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Miscellaneous

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Mineral-filled biopolyester coatings for paperboard packaging materials: barrier, sealability, convertability and biodegradability properties

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Abstract: Changing trends in packaging materials has been driven by increasing environmental awareness as well as legislation. In this context, paperboard-based packaging have become increasingly popular due to its bio-based origin, potential biodegradability and physical properties. However, conventional systems lack behind in barrier performance and heat sealability. Hence, the addition of functional layers have been considered as alternative solutions to this challenge. Here we propose a biodegradable PLA-based polymer coating filled with minerals (0–10 wt% loading), namely, talc, kaolin and calcium carbonate, all of which were used in surface application on uncoated folding box board. For this purpose, we used a pilot-scale extrusion unit that produced materials that were tested for key properties. We found that the presence of filler in the PLA layer improved both water vapor (up to 16 %) and oxygen (up to 56 %) barrier properties. Moreover, the main effect of the fillers was observed in heat sealability, which was improved *via* adhesion at low temperatures, resulting in full fiber tear. Cup forming was less effected by filler loading in the PLA coating while repulping tests indicated the presence of large flakes of the polymer coating in 1 %-consistency slurries. Finally, biodegradability was slightly delayed in filler-containing samples (biodegradation within 10–60 days), most likely due to the nucleating effect of the fillers. Nevertheless, all

the samples can be classified as biodegradable. Overall, our results represent a step forward in scale-up adoption of PLA-based coatings most useful in the development of packaging materials.

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

Introduction

Paperboard is one of the most used packaging materials (Cameron 2020) which can be explained by its multiple advantages e. g. its renewable origin, physical properties, convertability, biodegradability, and recyclability (Andersson 2008, Rastogi and Samyn 2015, Seoane et al. 2018). However, among these features, a packaging material often requires barrier properties and heat sealability (Lahti et al. 2017). Extrusion coating is one of the most commonly used technology to apply barrier coating layer on to paperboard substrate. Yet, fossil-based and durable materials e. g. polyolefins are mainstream for barrier coatings (Rastogi and Samyn 2015). Nevertheless, one of the key drivers for the packaging industry are the sustainability and regulatory aspects (Cameron 2020), and alternative barrier coating materials have been widely researched (Helanto et al. 2019). PLA, has offered a bio-based and biodegradable alternative for paper and paperboard barrier coatings (Lahtinen et al. 2011, Lahtinen et al. 2012, Cheng et al. 2015, Khajeheian et al. 2016, Koppolu et al. 2019, Sundar et al. 2020, Helanto et al. 2022). PLA has disadvantages e. g. its poor thermal and gas resistance and brittleness (Sonjui and Jiratumnukul 2014, Zou et al. 2015, Khuenkeao et al. 2016, Phetwarotai and Aht-Ong 2016, Amirabadi et al. 2018), which have been enhanced e. g. by blending with flexible polymers, plasticizers or fillers (Zou et al. 2015, Khuenkeao et al. 2016, Phetwarotai and Aht-Ong 2016).

Mineral fillers such as platy talc ($Mg_3Si_4O_{10}(OH)_2$) (Courgneau et al. 2012, Jain et al. 2012, Ouchiar et al. 2015, Buzarovska et al. 2016, Ouchiar et al. 2016, Ghassemi et al. 2017, Amirabadi et al. 2018, Lee et al. 2020, Helanto et al.

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2021a, Helanto et al. 2021b, Helanto et al. 2022), platy kaolin (composed mainly of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)) (Matusik et al. 2011, Ouchiar et al. 2015, Segura González et al. 2015, Ouchiar et al. 2016, Helanto et al. 2021a, Helanto et al. 2022), and more irregularly shaped calcium carbonate (CaCO_3) (Sabzi et al. 2012, Piekarska et al. 2017, Rocha et al. 2018, Aliotta et al. 2019, Helanto et al. 2021a, Helanto et al. 2022) have been combined with PLA matrix to improve its properties. Fillers have multiple ways of enhancing the barrier properties. It has been reported, that fillers can be working as nucleating agents for crystal formation in polymer matrix which has promoted barrier properties (Buzarovska et al. 2016). The platy shape of talc and kaolin are creating tortuosity to the coating matrix and hindering the diffusion of permeating molecules (Jain et al. 2010). In addition, fillers have also been seen beneficial promoting compatibility of immiscible polymer blends (Jain et al. 2010, Helanto et al. 2021b) or increased the hydrophobicity of the matrix (Yu et al. 2012), and therefore having a positive effect on the barrier properties. Negative effects of filler additions in barrier point of view are naturally e. g. unfavorable filler orientation (Evstatiev et al. 2013), pinhole generation and agglomerates (Massey 2003, Helanto et al. 2022).

