Continuous Processing of Nanocellulose and Polylactic Acid into Multilayer Barrier Coatings

Rajesh Koppolu,*‡ Johanna Lahti,§ Tiffany Abitbol,* Agne Swerin,‖ Jurkka Kuusipalo,‡ and Martti Toivakka,*

*Laboratory of Paper Coating and Converting, Center for Functional Materials, Åbo Akademi University, 20500 Turku, Finland
‡Paper Converting and Packaging, Tampere University of Technology, 33100 Tampere, Finland
§Bioeconomy—Biorefinery and Energy, RISE Research Institutes of Sweden, 114 28 Stockholm, Sweden
‖Division of Surface and Corrosion Science, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden

ABSTRACT: Recent years have seen an increased interest toward utilizing biobased and biodegradable materials for barrier packaging applications. Most of the abovementioned materials usually have certain shortcomings that discourage their adoption as a preferred material of choice. Nanocellulose falls into such a category. It has excellent barrier against grease, mineral oils, and oxygen but poor tolerance against water vapor, which makes it unsuitable to be used at high humidity. In addition, nanocellulose suspensions’ high viscosity and yield stress already at low solid content and poor adhesion to substrates create additional challenges for high-speed processing. Polylactic acid (PLA) is another potential candidate that has reasonably high tolerance against water vapor but rather a poor barrier against oxygen. The current work explores the possibility of combining both these materials into thin multilayer coatings onto a paperboard. A custom-built slot-die was used to coat either microfibrillated cellulose or cellulose nanocrystals onto a pigment-coated baseboard in a continuous process. These were subsequently coated with PLA using a pilot-scale extrusion coater. Low-density polyethylene was used as for reference extrusion coating. Cationic starch precoating and corona treatment improved the adhesion at nanocellulose/baseboard and nanocellulose/PLA interfaces, respectively. The water vapor transmission rate for nanocellulose + PLA coatings remained lower than that of the control PLA coating, even at a high relative humidity of 90% (38 °C). The multilayer coating had 98% lower oxygen transmission rate compared to just the PLA-coated baseboard, and the heptane vapor transmission rate reduced by 99% in comparison to the baseboard. The grease barrier for nanocellulose + PLA coatings increased 5-fold compared to nanocellulose alone and 2-fold compared to PLA alone. This approach of processing nanocellulose and PLA into multiple layers utilizing slot-die and extrusion coating in tandem has the potential to produce a barrier packaging paper that is both 100% biobased and biodegradable.

KEYWORDS: nanocellulose, polylactic acid, barrier coatings, roll-to-roll process, multilayer coatings

INTRODUCTION

As of 2012, the annual generation of municipal solid waste is about 1.3 billion tons around the world and is predicted to reach about 2.2 billion tons by 2025.1 Food packaging amounts to 20% of the total municipal solid waste, and depending on the country, 40–85% of food packaging ends up either in landfills or in the oceans.2,3 This poses an urgent need to replace packaging that contains nonbiodegradable, fossil fuel-based plastics with bio-based and biodegradable alternatives. Nanocellulose, polylactic acid (PLA), starch, methylcellulose, chitosan, soy protein, gelatin, and poly-hydroxyalkanoate (PHA) are some examples of such biomaterials that could potentially be used to replace plastics in various packaging applications. Numerous scientific publications and review articles discuss each of the above materials in more detail.4–15

In recent years, nanocellulose has been attracting interest as a promising biomaterial for packaging applications.16 Depending on the source and the processing technique, nanocellulose consists of microfibrillated cellulose (MFC) with diameters of 20–60 nm, lengths up to a few micrometers, and crystallinities of 60–70% on the one end of the spectrum17 and cellulose nanocrystals (CNCs) with diameters of 5–20 nm, lengths of 100–500 nm, and crystallinities close to 90% on the other end of the spectrum.18 Nanocellulose-based films and coatings exhibit excellent barrier against oxygen, grease, and mineral oils.19–23 However, nanocellulose is sensitive to moisture, with most of the barrier properties degrading when the relative humidity (RH) approaches 90%.24 Most of the nanocellulose suspensions have high viscosity and yield stress at already low
solid content\textsuperscript{25} and have poor adhesion to various substrates.\textsuperscript{26} This poses additional challenges for high-speed processing.

