Supporting information for "Tailoring the Performance of Nanocellulose-based Multilayer-Barrier Paperboard using Biodegradable-Thermoplastics, Pigments, and Plasticizers"

Rajesh Koppolu[1,4*], Johanna Lahti[2,4], Tiffany Abitbol[3,5], Christian Aulin[3,6], Jurkka Kuusipalo[2], and Martti Toivakka[1]

[1]Laboratory of Natural Materials Technology, Åbo Akademi University, Turku, 20500 Finland
[2]Paper Converting and Packaging, Tampere University, Tampere, 33100, Finland
[3]RISE Research Institutes of Sweden, Stockholm, 11428, Sweden
[4]Biomaterial Processing and Products, VTT Technical Research Center of Finland, Espoo, 02150, Finland
[5]Materials Science and Engineering, EPFL - École Polytechnique Fédérale de Lausanne, Lausanne, CH-1015, Switzerland
[6]Holmen Iggesund, Stockholm, 11451, Sweden
[*]Corresponding author. Email: rajesh.koppolu@vtt.fi

1 Nanocellulose production process

MFC production

MFC was produced by passing a 2.5% solids content bleached softwood kraft pulp through a ultrafine grinder (Masuko MKZB15-50J Supermasscolloider) with specialized plates until the fines content was over 90%, which was measured using a MorFi fiber and shive analyzer. The resulting MFC suspension was pressed to a 20% solids content cake for shipping and was finally diluted to 2.5 % for roll-to-roll coating.

CNF production

A dissolving grade pulp was carboxymethylated to a charge density of 600 $\pm$ 50 $\mu mol.g^{-1}$ (measured using conductometric titration, as described in the work from Wågberg et al. (1987)). The carboxymethylated pulp was later fibrillated using a high-pressure microfluidizer (Microfluidics M110EH Microfluidizer®), using a 400 plus 200 μm chamber configuration. The defibrillation was further continued by three extra passes through the microfluidizer in a 200 plus 100 μm chamber configuration to obtain the CNF suspension at 2% solids content, and was used as such for roll-to-roll coating.

2 Rheology

Description of rheology measurements

A modular compact rheometer, MCR 702 (Anton-Paar GmbH, Austria) was used to measure rotational and oscillatory rheology parameters for the suspensions using Couette geometry (bob diameter - 26.65 *mm*, effective bob length - 40 *mm*, cup diameter - 28.93 *mm*, working gap - 5.7 *mm*) with smooth surfaces at 25 ^oC. Prior to each measurement, the samples were pre-sheared at 100 s^{-1} for 60 *s* and allowed to equilibrate for 120 *s* to remove any pre-existing heterogenities in the suspension (Naderi et al.,

2016). Rotational viscosity measurements were performed in controlled shear rate mode with logarithmic shear rate ramp-up/down from 0.01 - 1000 - 0.01 s^{-1} (10 points/decade) with dynamic acquisition time that changes logarithmically from 60 - 1 - 60 s and an additional 4 s at 1000 s^{-1}. Data from the ramp-down curve was considered for analysis to avoid any transient viscosity effects that might show up in the ramp-up curve. Oscillatory strain sweep measurements were performed to evaluate linear viscoelastic (LVE) range and yield stress of the suspensions. Oscillatory strain was logarithmically varied from 0.01 - 100 % (10 points/decade) with logarithmic decrease in acquisition time from 100 - 10 s at a constant angular frequency of 10 $rad.s^{-1}$.