Heat sealability is one of the most vital property of extrusion coated paperboard used in packaging applications, enabling the structure and mechanical strength of the packaging and avoiding seam leakages. (Kuusipalo 2008) Heat sealing is commonly utilizing heat, pressure and time to form seams in thermoplastic containing packaging structures (Kuusipalo 2008, Yam 2009). Hot bar heat sealing is still the most used sealing method, but also e. g. ultrasonic (Kuusipalo 2008, Yam 2009), and hot air sealing methods are widely utilized (Kuusipalo 2008, Lahti et al. 2017). Paper cups and trays are examples of utilizing different heat-sealing techniques (Kuusipalo 2008). PLA has been reported to form good heat seal below, but near to its melting point (Auras et al. 2004). In PLA coated paperboards, the increased crystallinity of PLA has been noticed to increase the heat sealing temperature (Lahtinen et al. 2009). Also the minimum concentration (1 w/v%) of PLA resulting good heat seal in solvent casted paperboard coatings have been reported (Rhim and Kim 2009).

Recycling and biodegradation of paperboard based packaging materials are offering alternatives to energy recovery and landfill end-of life options. Recyclability of a packaging material has become one of the key demands of packaging value chain (Ojanen et al. 2021). It has been reported, that good repulpability of a paperboard based material is one of the key requirements of its efficient recycling (Schoukens et al. 2014). Coated paperboard can be

repulped in a hydropulper located at paper or paperboard mill (Kirwa 2013, Robertson 2021). The hydraulic forces are separating the layers from each other, and the diluted fiber slurry is removed from the bottom of the pulper, while coating residues and bale wires etc. are often removed with a help of a ragger wire (Robertson 2021). The repulpability of different barrier materials vary e. g. conventional PE coated paperboard repulp different compared to some dispersion coated alternatives. Material repulpability can be improved with different chemical treatments (Ojanen et al. 2021). Biodegradability of PLA based materials is naturally a widely studied topic (Ray et al. 2003, Kosior et al. 2006, Tokiwa and Calabia 2006, Kale et al. 2006, Kale et al. 2007a, Kale et al. 2007b, Pantani and Sorrentino 2013, Musioł et al. 2016, Yu et al. 2020). Chemical structure, thermal characteristics and the surface properties of the polymer are key elements effecting on the biodegradability. In addition, biodegradability depends on the surrounding conditions (Tokiwa and Calabia 2006). PLA has several degradation routes, e. g. by hydrolysis, enzymes, micro-organism, or by ultra-violet light (Pantani and Sorrentino 2013, Yu et al. 2020). Fillers have also been reported to effect on the biodegradability of PLA matrix (Ray et al. 2003, Thellen et al. 2005, Ozkoc and Kemalolu 2009).

In this study, uncoated folding box board was extrusion coated with a pilot-scale extrusion unit with PLA-based polymer with incorporation of 0–10 wt% of talc, kaolin or surface treated calcium carbonate. The effect of the fillers were studied in terms of barrier properties (WVTR, OTR), heat sealability (hot bar, hot air), cupformability, repulpability and biodegradability.

