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Published in:
Nordic Pulp and Paper Research Journal

DOI:
10.1515/npprj-2021-0070

Published: 28/03/2022

Please cite the original version:
Coating

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https://doi.org/10.1515/npprj-2021-0070
Received November 19, 2021; accepted December 29, 2021; previously published online January 12, 2022

Abstract: We study the incorporation of minerals (talc, kaolin and surface-treated calcium carbonate) in paperboard coatings based on PLA to improve their performance, often limited by the low crystallinity and moderate gas barrier of the polymer. Masterbatches of PLA-based blends mixed with the mineral fillers were melt-blended in a twin-screw extruder and applied as a coating on paperboard in a pilot-scale unit operating at velocities up to 140 m/min. Thermal imaging was used during the extrusion coating and the effect of the fillers was investigated as far as processability and their effect on the mechanical performance. A reduction of neck-in and improved adhesion between the coating and the substrate were achieved at intermediate mineral loadings. Excess filler and low coating weight generated pinholes, leading to a reduction of the integrity and mechanical properties of the coatings. Overall, we define the performance window for continuous, pilot-scale coating of paperboard with a biopolyester filled with mineral particles, opening the opportunity to realize operations in industrial settings.

Keywords: biopolymer; coating; extrusion; filler; packaging.

Introduction

The packaging industry has been influenced by various factors, including the global and regional economics and demographics, sustainability and regulatory aspects. Paperboard is used for packaging, representing the second largest material used in such field (Cameron 2020) while food applications are the largest end-use (Emblem and Emblem 2012, Cameron 2020). Paperboard packaging plays a significant role due to its suitable features (Triantafyllou et al. 2007), such as mechanical strength, versatility in converting operations, lightweight, renewability, biodegradability, and recyclability ( Andersson 2008, Rastogi and Samyn 2015, Seoane et al. 2018). Unfortunately, some of the drawbacks that still need to be addressed in paperboard packaging include materials’ porosity and hydrophilicity, both of which exert a negative impact in the barrier performance against moisture, gases, and oil/grease, which are required in to extend the shelf-life of food packaging. Hence, such properties need to be enhanced, for instance, by using internal sizing or by application of barrier coatings (Andersson 2008, Rastogi and Samyn 2015).

Extrusion coating represents the most commonly used technique to apply barrier layers on paperboard. It is a continuous process that is expected to result in uniform, solvent-free and defect-free coatings. Compared to other coating techniques, for example, dispersion coating or solvent casting, extrusion coating is most effective at relatively high coating weights (Rastogi and Samyn 2015). Current food packaging barrier coatings are mainly fossil-based, and non-biodegradable, including polyolefins, waxes, ethylene-vinyl alcohol (EVOH) and poly(vinylidene chloride) (PVDC). (Sonjui and Jiratumnukul 2014, Rastogi and Samyn 2015) Meanwhile, bio-based, and biodegradable packaging materials have been widely studied but mostly in lab-scale experiments. Hence, the packaging industry is still anticipating solutions that can be implemented in continuous processes that lead to durable packaging materials (Helanto et al. 2019).

PLA has been considered as a promising renewable and biodegradable polymer for packaging applications. This is despite some PLA’s drawbacks, which include low
thermal resistance, brittleness, low crystallinity, and poor solvent resistance and gas barrier performance. (Sonjui and Jiratumnukul 2014, Zou et al. 2015, Khuenkeao et al. 2016, Phetwarotai and Aht-Ong 2016, Jain et al. 2018, Helanto et al. 2019) To meet these challenges, flexible polymers, plasticizers, fillers, and nucleating agents have been introduced in PLA matrices (Zou et al. 2015, Khuenkeao et al. 2016, Phetwarotai and Aht-Ong 2016). Filler addition has been reported to benefit PLA’s mechanical, thermal and barrier performance, and can potentially reduce the end-product cost. However, the properties of polymer/filler systems are also affected by factors such as polymer – filler interactions, orientation and geometry of filler particles as well as loading levels (Jain et al. 2012, Zou et al. 2015, Helanto et al. 2019). Permeation tends to occur in defect areas present in coating layers, for example, in cracks, voids, and pinholes. In addition, the mechanical characteristics of the coated paperboard was evaluated. The results of this study represent an opportunity to explore the processing conditions that lead to optimal coatings, for instance, those for use in food packaging. We note that the barrier, converting and end-of-life properties of the produced materials will be the subject of discussion of a second part of this study (Helanto et al. 2021c).