Influence of CMC addition on yield stress

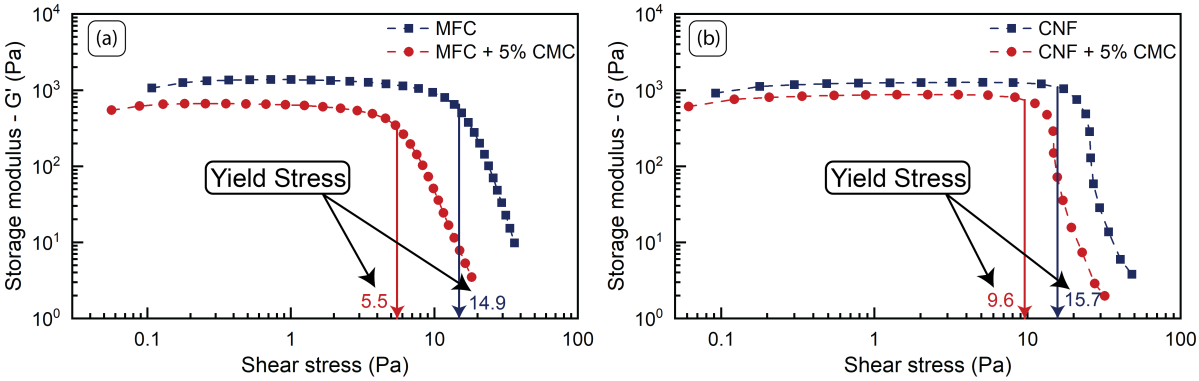

Figure S 1: Storage modulus (G') vs. shear stress for, (a) MFC and MFC + 5% CMC (both suspensions at 2.5% solids content); (b) CNF and CNF + 5% CMC (both suspensions at 2% solids content)

CMC addition clearly reduces yield stress of the suspension, which in turn has a positive impact on coating uniformity. Lower yield stress also makes it easier to pump such high-viscosity suspensions.

Viscosity curves for MFC-kaolin suspensions

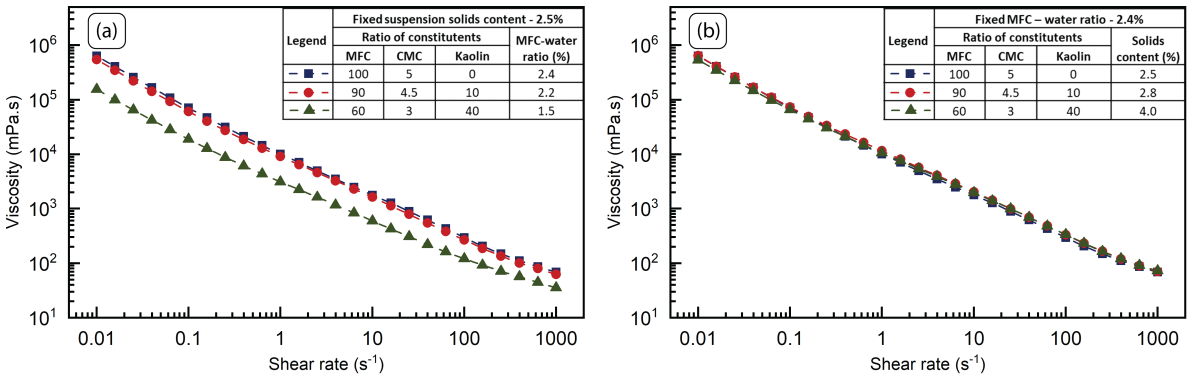

Figure S 2: Viscosity vs. shear rates for MFC-kaolin suspensions, (a) fixed suspension solids content of 2.5% with varying MFC-kaolin and MFC-water ratios; (b) fixed MFC-water ratio of 2.4% with varying MFC-kaolin ratio and suspension solids contents

It can be clearly seen from Figure S2 that viscosity of MFC-kaolin suspensions mainly depends on MFC-water ratio. Therefore, the solids content of MFC-kaolin suspensions was adjusted to maintain a constant

MFC-water ratio during R2R coating. This results in a higher solids content at higher kaolin addition levels, which in-turn reduces the energy needed to dry the wet coated layer and allows for a higher coating speed.

3 Experimental procedure for barrier measurements

Mineral oil barrier

10 *ml* of n-heptane (Sigma Aldrich) was first placed in an aluminum cup with a threaded flanged ring (EZ-Cup Vapometer Permeability Cup from Thwing-Albert, U.S.A). A few pieces of sponge were placed in the cup to achieve quick saturation vapor pressure for n-heptane. The coated sample was placed in-between two Viton™ gaskets and then placed on the top of the cup (coated side facing n-heptane). Finally, a teflon ring was placed on top and the whole assembly was sealed using the threaded upper ring. The amount of n-heptane vapors escaped through the coated sample during a 24 hour period was reported as $g.m^{-2}.day^{-1}$.

Grease barrier

This test was done according to ASTM F119-82 with slight modifications. The coated samples were first placed on top of a scanner (Espon V39) with coated side facing up. Two pieces of Whatman® filter paper (Grade 1, 20 *mm* diameter) were placed on the test sample, and 6 drops of Olive oil (Sigma Aldrich) were added onto the filter paper. 50 *g* weights (20 *mm* diameter) were finally placed on the oil-filled filter paper and the whole setup was placed in an oven at 40 ^oC. The underside of the samples were scanned at an interval of 30 *min* over a period of 500 hours. The scanned images were then analyzed using an image processing software (Fiji-ImageJ), and the time taken for the oil to penetrate to the underside and cover 1% of the sample area was reported.