One approach to protect nanocellulose from moisture is to have a multilayered structure consisting of alternating layers of nanocellulose and hydrophobic polymers, and this multilayer structure can further be made environmentally friendly by utilizing biopolymers. Several research groups have demonstrated this concept by employing various biopolymers such as guar gum, alkyd resins, polyglycolic acid, polyvinyl alcohol, PHAs, shellac, polypyrrole, chitin, and PLA.\textsuperscript{40,41} However, oxygen permeability of optimally prepared CNC/PLA composite films by solution casting of CNC/PLA composite films reduced in water vapor and oxygen permeances, respectively, by several orders of magnitude lower than that of PLA.\textsuperscript{20,42,43}

Of the above-mentioned biopolymers, PLA as such has already found its use in several packaging applications, such as shopping bags, fruit boxes, yogurt, and single-use beverage cups.\textsuperscript{36} PLA is typically produced via condensation polymerization of lactic acid, which is in turn produced by fermenting carbohydrates mostly sourced from corn sugar, potato starch, and sugarcane.\textsuperscript{27} Because PLA is thermoplastic, traditional manufacturing techniques that are used to process thermoplastics, such as polystyrene and low-density polyethylene (LDPE), can be used.\textsuperscript{38} Similar to nanocellulose, PLA has excellent barrier against grease and mineral oils,\textsuperscript{39} while barrier to water vapor is higher for PLA.\textsuperscript{40,41} However, oxygen permeability of optimally prepared films of nanocellulose is a few orders of magnitude lower than that of PLA.\textsuperscript{20,42,43}

Processing nanocellulose and PLA as a layered system could complement the shortcomings of each other and the packaging thus produced can have superior barrier properties than its individual components. A common approach is to add CNCs, typically less than 5\% into a PLA matrix and cast the suspension either into films or as a coating on a substrate. Typical solvents used in this process include chloroform, acetone, tetrahydrofuran, and hexafluoro-2-propanol, which are eventually evaporated slowly after the casting process.\textsuperscript{44–48} Sanchez-Garcia and Lagaron\textsuperscript{49} have achieved 80 and 90\% reduction in water vapor and oxygen permeances, respectively, by solution casting of CNC/PLA composite films. Herrera et al.\textsuperscript{49} have made CNC/PLA composite films by hot melt extrusion followed by compression molding. Although they have not measured the barrier properties of the composite films, the relatively simple and fast manufacturing process shows promise for future commercialization. Aulin et al.\textsuperscript{28} deposited alternating layers of cellulose nanofibers (CNFs) and a cationic polyelectrolyte, polyethyleneimine (PEI), on PLA sheets. Water vapor permeance of such sheets was reduced by 50\% and the oxygen permeability was close to polyvinyl alcohol and ethylene vinyl alcohol films.

Most of the approaches discussed above are batch-scale processes that often require long drying/evaporation times or multiple time-consuming steps. The objective of this work is to explore the possibility to combine slot-die coating of nanocellulose\textsuperscript{50,51} and extrusion coating of PLA and process them as thin multilayer coatings onto a paperboard in a continuous process. Barrier properties of these coatings are given special attention.

\section*{Materials and Methods}

\textbf{Base Substrate.} A pigment-coated paperboard (Trayforma Special, Stora Enso, Finland) was used as the base substrate in this work, referred to as “baseboard” from here on. This baseboard had a basis weight of 204 ± 1.5 g/m\textsuperscript{2} and thickness of 270 ± 1.5 μm. Compared to an uncoated paperboard, the pigment-coated paperboard has a smoother surface and smaller pore size, which results in improved coverage and retention of the nanocellulose coating on the surface of the baseboard.\textsuperscript{26} A laboratory-scale roll-to-roll reverse gravure coater (RK PrintCoat Instruments Ltd., United Kingdom) was first used to apply 0.3 wt \% cationic starch solution (gravure roll: 70 lpi × 127 μm with surface volume ~78.5 cm\textsuperscript{3}/m\textsuperscript{2}; dry coating grammage <1 g/m\textsuperscript{2}) on top of the baseboard to improve its adhesion with nanocellulose. The reason for using cationic starch as a primer for nanocellulose coatings is discussed in more detail by Koppolu et al.\textsuperscript{27,28}