### Materials and methods

#### Materials

Uncoated folding boxboard (MetsäBoard Natural FSB Cup 200 g/m², 275 μm caliper, Metsä Board Oyj) was used as a baseboard in this study. A commercial PLA/biodegradable polyester polymer (MATER-BI® EX51AO) was sourced from Novamont. Talc (Finntalc M05SL, particle size 2.2 μm, Mondo Minerals/Elementis), kaolin (Hydrite SB 100, particle size 1 μm (40 %), Imerys), and modified calcium carbonate (Omya Smartfill 55–OM, particle size <2 μm (55 %), Omya) were used as fillers. Neat MATER-BI® polymer samples are herein named as “Ref.”, whereas the polymer and filler-containing samples were named after the filler.
type, where “T”, “K” and “C” indicate talc, kaolin and calcium carbonate, respectively, tagged with the filler content (wt%). For example, the sample containing MATER-BI® and 5 wt% of talc is referred as T5.

Compounding

Masterbatches were melt-compounded with a counter-rotating twin-screw extruder (25-mm Coperion ZSK 26 Mc, 32L/D ratio). The biopolymer/filler masterbatches were prepared at 70 % polymer/30 % filler ratio (dry wt%) using a gravimetric side feeder (K-Tron, K-ML-KT20, 200 rpm). For all of the masterbatches, the extruder temperature profile was set at 195/195/185/180/175/170/165/160 °C going from the feeding zone to the die under a screw speed of 400 rpm and a yield of 20 kg/h. The extruded masterbatches were cooled in water bath and air and then pelletized.

Extrusion coating

A roll-to-roll extrusion unit (D = 60 mm, L/D = 30) (Tampere University 2021) was used to produce the coated paperboard samples and extruded films. The neat polymer and the masterbatches were dried (45–50 °C/20 h). Prior to extrusion coating, the system was manually mixed at the given filler concentration. The applied temperature profile used in the extruder, from feeding to the die (T-die) zone, corresponded to 220/240/255/265 °C operated under a back pressure of 95–108 bar and screw rotation speed of 80 rpm. The paperboard substrate was pre-treated with a flame, and the air gap was set to 160 mm, nip pressure to 6 bar and the line speed was varied from 40 to 140 m/min. The applied chill roll temperature was ~20 °C (matte type). The films used for mechanical testing were prepared as extrusion-coated paperboard but feeding silicon paper sheets in between of paperboard and the polymer film to avoid adhesion. An example of extrusion coating process is shown in Figure 1.

Temperature profiling was conducted by using thermal imaging (Testo 825-2i) during the extrusion coating process of the samples at a line speed of 80 m/min. Thermal imaging points included: 1) paperboard web before the nip; 2) polymer film (melt curtain); 3) chill roll, and 4) coated paperboard after chill roll (Figure 1). Three temperatures were analyzed across the machine width (from the edges and the middle). Due to the variations seen in the edge temperatures, the temperature registered in the middle is reported.

Table 1: Samples and nomenclature used for extrusion-coated paperboard.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Name</th>
<th>Coating speed (m/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MATER-BI Ref.</td>
<td>Ref.</td>
<td>60–140</td>
</tr>
<tr>
<td>MATER-BI + Talc 1 wt%</td>
<td>T1</td>
<td>60–120</td>
</tr>
<tr>
<td>MATER-BI + Talc 3 wt%</td>
<td>T3</td>
<td>40–100</td>
</tr>
<tr>
<td>MATER-BI + Talc 4 wt%</td>
<td>T4</td>
<td>40–80</td>
</tr>
<tr>
<td>MATER-BI + Talc 5 wt%</td>
<td>T5</td>
<td>60–120</td>
</tr>
<tr>
<td>MATER-BI + Kaolin 1 wt%</td>
<td>K1</td>
<td>60–120</td>
</tr>
<tr>
<td>MATER-BI + Kaolin 3 wt%</td>
<td>K3</td>
<td>60–120</td>
</tr>
<tr>
<td>MATER-BI + Kaolin 5 wt%</td>
<td>K5</td>
<td>60–120</td>
</tr>
<tr>
<td>MATER-BI + CaCO3 1 wt%</td>
<td>C1</td>
<td>60–120</td>
</tr>
<tr>
<td>MATER-BI + CaCO3 5 wt%</td>
<td>C5</td>
<td>60–120</td>
</tr>
<tr>
<td>MATER-BI + CaCO3 10 wt%</td>
<td>C10</td>
<td>60–120</td>
</tr>
</tbody>
</table>

Figure 1: Points used for thermal imaging during extrusion coating. 1) paperboard web, 2) polymer melt curtain, 3) chill roll, and 4) coated paperboard.