4 Description of coating process

A laboratory scale roll-to-roll mini-pilot coater (R.K. PrintCoat Instruments, U.K.) was modified in-house and fitted with a custom-built slot-die applicator to coat nanocellulose suspensions onto the paperboard. Figure S3a shows the schematic of the slot-die coating process. Nanocellulose suspension is supplied to the slot-die from a pressurized feed vessel via a gear pump. Inside the slot-die, the suspension first enters into a distribution channel (diameter 25 *mm*) and then passes through a narrow gap (slot-gap) before exiting the slot-die. Pressure drop across this gap results in high-shear rates which reduces the apparent viscosity of shear-thinning nanocellulose suspension. The low-viscosity suspension exiting the slot-die is then applied onto a moving substrate to obtain a uniform wet-coated layer. The slot-die has a coating width of 100 *mm* and length of the narrow slot-gap region is ca. 50 *mm*. Depending on the fibril size, suspension solids content, and viscosity, slot-gap is adjusted between 500 -1000 μm to avoid clogging the slot entrance. Figures S3b and c show a close-up and cross-section of the slot-die applicator, respectively. The slot-die is fixed at a 3 o'clock position with a downward offset of 5 *mm* against the backing roll center line (see Figure S3a), thus allowing the slot-die's top lip to function as a metering device. The advantage is that, this allows the coater's line speed to be set independent of the minimum flow rate required to achieve sufficient fluidization (low viscosity) of the nanocellulose suspension. Wet coating thickness is set by the gap between substrate and slot-die's top lip, and coating speed depends on the wet coating thickness, suspension solids, and maximum drying capacity of the coater.

