Supporting Information for: Nanopapers for Organic Solvent Nanofiltration

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Supporting Figures:



Fig. S1. Correlation between grammage and thickness of NFC-O and -K papers.



Fig. S2. P (water) = f(time): NFC-O-paper with 30 gsm.

Materials:

Aluminium chloride hexahydrate (purity \geq 97%) was purchased from BDH (Poole, UK), tetrahydrofuran (GPC grade) from Fisher Chemical (Loughborough, UK), n-hexane (HPLC grade) from VWR (Leuven, B), PS-standards from Alfa Aesar (Heysham, UK) and PEG-standards from Polymer Labs (Shropshire, UK).

Nanofibrillated cellulose (NFC-K) was produced by mechanical grinding of elemental chlorine free (ECF) never-dried bleached birch kraft pulp (UPM-Kymmene Corporation, Pietarsaari, Finland) as also described in Lee et al.¹⁴. The carbohydrate composition of the pulp and the NFC produced from were similar. The composition was 73% glucose, 26% xylose and 1% mannose.¹ The pulp furthermore contained 0.2% residual lignin and 0.09% residual extractives.² The charge of the pulp was approximately 0.04 mmol/g, which was determined using the standard titration method (SCAN CM 65:02). The grinding process of the kraft pulp was conducted using a Masuko Mass Colloider (MKZA10-15J Supermasscolloider, Masuko Sangyo Co., Kawaguchi, Japan). The pulp was passed through the grinder seven times and the final consistency of the aqueous gel-like NFC-K was approximately 1.8 wt-%. NFC-K fibrils possess a fibrous structure with diameters of approximately 50-100 nm and lengths of several micrometres.¹⁴

TEMPO-oxidized cellulose nanofibrils (NFC-O) with the trade name of UPM Biofibrils was supplied as 2.5 wt-% aqueous dispersion by UPM-Kymmene Corporation, Helsinki, Finland, for testing purposes. Prior to mechanical disintegration, the never-dried bleached birch kraft pulp with the similar chemical composition as above was TEMPO-oxidized as described elsewhere^{3,4}. The charge of the oxidized pulp was 1.03 mmol/g determined by conductometric titration as reported by the supplier. The fibril diameter distribution varied within 5-25 nm (55% of fibrils possess the diameter of 10-15 nm) as also reported by the supplier. In addition to this, the size of the fibrils was analysed using Atomic Force Microscopy (AFM). AFM imaging was performed using a Nanoscope IIa Multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA, USA). The nanofibril samples were prepared by spin coating a dilute NFC dispersion on a silica surface as described in Ahola et al.⁵ The images were scanned in tapping mode in air using silicon cantilevers (µMasch, Tallinn, Estonia) with nominal resonance frequencies of 320-360 kHz. No image processing except flattening was made and at least 5 areas on each sample were characterised. The diameter of the fibrils analysed using AFM gives a slightly higher average value of approximately 30 nm. This is due to the fact that the actual width of the fibrils is lower as that gained by AFM due to the finite AFM tip dimensions and curvature.

¹ P. Eronen, M. Osterberg, S. Heikkinen, M. Tenkanen and Laine J., *Carbohydr. Polym.* 2011, **86**, 1281–1290.

² S. Asikainen, A. Fuhrmann and L. Robertsen, Nord. Pulp Pap. Res. J. 2010, 25, 269–276.

³WO Pat., WO 2012/168562 A1, 2012.

⁴ R. Pönni, T. Pääkkönen, M. Nuopponen, J. Pere and T. Vuorinen, *Cellulose*, 2014, under revision.

⁵ S. Ahola, J. Salmi, L.-S. Johansson, J. Laine and M. Österberg., *Biomacromolecules*, 2008, **9**, 1273-1282.



Fig. S3. AFM topography image with typical height profile (left) and fibril diameter-distribution provided by supplier (right) of NFC-O. The AFM image size is 2 μ m × 2 μ m