\textbf{Slot-Die Coating.} The primer-coated baseboard was subsequently coated with either MFC or CNCs in a roll-to-roll process using slot-die as a coating applicator. MFC was supplied as a 3 wt \% suspension by The Process Development Center of University of Maine (USA). They were produced by passing bleached softwood kraft pulp through a refiner with specialized plates until the fines content was over 90\%, which was measured using a MorFi fiber and shive analyzer. The suspension thus obtained was diluted to 2.5 wt \% for coating, and 5 wt \% carboxymethyl cellulose—CMC (Finnfix 4000G, CP Kelco, Finland), with respect to dry MFC, was added as a plasticizer. CNCs were supplied as a 3 wt \% suspension by Melodea Ltd., which used sulfuric acid hydrolysis on dissolving pulp to produce the CNC suspension. 20 wt \% sorbitol (n-sorbitol—99\%, Sigma-Aldrich), with respect to dry CNCs, was added as a plasticizer. Figure 1 shows the transmission electron microscopy (TEM) images of MFC and CNCs.

The same RK coater that was used for coating cationic starch was modified in-house and fitted with a custom-built slot-die to coat the nanocellulose suspensions onto the primer-coated baseboard. Continuous slot-die coating of various types of nanocelluloses onto paperboard has been described in detail elsewhere.\textsuperscript{26,50,51} Briefly, nanocellulose suspension was fed into a slot-die (34 mm length, 74 mm width, 500–1000 μm slot gap, and 16 mm distribution channel diameter) via an air-pressurized feed vessel. The slot-die was installed at a 3 o’clock position relative to the backing roll and was used as both an applicator and a metering device. The pressure drop across the narrow gap in the slot creates high shear rates, which reduces the apparent viscosity of the shear-thinning nanocellulose suspension,\textsuperscript{25,50} thus allowing its application as a thin layer on the substrate. Two coating grammages each, of MFC and CNCs (a total of four different coatings), were produced at a line speed of 3 m/min. All the coatings were calendared using a laboratory-scale soft nip calender (DT Paper Science, Finland) at a line load of 100 kN/m and 60 °C temperature, with the coated side facing the metal roll.

\textbf{Extrusion Coating.} The nanocellulose-coated paperboard was finally coated with commercial-grade LDPE or PLA using a pilot-scale extrusion coater at the Tampere University of Technology. LDPE was
used as a reference to compare barrier properties with PLA. Prior to extrusion coating, the nanocellulose paperboard was corona-treated online to improve the adhesion of the polymer to the surface of nanocellulose. The final paperboard thus obtained consisted of three different coatings, a cationic starch precoating followed by nanocellulose middle coating and a final polymer coating. Although herein the three coatings were done separately, they could be integrated into a single coating/converting line. Figure 2 shows the schematic of such an integrated coating/converting line.

**Characterization.** All the samples were conditioned at 23 °C and 50% RH for at least 24 h before characterizing them. The large variation in the thickness and basis weight of the baseboard makes it difficult to accurately determine the thicknesses and coating grammages of the relatively thin nanocellulose coatings. Therefore, ion beam cutting was used to prepare cross sections of the samples and a scanning electron microscope was used to image the cross sections. Coating thicknesses of the individual layers were measured from the images and coating grammages calculated by multiplying the thicknesses with the corresponding densities. Air permeability of the coatings was measured using an L&G Air Permeance Tester (Sweden) with a measurement range of 0.003–100 μm/Pa·s.

Water vapor transmission rate (WVTR) was determined according to the ASTM standard, E96/E96 M-05. Two different conditions, 23 °C/50% RH and 38 °C/90% RH, were used, and the average of four parallel measurements was reported as g/m²·day. A similar method was used to measure the heptane vapor transmission rate (HVTR) at 23 °C/50% RH as suggested by Miettinen et al. Here, the salt was replaced by n-heptane and HVTR was determined by measuring the reduction in the weight of the cup because of permeation of heptane through the sample. An average value from three parallel measurements was reported as g/m²·day.