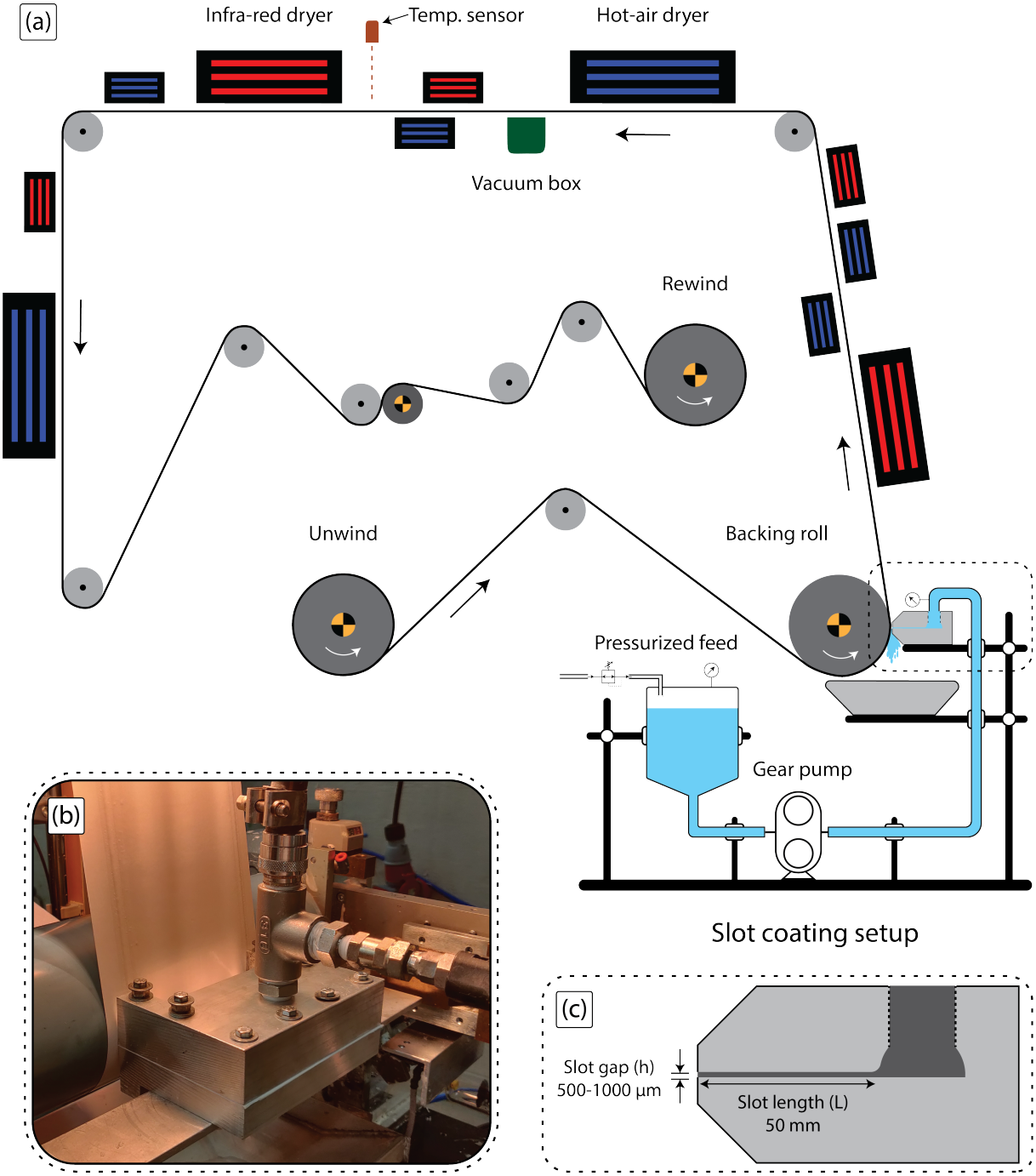

Figure S 3: (a) Schematic of roll-to-roll slot-die coating of nanocellulose; (b) Slot-die coating applicator; (c) Cross-section of the slot-die

5 HVTR for MFC-kaolin composite films

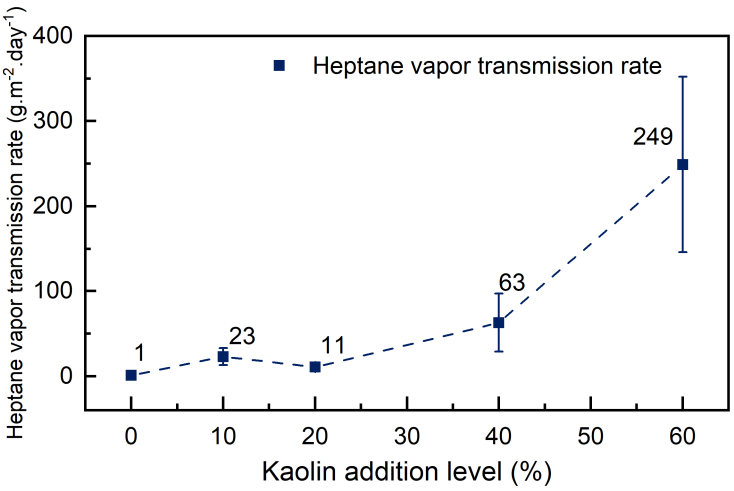

Figure S 4: Heptane vapor transmission rate of MFC-kaolin composite films

6 Mechanical properties of CNF films

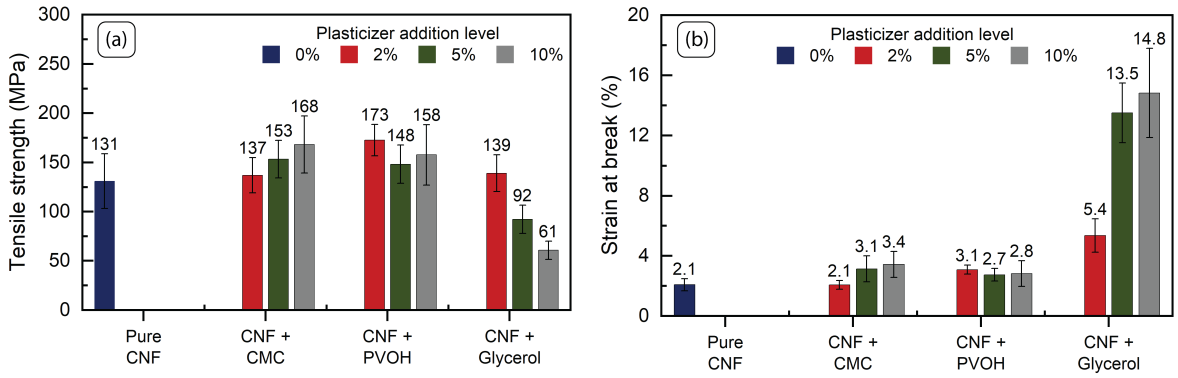

Figure S 5: (a) Tensile strength and (b) Strain at break for CNF films with CMC, PVOH, and Glycerol plasticizers

