2323-2327.
- [16] M. Henriksson, L.A. Berglund, P. Isaksson, T. Lindström, T. Nishino, *Biomacromolecules*, 9 (2008) 1579-1585.
- [17] L. Hu, G. Zheng, J. Yao, N. Liu, B. Weil, M. Eskilsson, E. Karabulut, Z. Ruan, S. Fan, J.T. Bloking, M.D. McGehee, L. Wagberg, Y. Cui, *Energy Environ. Sci.*, 6 (2013) 513-518.
- [18] J. Huang, H. Zhu, Y. Chen, C. Preston, K. Rohrbach, J. Cumings, L. Hu, *ACS Nano*, 7 (2013) 2106-2113.
- [19] K.-Y. Lee, T. Tammelin, K. Schulfter, H. Kiiskinen, J. Samela, A. Bismarck, *ACS Appl. Mater. Interfaces*, 4 (2012) 4078-4086.
- [20] M. Österberg, J. Vartiainen, J. Lucenius, U. Hippi, J. Seppälä, R. Serimaa, J. Laine, *ACS Appl. Mater. Interfaces*, 5 (2013) 4640-4647.
- [21] S.-J. Chun, E.-S. Choi, E.-H. Lee, J.H. Kim, S.-Y. Lee, S.-Y. Lee, *J. Mater. Chem.*, 22 (2012) 16618-16626.
- [22] A. Mautner, K.Y. Lee, P. Lahtinen, M. Hakalahti, T. Tammelin, K. Li, A. Bismarck, *Chem. Commun.*, 50 (2014) 5778-5781.
- [23] P. Vandezande, L. E. M. Gevers, I. F. J. Vankelecom, *Chem. Soc. Rev.*, 37 (2008), 365-405.
- [24] I. Soroko, Y. Bhole, A.G. Livingston, *Green Chem.*, 13 (2011) 162.
- [25] W. Zhang, *Experimental and Computational Analysis of Random Cylinder Packings with Applications*, Ph.D. Thesis, Louisiana State University, 2006.
- [26] K.-Y. Lee, A. Bismarck, *Cellulose*, 19 (2012) 891-900.
- [27] P. Eronen, M. Österberg, S. Heikkinen, M. Tenkanen, J. Laine, *Carbohydr. Polym.*, 86 (2011) 1281-1290.
- [28] S. Asikainen, A. Fuhrmann, L. Robertsen, *Nord. Pulp Pap. Res. J.*, 25 (2010) 269-276.
- [29] T. Vuorinen, T. Paeaekkoenen, M. Nuopponen, *WO2012168562A1* (2012).
- [30] A.P. Mathew, K. Oksman, Z. Karim, P. Liu, S.A. Khan, N. Naseri, *Ind. Crop. Prod.*, 58 (2014) 212-219.
- [31] Y.H. See Toh, X.X. Loh, K. Li, A. Bismarck, A.G. Livingston, *J. Membr. Sci.*, 291 (2007) 120-125.
- [32] J.F. Saeman, *Ind. Eng. Chem.*, 37 (1945) 43-52.
- [33] M. Ernst, A. Bismarck, J. Springer, M. Jekel, *Journal of Membrane Science*, 165 (2000) 251-259.
- [34] E. Gibbins, M. D'Antonio, D. Nair, L.S. White, L.M. Freitas dos Santos, I.F.J. Vankelecom, A.G. Livingston, *Desalination*, 147 (2002) 307-313.
- [35] M. Novellani, R. Santini, L. Tadrist, *Eur. Phys. J. B*, 13 (2000) 571-578.
- [36] J.K. Armstrong, R.B. Wenby, H.J. Meiselman, T.C. Fisher, *Biophys. J.*, 87 (2004) 4259-4270.
- [37] K.-Y. Lee, G. Buldum, A. Mantalaris, A. Bismarck, *Macromol. Biosci.*, 14 (2014) 10-32.

Figure captions

Fig. 1. ζ -potential = $f(\text{pH})$ for BC, NFC-K, NFC-O and CNC fibrils in water (left); and ζ -potential of NFC-O and CNC in water with different concentrations of AlCl_3 on a semi-log scale to highlight the efficacy of multivalent ions (right).

Fig. 2. Grammage [gsm] vs. thickness [μm] for papers made from BC (dot), NFC-O (square), CNC (rotated square), and NFC-K (up triangle).

Fig. 3. $P = f(\text{time})$: CNC paper with 55 gsm at 0.5 MPa. The permeance decreased during testing by a factor of 300.

Fig. 4. $P = f(\text{grammage})$: nanopapers made from BC (dot), NFC-K (up triangle), NFC-O (square) and CNC (down triangle). Please note: the error bars are smaller than the symbols.

Fig. 5. SEM (left) and AFM (right) images of (a) BC, (b) NFC-K, (c) NFC-O and (d) CNC.

Fig. 6. Rejection of PEG = $f(M_w)$ for BC (dot), NFC-K (up triangle), NFC-O (square) and CNC (down triangle): $MWCO$ is the molecular weight of which 90 % is rejected.

Figures

Fig. 1.

Fig. 2.

Fig. 3

Fig. 4.

Fig. 5.

Fig. 6.