Oxygen transmission rate (OTR) was measured according to ASTM F1927 using Mocon Ox-Tran 2/21 MH/SS. Three different test conditions were used, 23 °C/50% RH, 25 °C/75% RH, and 38 °C/90% RH. The measurement is time-consuming and the instrument can measure only one sample at a time; therefore, the values from just two parallel measurements are reported as cm³/m²·day. Finally, grease penetration rate for the coatings was determined according to ASTM F119, where olive oil was used as the reagent and the time taken in hours/days for the first traces of oil to appear on the bottom side of the sample (six parallel measurements) was reported.

### RESULTS AND DISCUSSION

MFC and CNC suspensions were coated onto the primer-coated baseboard using a roll-to-roll slot-die coating process. Two different coating grammages each for MFC and CNCs were produced and they were named as MFC_L, MFC_H, CNC_L, and CNC_H, with L and H representing low and high coating grammages, respectively. Nanocellulose-coated samples were calendered and then finally coated with either LDPE or PLA using a pilot-scale roll-to-roll extrusion coater. Reference coatings of LDPE and PLA on the baseboard were also produced for comparison. The coatings were characterized for their coating thicknesses, coating grammages, and barrier properties.

Table 1 summarizes the coating thicknesses and calculated coating grammages of all the nanocellulose and polymer coatings. Scanning electron microscopy (SEM) images in Figure 3 show full coverage of the baseboard by both CNCs and MFC. Air permeability of all the coatings was below the detection limit of the instrument, which also suggests full
Moreover, su which in general is susceptible to brittle failure. The layers could provide mechanical support to the PLA layer, cracking of the pigment coating layer shown in Figure 3c,d. This can be an artifact of sample preparation, which is apparent in the CNC/PLA interface did not show such behavior. This can be MFC/PLA interface showed local adhesion failure, while the both types of nanocelluloses. However, some regions at the surface of the nanocellulose + PLA multilayer structures need to be addressed in future studies.

Nanocellulose being hygroscopic absorbs water vapor from the air and swells in proportion to the amount of absorbed water. Upon swelling, the dense network structure that is responsible for providing barrier against oils, oxygen, and other gases starts to open up, resulting in the reduction of barrier properties of original film/coating. In contrast, both LDPE and PLA show barrier against water vapor, hence the reason for their wide use in packaging applications. Therefore, by having a layer of LDPE or PLA on top of nanocellulose, one can protect it from water vapor and maintain the desired barrier properties seen at low RH conditions. Figure 4a shows the WVTRs at 50 and 90% RHs for all the coatings, and Figure 4b,c shows the WVTRs at 50 and 90% RH, respectively, for just the multilayer coatings. As expected, both CNC and MFC coatings showed slight but not significant reduction in WVTR at both the conditions compared to baseboard. LDPE coating on nanocellulose drastically reduced WVTR by about 96% at both low and high humidities. A similar reduction trend was observed for the coatings with PLA; however, WVTR was slightly higher than those with LDPE. This is expected because PLA is susceptible to hydrolytic degradation, which is proportional to the temperature and humidity of the surroundings. Nevertheless, PLA coating reduced WVTR by over 85%, even at a high RH of 90%. In addition, WVTR for all the nanocellulose + polymer coatings remained lower than their corresponding control polymer (LDPE or PLA) coatings irrespective of the test conditions.

One of the main reasons for the interest in using nanocellulose for packaging applications is its superior barrier against oxygen and other gases. By preventing oxygen from entering the package, one can improve the shelf life of food by delaying its decay. On the other hand, an effective gas barrier can prevent the food odors from escaping the package. Table 2 summarizes the OTR at three different test conditions, 23 °C/50% RH, 25 °C/75% RH, and 38 °C/90% RH. Oxygen transmission is sensitive to pinholes/defects in the coatings. The probability of pinholes/defects in a nanocellulose coating increases in a roll-to-roll process because of the extreme drying conditions used to dry the wet suspension. In contrast, during film casting, self-assembly of nanocellulose crystals/fibers takes place slowly, thus promoting the formation of a defect-free film. Because of this reason, CNC and MFC coatings showed a large scatter in OTR data and therefore were not reported. However, when LDPE or PLA was extruded on top of the nanocelluloses, the molten polymer may have filled any pinholes/defects present in the nanocellulose coating, resulting in a steep decrease and lower scatter in OTR values. Between LDPE and PLA, the latter had higher barrier against oxygen and this explains the lower OTR values for nanocellulose + PLA coatings. At 50% RH, both CNCs and MFC showed similar OTR, but as the humidity is increased, MFC demonstrated higher resistance to oxygen transmission than