There is a slight increase in strain at break for CNF films with CMC or PVOH as plasticizers. On the other hand adding glycerol to CNF increases the strain at break for CNF films from 2.1 to 5.4% at 2% addition level, and to 14.8% at 10% addition level. Therefore, adding glycerol could result in a flexible CNF coated layer, which could have a positive impact on barrier properties. Glycerol addition lowers the tensile strength of CNF films, but it is less of an issue when CNF is applied as a thin layer on paper substrates where the strength is provided by the base substrate.

7 Peel test example figure

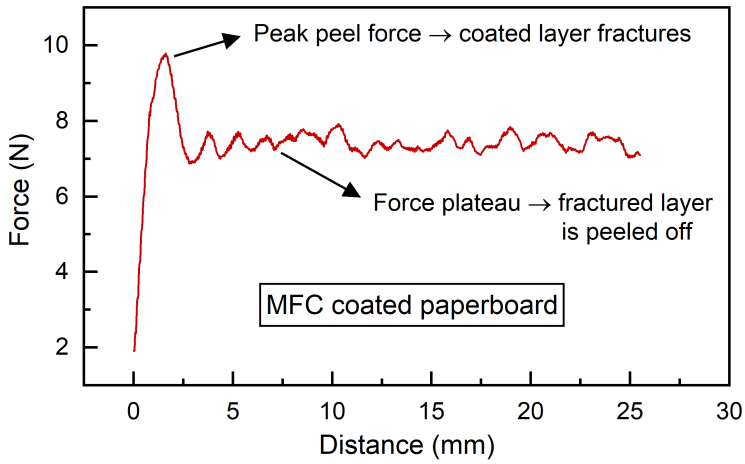

Figure S 6: Adhesion test - peel force vs. distance for MFC coated paperbaord

8 SEM surface and cross-section images

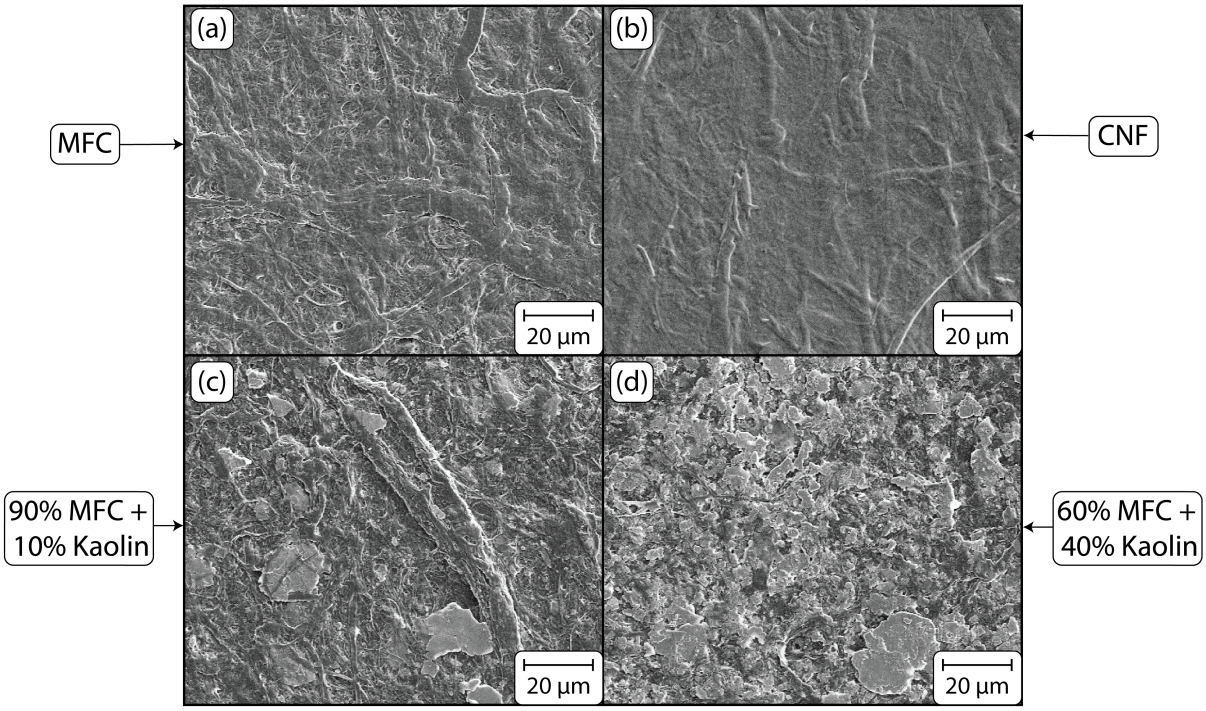