Neck-in was determined by measuring the width of polymer coating compared to the information of applied die width, which was 570 mm and 590 mm during the extrusion coating. Three parallel measurements were performed, and the average is reported.

The adhesion was determined visually from the middle of the paperboard sample by manual peeling. An X-shaped cut was carefully performed with the coating surface using a sharp knife, and the coating layer was peeled manually in the machine direction (both directions, to the running direction and opposite) and fiber tear was evaluated according to the qualitative scale presented in Table 2.

Coating layer characteristics

Morphological analyses were carried out with the extrusion-coated samples, which were cut and sputtered with a thin layer of gold prior to imaging using a scan-
Figure 2: Pinhole analysis of the coated paperboard samples. Imaging was carried out with a camera under UV illumination (254 nm wavelength) and further analyzed with Matlab software (area of 2670 × 3530 pixels). A) Original image, B) Blue channel image, C) Selecting area of interest (marked with red), and D) binarized image where white areas represent the pinholes. Herein, the sample used was coated paperboard (coating weight 15.08 g/m²) with 5 wt% of kaolin and extrusion coating machine speed of 90 m/min. The number of pinholes was calculated to be 654, the adhesion ranking was 4.5.

Table 2: Qualitative adhesion scale of extrusion coated paperboard. The degree of fiber tear is evaluated (0–5) in the manual peeling method.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No adhesion</td>
</tr>
<tr>
<td>1</td>
<td>Weak adhesion</td>
</tr>
<tr>
<td>2</td>
<td>Adhesion but no fiber tear</td>
</tr>
<tr>
<td>3</td>
<td>Under 50 % fiber tear</td>
</tr>
<tr>
<td>4</td>
<td>Over 50 % fiber tear</td>
</tr>
<tr>
<td>4.5</td>
<td>Over 90 % fiber tear</td>
</tr>
<tr>
<td>5</td>
<td>100 % fiber tear</td>
</tr>
</tbody>
</table>

For the pinhole analysis, we used a colored solution as a tracer: 500 ml of ion exchanged water and 5.34 g of a non-ionic surfactant (Triton X-100) were stirred using a magnetic stirrer (10-min). The particles in the solution were mixed utilizing ultrasound at 37 Hz for 10 min. 5 g of beetroot color (Red beet juice powder, Diana Naturals) was added to the solution followed by 10-min stirring. The colored solution was applied using a pipette on each sample’s surface and dried using paper towels. Colored samples were photographed using a Nikon D5200 camera under UV light (wavelength of 254 nm) (Figure 2A). The acquired images were of 6000 × 4000 pixels in dimension, and the horizontal and vertical resolution were both 300 dpi. The images were further analyzed using Matlab software. Figure 2 demonstrates the image analysis procedures: the original image is pre-processed by extracting the blue color chan-
nel (Figure 2B). After this, the area of interest was selected using Matlab function `imcrop` (Figure 2C) allowing to select the area where the paperboard sheet is found. The dimensions of the area where pinholes were found were pre-defined, a target size of 2670 × 3530 pixels was used to extract the central area from the sheet to eliminate any excess white areas. Once the pre-defined area was extracted, the image was binarized using Matlab function `imbinarize` with adaptive method (Figure 2D). To avoid false count of white pixels, a new target size of 2650 × 3510 pixels was defined and used to exclude random white pixels from the edges. In the binarized image, the number of white pixel areas indicates the number of pinholes. Lastly, Matlab function `bwconncomp` was used to find the connected white pixel areas.

Tensile and elongational characteristics were defined by Zwick Roell Z010 material tester (max load 10 kN) as described in ISO 527-2:2012 and measured at 23 ± 2°C and 50 ± 10% RH conditions. The specimens were conditioned according to ISO 291 for at least 88 hours prior to testing. A preliminary crosshead separation of 110 mm and a crosshead speed of 5 mm/min were used. Five replicates were measured and the average is reported. Tensile strength (maximum), tensile strength at break, elongation at break and elastic modulus were determined.