Table 1. Coating Thicknesses and Coating Grammages along with Standard Deviations (15 Samples) for Different Coating layers

| coating layer | coating thickness (µm) | coating grammage (g/m²) |
|---------------|------------------------|-------------------------|
| CNC_L         | 4.3 ± 0.4              | 6.7 ± 0.6               |
| CNC_H         | 7.2 ± 0.7              | 11.2 ± 1.1              |
| MFC_L         | 4.1 ± 0.5              | 6.4 ± 0.8               |
| MFC_H         | 7.8 ± 0.3              | 12.1 ± 0.5              |
| LDPE          | 16.0 ± 1.2             | 14.9 ± 1.2              |
| PLA           | 18.7 ± 1.0             | 23.4 ± 1.3              |

“L” and “H” represent low and high coating grammages respectively.

* Determined using SEM cross sections. Calculated from thickness assuming the following densities: CNCs and MFC 1.55 g/cm³, LDPE 0.93 g/cm³, and PLA 1.25 g/cm³.

coverage. For comparison, the air permeabilities of the baseboard before and after primer coating were 0.009 and 0.016 µm/Pa·s, respectively, and the lower limit of the instrument is 0.003 µm/Pa·s. PLA formed a uniform layer on both types of nanocelluloses. However, some regions at the MFC/PLA interface showed local adhesion failure, while the CNC/PLA interface did not show such behavior. This can be an artifact of sample preparation, which is apparent in the cracking of the pigment coating layer shown in Figure 3c,d. Moreover, sufficient adhesion between nanocellulose and PLA layers could provide mechanical support to the PLA layer, which in general is susceptible to brittle failure. The brittleness and especially the influence of creasing on barrier properties of nanocellulose + PLA multilayer structures need to be addressed in future studies.

Figure 3. SEM cross sections of (a) CNC_L; (b) CNC_L + PLA; (c) MFC_H; and (d) MFC_H + PLA. Scale bars: 10 µm.
CNCs. This is because, as the humidity increases, nanocellulose swells, and this might lead to cracks in the nanocellulose layer. The entangled fibrils of MFC could physically counteract the swelling, thus resulting in less cracks and consequently lower OTR compared to the crystalline CNCs. One thing to note here is that the nanocellulose layer had protection from humidity by the polymer from only one side while the other side was still open for water vapor to penetrate into the structure of nanocellulose. This might also be another reason for the increase in OTR with increasing humidity. For future work, it would be interesting to look at the influence of two-sided polymer coating on oxygen transmission values, especially at elevated humidities. The OTR values obtained for nanocellulose + PLA coatings at 50% RH are comparable to those reported by Aulin et al. for their PLA/CNF/PEI composites produced via layer-by-layer deposition.

Figure 4. (a) WVTR of all the coatings at 23 °C/50% RH and 38 °C/90% RH; (b) and (c) WVTR of multilayer coatings at 23 °C/50% RH and 38 °C/90% RH, respectively, along with standard deviations.

Table 2. OTR (cm³/m²·day) for Different Coatings at 23 °C/50% RH, 25 °C/75% RH, and 38 °C/90% RH; HVTR (g/m²·day) at 23 °C/50% RH

| Coating          | OTR (cm³/m²·day)* | HVTR (g/m²·day) |
|------------------|-------------------|-----------------|
| baseboard        | 1707 ± 78         | 1707 ± 78       |
| LDPE             | 398 ± 25          | 398 ± 25        |
| CNC_L + LDPE     | 26 ± 21           | 26 ± 21         |
| CNC_H + LDPE     | 40 ± 19           | 40 ± 19         |
| MFC_L + LDPE     | 10 ± 1            | 10 ± 1          |
| MFC_H + LDPE     | 28 ± 7            | 28 ± 7          |
| PLA              | 13 ± 9            | 13 ± 9          |
| CNC_L + PLA      | 35 ± 22           | 35 ± 22         |
| CNC_H + PLA      | 37 ± 24           | 37 ± 24         |
| MFC_L + PLA      | 32 ± 21           | 32 ± 21         |
| MFC_H + PLA      | 9 ± 2             | 9 ± 2           |