Figure S 7: SEM surface images for, (a) MFC, (b) CNF, (c) 90% MFC + 10% Kaolin, and (d) 60% MFC + 40% Kaolin

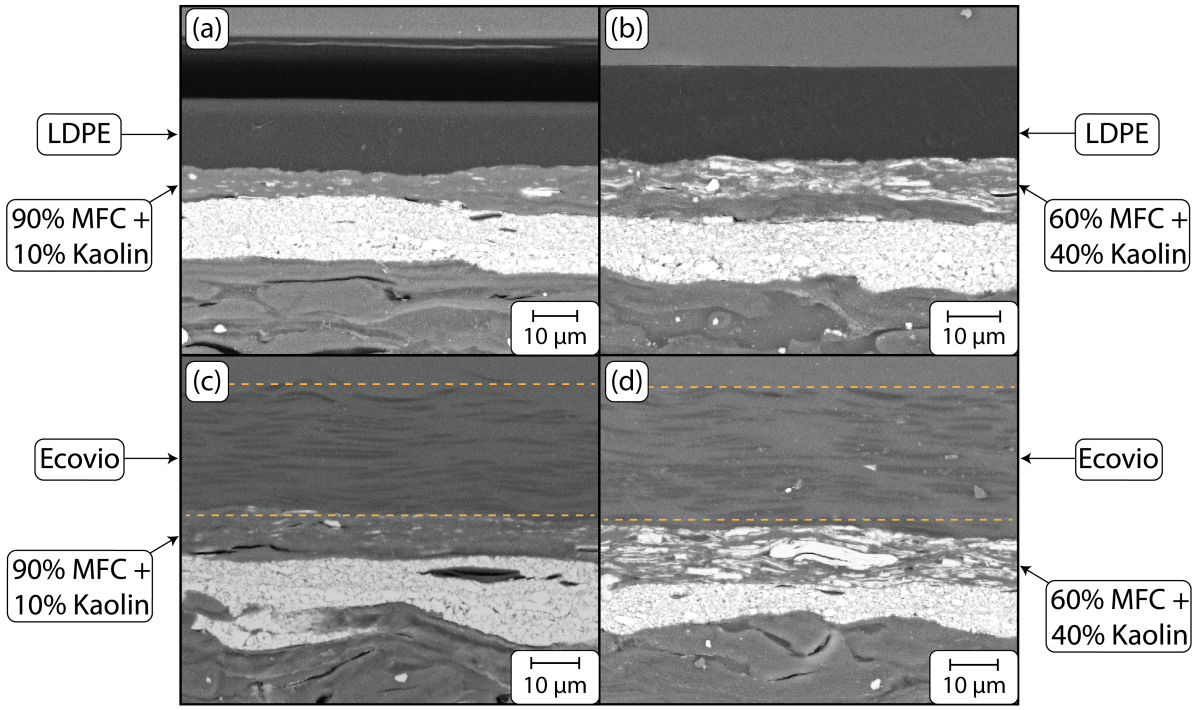

Figure S 8: SEM cross-sections for multilayer-coated samples, (a) LDPE on MFC+10% kaolin, (b) LDPE on MFC+40% kaolin, (c) Ecovio on MFC+10% kaolin, and (d) Ecovio on MFC+40% kaolin

References

Naderi, A., Lindström, T., Sundström, J., Flodberg, G., and Erlandsson, J. (2016). A comparative study of the properties of three nanofibrillated cellulose systems that have been produced at about the same energy consumption levels in the mechanical delamination step. *Nordic Pulp & Paper Research Journal*, 31(3):364–371.

Wågberg, L., Winter, L., Ödberg, L., and Lindström, T. (1987). On the charge stoichiometry upon adsorption of a cationic polyelectrolyte on cellulosic materials. *Colloids and surfaces*, 27(4):163–173.