### Results and discussion

#### Temperature profiles

Polymer coating temperature is one important factor affecting the adhesion development onto paperboard (Krook et al. 2005). The temperature profiles were determined using thermal imaging to account for possible changes caused by the addition of the fillers, Table 3. Although the paperboard substrate, line speed and pre-treatment were all the same, variations were observed in the web temperature (paperboard web before the nip). The likely reason for this fluctuation in the running order of the sample points, which is not the order of the appearance in the Table 3. The sample points run at first had lower web temperatures than the later run sample points. However, the web temperatures of T3 and T4 cannot be fully explained by this, and are more likely caused by reflections in thermal imaging. Some indication of the filler effect was observed in the film (melt curtain). As far as the effect of talc or kaolin, the filler loading increased the temperature of the film. However, this was not observed in the samples containing calcium carbonate, where the highest temperature was reached at the lowest filler content (1 wt%) followed by 7 °C decrease at 5–10 wt% content. Overall, only samples with 3–5 wt% of talc and 1 wt% of calcium carbonate had higher film temperatures than the neat polymer. A higher temperature (low viscosity) and coating weights have been seen to favor the adhesion by a longer cooling and thus deeper penetration of the polymer coating into the paperboard. (Krook et al. 2005) The chill roll and coated web temperatures were observed to remain somewhat unchanged.

#### Neck-in

Neck-in means the narrowing of the polymer film in the air gap. Lower neck-in is desired and indicate wider film width, which relates to a cost impact in the extrusion coating process. (Kang et al. 2009) Typically, biodegradable polymers produce a higher neck-in value compared, for example, with LDPE (Durling 2017). The effect of the filler addition on neck-in is presented in Figure 3. The polymer melt temperature, air gap and the line speed were the same for all sample points. Compared to the neat polymer (Ref.), lower neck-in values were obtained upon loading with the filler types. Kaolin (3–5 wt%) decreased the neck-in the most, but also a decrease was achieved with talc (4–5 wt%) and calcium carbonate (5 wt%). With talc and kaolin, the film temperature in the air gap increased with increasing filler loading but it did not increase the neck-in, even though the increased temperature could cause such a phenomenon (Durling 2017). On the other hand, higher aspect
ratio filler has been seen beneficial in reducing the neck-in by increasing the storage moduli and melt tension (Wang et al. 2001). The platy fillers, talc and kaolin, have higher aspect ratio than calcium carbonate (Leong et al. 2004), which could explain the difference seen in the neck-in reduction for talc and kaolin compared to calcium carbonate. Neck-in slightly increased at the lower filler content for talc (1–3 wt%), and kaolin (1 wt%), and with calcium carbonate at 1 wt% and 10 wt%. Increased neck-in could have been caused by the reduction in molecular mass of the polymer, upon compounding with the inorganic fillers (Liu et al. 2014). In the extrusion process, fillers can reduce the molecular weight of the matrix polymer, as a result of depolymerization, random chain scissions, intermolecular/intramolecular transesterification, or hydrolysis. (Dhar et al. 2017)

Among the extrusion process parameters, polymer of high and wide molecular distribution (Kuusipalo 2001), high elasticity (Kang et al. 2009, Khajeheian et al. 2018), and long-chain branching, all decreases the neck-in (Kang et al. 2009). Positive development of neck-in for PLA-based extrusion coatings have also been reported by others. Khajeheian et al. studied linear and peroxide-modified branched PLAs and noticed a reduction in neck-in values, which were explained by the increased elasticity. (Khajeheian et al. 2018). In reactive extrusion film casting process, the neck-in was reduced with PLA/cellulose nanocrystal (CNC) films prepared with different compatibilizers. The improvement in neck-in was explained by factors such as degree of crosslinking or branching, enhanced molecular weight, gel fraction yield, and share of degraded low molecular weight fragments. (Dhar et al. 2017)