*aOnly two measurements were performed. Therefore, both the values are reported.*
Any packaging that is used for food contact applications should have a barrier against migration of mineral oils from the printing inks into the interior of the packaging. Of all the mineral oils, heptane is one of the smallest; therefore, a barrier against heptane could be considered as an indicator for the barrier against larger molecular-weight oils. The HVTR values for the coatings at 23 °C and 50% RH are summarized in Table 2. Compared to baseboard, the HVTR of nanocellulose containing coatings reduced by 98%. LDPE as such has a moderate barrier against heptane.\textsuperscript{56} Having a multilayer nanocellulose + LDPE coating resulted in an order of magnitude lower HVTR compared to just LDPE coating. PLA in itself had a similar barrier as nanocellulose against heptane. Therefore, nanocellulose + PLA coatings did not show any differences in HVTR.

Resistance to penetration against grease is another important consideration for food packaging used for storing butter, vegetable oils, and meat products. All the coatings were tested for their resistance against penetration of olive oil at 40 °C. Figure 5 summarizes the time taken in days for the oil to penetrate through the sample to the other side. Six samples for each coating type were used, and the start point of the bar for each coating type indicates when the first sample failed and the end point indicates when the sixth (final) sample failed. Olive oil penetrated through the baseboard in a matter of minutes; therefore, it was omitted from the figure. LDPE and PLA reference coatings had grease barriers close to 6 and 25 days, respectively, and they have short bars because of homogeneity in their coating layer. Nanocellulose coatings on the other hand had longer bars because of possible coating defects. Coatings containing CNCs in general showed higher grease barrier than the coatings with MFC. This can be attributed to the higher crystallinity of CNCs. In addition, higher coating grammages showed higher barrier because the oil had to penetrate a longer distance. When LDPE and PLA was coated on top of nanocellulose, the grease barrier increased considerably with the first sample failing after 40 days, and in some cases, the oil did not go through even after 84 days, thus proving that this multilayer concept has excellent barrier against penetration of grease. It would be interesting to look at the grease barrier at higher RHs and for creased samples. Because of the time-consuming nature of the measurements, they were not considered for this work but will be a focus for future studies.

![Figure 5. Grease penetration rate for different coatings](image)

**CONCLUSIONS**

Two different continuous coating methods, slot-die coating of nanocellulose (MFC and CNCs) followed by extrusion coating of PLA, were used in tandem to coat the two promising bio-based/bio-degradable materials in a multilayer structure onto a paperboard.

Extrusion coating of LDPE done on the nanocellulose-coated paperboard was used as a reference to compare barrier properties with PLA-based coatings. Cationic starch and corona treatment were used to improve the adhesion at nanocellulose/baseboard and nanocellulose/PLA (or LDPE) interfaces, respectively. The WVTR of these multilayer coatings remained lower than the control PLA and LDPE coating even at a high RH of 90%. Compared to just PLA, nanocellulose + PLA multilayer coating reduced OTR by as much as 98%. A similar reduction was observed with HVTR when compared to the baseboard. Grease barrier of these coatings was improved by 5-fold compared to nanocellulose alone and 2-fold compared to PLA alone. Therefore, this approach of processing nanocellulose and PLA together complements the shortcomings of each other and produces a paperboard with superior barrier properties that is both bio-based and biodegradable. Additionally, it should also be noted that OTR, HVTR, and grease barrier for nanocellulose + LDPE coatings have greatly improved compared to just LDPE coating. Moreover, the fact that these coatings were already produced using continuous roll-to-roll processes makes them an attractive option for future commercialization.

**AUTHOR INFORMATION**

**Corresponding Author**
E-mail: Rajesh.Koppolu@abo.fi. Phone/Fax: +358-2-215 4232.

**ORCID**
Rajesh Koppolu: 0000-0002-0966-7587
Agne Swerin: 0000-0002-6394-6990

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**ABBREVIATIONS**
CMC, carboxymethyl cellulose
CNCs, cellulose nanocrystals
CNFs, cellulose nanofibers
HFP, hexafluoro-2-propanol
HVTR, heptane vapor transmission rate
LDPE, low-density polyethylene
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