**Adhesion**

The adhesion between polymer and substrate is one of the most critical properties of extrusion-coated paperboard, which can be obtained by wetting of a polymer melt onto a paperboard surface, and by chemical and/or mechanical bonding (Durling 2017). A strong correlation was observed with the coating weight and the adhesion, as expected. The lowest coating weight of each sample point with good adhesion (≥4, over 50 % fiber tear) is presented in Figure 4. Lower coating weights with good adhesion were achieved for all the fillers. However, most of the samples included pinholes. The only pinhole-free sample, which resulted good adhesion with lower coating weight, was achieved with calcium carbonate (C1 14.9 g/m² and C5 15.0 g/m²). From the adhesion point of view, a significant improvement was achieved with 5 wt% talc, which resulted in the lowest coating weight (7.5 g/m²). The coating weight of the sample with good adhesion was reduced by increasing kaolin content. Also, a somewhat similar behavior was seen for calcium carbonate. The relation to coating weight, which was somewhat linear, remained with all the other samples except for 5 wt% of talc, where all the measured adhesions remained constant (4.5) apart from the coating weight, and also 5 wt% of kaolin had very limited effect (constant 4.5 when <20 g/m², 5 when >20 g/m²). Filler additions improved the adhesion development at lower
coating weights, but the correlation of the increased coating weight and adhesion mainly remained. Higher coating weight affects the cooling time in the nip and the extent of coating penetration in the paperboard (Morris 2008). Fillers could have maintained the heat of the melt polymer film a bit longer and therefore improved the adhesion development.

Other authors have mainly experienced decreased adhesion caused by filler additions. It has been reported that nanomontmorillonite (0–8 wt%) filler addition to PE reduces adhesion in extrusion coating process. The reduction was explained by the increased viscosity and thus reduced penetration into the paperboard surface. (Krook et al. 2005) Similar behavior has been reported in dispersion coatings, where filler additions e.g. talc and kaolin have decreased the adhesion to the substrate compared to unfilled coatings. (Schuman et al. 2005) Increased viscosity has also been the reason for reduced adhesion obtained with blends of linear and peroxide-modified branched polylactide compared to neat linear poly(L-lactide). (Khajehian et al. 2018) In contrast, the adhesion of PLA to printing paper surface has been improved with modified gelatin additives in PLA matrix (Cheng et al. 2015).

**Morphology**

Polymer coated paperboard cross section SEM images are shown in the Figure 5. Arrows are used to indicate the coating layer on the surface of the paperboard. The filler particles were dispersed throughout the coating thickness. It has been reported that talc particles tend to align parallel to the film surface in typical packaging materials (Castillo et al. 2013). Indication of parallel orientation to the film surface was also seen with platy fillers, talc (T5, Figure 5) and kaolin (K5, Figure 5). This orientation is beneficial for barrier development, e.g., by increasing the diffusion path.
of the permeating molecules (Castillo et al. 2013). In the SEM imaging, the softness (in cutting) and sensitivity of the biopolymer coating under radiation and charging are seen as white areas in samples K5 and C5 (Figure 5). SEM images support the observation made for the adhesion (at 4–4.5 levels), as noted for the samples presented in Figure 5. Polymer coatings appeared to be well attached to the paperboard surface, with no large areas of “air pockets” between the polymer layer and the paperboard substrate.

Pinholes

The type of filler and its loading as well as coating weight are some of the most significant contributors to pinhole formation. Table 4 presents pinhole data of samples that displayed pinholes. For samples T3, K1, K3, C5 and C10, there are also one pinhole-free sample presented in Table 4. In addition, adhesion results, coating weights of samples are also included.

The results show varying numbers of pinholes within the samples. It is observed that as the machine speed increases, and coating weight decreases and the number of pinholes tend to grow. Among the samples having pinholes, K3 ran with 90 m/min machine speed and had the least number of pinholes. The sample T5 ran at 110 m/min machine speed and presented the largest number of pinholes. In general, T5 samples ran with machine speed over 90 m/min and K5 samples ran with machine speed over 80 m/min have significantly larger numbers of pinholes. T3, T4, K3, C5 and C10, which ran at a machine speed <110 m/min, presented less than 100 pinholes. The samples analyzed here do not show clear dependency between numbers of pinholes and filler content as it has been observed by Krook et al. (Krook et al. 2005) with low density polyethylene and montmorillonite nanocomposite. Here, calcium carbonate at 10 % dosage level results in moderate numbers of pinholes. No correlation/dependency was found between the pinhole results and the mechanical characteristics of the films (Table 5) nor the neck-in results (Figure 3).

The effects on number of pinholes of coating weight, adhesion, filler content and machine temperatures were analyzed. When the machine speed increased, the coating weight decreased for most of the samples. The most significant relationship was observed between coating weight and number of pinholes. The pinhole-free sample points presented in Table 4 have consistently higher coating weights. Figure 6 shows the coating weight and pinholes of three sample with same filler content, T5, K5 and C5. Samples with largest numbers of pinholes have relatively good adhesion, at level 4.5. However, it is also observed that samples with less pinholes have also good adhesion levels. The effect of filler content was minor. For
Table 5: Mechanical characteristics of the coating layer (measured without the paperboard substrate). Reference (Ref.) polymer is PLA/polyester and other sample points are filled with 1–10 wt% of talc (T), kaolin (K) or calcium carbonate (C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength, MPa</th>
<th>Tensile Strength at Break, MPa</th>
<th>Elongation at break, %</th>
<th>Elastic Modulus, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>26.9 ± 2.3</td>
<td>11.9 ± 1.3</td>
<td>1.8 ± 0.1</td>
<td>1932 ± 134</td>
</tr>
<tr>
<td>T1</td>
<td>24.7 ± 1.9</td>
<td>10.7 ± 0.8</td>
<td>1.8 ± 0.2</td>
<td>1817 ± 113</td>
</tr>
<tr>
<td>T3</td>
<td>20.2 ± 2.9</td>
<td>8.5 ± 1.4</td>
<td>1.5 ± 0.1</td>
<td>1607 ± 222</td>
</tr>
<tr>
<td>T4</td>
<td>26.2 ± 1.9</td>
<td>12.1 ± 1.1</td>
<td>1.7 ± 0.2</td>
<td>1947 ± 88</td>
</tr>
<tr>
<td>T5</td>
<td>14.4 ± 1.3</td>
<td>6.1 ± 1.0</td>
<td>1.2 ± 0.1</td>
<td>1433 ± 137</td>
</tr>
<tr>
<td>K1</td>
<td>19.2 ± 4.3</td>
<td>5.4 ± 1.4</td>
<td>1.9 ± 0.3</td>
<td>1401 ± 374</td>
</tr>
<tr>
<td>K3</td>
<td>18 ± 5.4</td>
<td>7.8 ± 2.4</td>
<td>1.4 ± 0.3</td>
<td>1639 ± 247</td>
</tr>
<tr>
<td>K5</td>
<td>13.5 ± 4.6</td>
<td>5.9 ± 2.0</td>
<td>1.2 ± 0.2</td>
<td>1429 ± 382</td>
</tr>
<tr>
<td>C1</td>
<td>26.3 ± 2.3</td>
<td>11.5 ± 1.0</td>
<td>1.9 ± 0.1</td>
<td>1834 ± 131</td>
</tr>
<tr>
<td>C5</td>
<td>22 ± 1.3</td>
<td>10.4 ± 0.9</td>
<td>1.5 ± 0.1</td>
<td>1771 ± 98</td>
</tr>
<tr>
<td>C10</td>
<td>15 ± 2.9</td>
<td>6.4 ± 1.4</td>
<td>1.1 ± 0.2</td>
<td>1523 ± 158</td>
</tr>
</tbody>
</table>

Figure 6: The effect of coating weight (lines) on pinhole count (bars) in area of 2670 × 3530 pixels of coated paperboard with 5 wt% of talc, kaolin or calcium carbonate.

example, T5 sample ran at different machine speeds and have the same filler content but the number of pinholes ranged from <10 to >3000. However, the percentage of filler material incorporated to the polymer matrix affects the number of pinholes generated within the same filler material. Calcium carbonate resulted in a rather low numbers of pinholes even at the highest filler material dosing level.

When the machine speed was increased, the coating weight decreased. The samples with lowest coating weights also had the largest number of pinholes. When comparing T5 and K5 samples to K3 and C10 counterparts, the number of pinholes generated within the same filler level.

Mechanical characteristics

The mechanical properties of the extrusion coatings were analyzed for self-standing films (not attached to the paperboard substrate) to better identify the effect of the fillers, Table 5. Tensile strength and elongation of the extrusion coating decreased with filler content. However, the decrease in tensile strength was not significant compared to the neat polymer (1 and 4 wt% talc or in sample with 1 wt% of calcium carbonate). Kaolin had the lowest tensile strength among the fillers. The elastic modulus of the samples was decreased with increasing filler content except for T4 and K3. The elastic modulus of T4 was higher than the neat polymer. Micro-sized fillers have been reported to have an unfavorable effect on the mechanical characteristics in biopolymers due to their ability to be stress concentrators (Castillo et al. 2013). Also, other aspects such as polymer-filler and filler-filler interactions and filler orientation impact the properties of the composite (Chow et al. 2004). In our study, the polymer-filler interactions should be considered. Kaolin has only one silicate layer for polymer macromolecules to interact, while talc has two (Ouchtar et al. 2015), and calcium carbonate used is functionalyzed and designed for PLA (Welker et al. 2021) by fatty acid modification (Aliotta et al. 2020). In addition, kaolin has the tendency to form associative structures with the individual flakes under the influence of hydrogen bonding. These aggregates can reduce the tensile properties by debonding from the polymer matrix, acting as stress concentrators. Leong et al. (2004) observed improved tensile strength of PP composites with talc and kaolin addition, but a reduced tensile strength was observed with calcium carbonate. The results were rationalized in terms of the platy filler shape and high aspect ratio, and along with the wetting by the polymer matrix and reduced voids between the filler and the polymer. (Leong et al. 2004)

For talc, the mechanical properties obtained at 4 wt% loading can be explained based on our earlier observations, related to the miscibility change in the matrix polymer (PLA and biopolyester) in such condition (Helanto et al. 2021a). In this study, among the used fillers, calcium carbonate produced composite films with the highest tensile strength and elongation. Similarly, in our earlier work we concluded that the same calcium carbonate outperform the other fillers in terms of the elongation of injection- and compression-molded PLA composites (Helanto et al. 2021b).
Conclusions

We investigated the effect of talc, kaolin and calcium carbonate in PLA-based extrusion coatings. Masterbatches of PLA based blends containing the mineral filler were compounded with twin screw extruder, followed by extrusion coating in a pilot-line. The processability and mechanical properties of the filled composite samples were compared. The effect of filler addition was noted in the melt film curtain, where talc and kaolin were observed to increase the temperature of the film as the filler loading was increased. However, such effect was not observed in the case of calcium carbonate. The temperatures were increased above that of the neat polymer only with 3–5 wt% talc and 1 wt% calcium carbonate. The filler addition decreased the neck-in at higher loadings, but with minor loadings, the neck-in was slightly increased. The decreased neck-in (with talc and kaolin) was likely caused by the high aspect ratio of the fillers, while the decreased neck-in is likely a result of the reduced molecular weight. Adhesion correlated strongly with the coating weight, as expected. Fillers promoted adhesion at low coating weights. For all the filler types, and compared to the neat polymer coating, lower coating weights were achieved with good adhesion. The lowest coating weight (7.5 g/m², with pinholes) exhibit good adhesion at 5 wt% talc addition. Samples with calcium carbonate showed a relatively small number of pinholes even though the coating weight was not the largest. Kaolin generated pinholes, 1 wt% addition level. Calcium carbonate generated pinholes at 5 wt% and 10 wt%. Talc at 5 wt% generated most of the pinholes. The mechanical properties of the extrusion coating were mainly decreased with filler loading. Filler additions (1 and 4 wt% talc and 1 wt% calcium carbonate) decrease the mechanical strength only to a limited extent. Kaolin addition decreased the tensile strength the most. The differences observed for the fillers relate to the filler-polymer interactions. All in all, the processability was improved with filler addition, but produced pinholes and reduced the mechanical properties. The effect of the filler addition on end-product, conversion and end-of-life properties are further investigated in the second part of this study (Helanto et al. 2021c).

Acknowledgments: The authors are grateful to Arctic Biomaterials Oy for the masterbatch compounding, Päivi Kauppinen for the assistance with the SEM images, Joni Myyryläinen for the assistance with the mechanical analysis, and Laura Koskinen for the assistance with the images. Research group of Paper Converting and Packaging Technology at Tampere University is acknowledged with appreciation for the extrusion coating trial, and the neck-in and the adhesion measurements.

Funding: The authors state no funding involved.

Conflict of interest: The authors declare no conflicts of interest.

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