Materials and methods

Materials

Baseboard utilized in this study was an uncoated virgin fiber folding boxboard grade produced by Metsä Board Oyj with basis weight of 200 g/m² and thickness of 275 µm. PLA based blend (MATER-BI® EX51A0) was used as the matrix polymer for the coating and was purchased from Novamont. Commercially available mineral fillers introduced to the coating were 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). Sample points have been named after the filler

type (“T” as talc, “K” as kaolin or “C” as calcium carbonate) and the filler content (wt%). As an example, paperboard coated with a mixture of matrix polymer and 3 wt% of kaolin is referred as K3. Neat matrix polymer containing sample points have been marked as “Ref.”.

Compounding and extrusion coating

Compounding and extrusion coating has been executed as described in our previous study (Helanto et al. 2022). Masterbatches of 70 wt% of matrix polymer and 30 wt% of mineral filler were melt compounded with twin-screw extruder (counter-rotating 25 mm Coperion ZSK 26 Mc, 32 L/D ratio with K-Tron gravimetric side feeder K-ML-KT20, 200 rpm). Temperature profile was common for all the masterbatches and was set to 195/195/185/180/175/170/165/160 °C (from feeding to die zone). Applied screw speed was 400 rpm with the yield of 20 kg/h. Extrusion was followed by cooling and pelletizing.

Extrusion coating of the paperboard took place at a pilot-scale extrusion coating line of $D = 60$ mm and $L/D = 30$ with a T-die. The matrix polymer and the masterbatches were pre-dried at 45–50 °C for 20 hours and mixed to filler consistency of 1–10 wt% prior to extrusion coating. The applied temperature profile, back pressure, screw rotation speed, air gap and nip pressure were 220/240/255/265 °C, 95–108 bar, 80 rpm, 160 mm, and 6 bar. Flame pre-treatment were used for the paperboard. Variation of line speed were used (40–140 m/min). Chill roll type was matte and the temperature was set to ~20 °C.

Barrier properties

The gravimetric analysis, based on modified ISO 2528 standard, of water vapor transmission rate (WVTR) was executed from the extrusion coated paperboards. The gravimetric change of the measuring cup (containing anhydrous CaCl_2 and covered with the sample) was observed as a function of time in 23 °C/50 % RH and 38 °C/90 % RH conditions in alternating climate chamber (BINDER, KMF 240). MOCON Ox-Tran 2/21 MH/SS oxygen transmission rate analyzer was used to analyze the oxygen transmission rate (OTR) of the extrusion coated paperboards based on the ASTM D3985-05 standard. The measurements were implemented under 23 °C/50 % RH conditions with 100 % oxygen from a testing area of 5 cm². The results of WVTR and OTR are averages of two parallel measurements normalized to polymer coating thicknesses

Convertability

Heat sealing

Hot bar heat sealing was executed with GL Instruments hot press equipment (010806A, UK). Extrusion coated paperboard samples (coating weight of 15–29 g/m²) were heat sealed top against back side with one side heated metal bar against ceramic plate. Applied sealing force was 300N, pressure 3 bar, pressing time 3 seconds, and sealing temperature varied from 120 °C to 200 °C. After heat sealing, the samples were let to cool down to room temperature before manual tearing. The heat sealability was evaluated by fiber tear (scale 0–5, Table 1) observed by manual tearing method.

Table 1: Evaluation scale (0–5) used in the manual tearing test.

Scaling	Description
0	No seal
1	Weak adhesion
2	Adhesion but no fiber tear
3	Under 50 % fiber tear
4	Over 50 % fiber tear
4.5	Over 90 % fiber tear
5	100 % fiber tear

Hot air sealing was executed with hot air sealing machine (Lahti et al. 2017) located in Tampere University. Extrusion coated paperboard samples (coating weight of 14–20 g/m²) were heat sealed top against back side. Applied sealing force was 400N, network pressure 6 bar, heating time 1.24 seconds, open time 0 seconds, pressing time 1.9 seconds, and sealing temperature varied from 350 °C to 440 °C. After heat sealing the samples were let to cool down to room temperature before manual tearing. The heat sealability was evaluated by fiber tear (scale 0–5, Table 1) observed by manual tearing method. Three parallel measurements were performed to obtain the temperature resulting 100 % fiber tear.

Cup forming

Cup forming was executed with a cup forming machine (50 cups/min) at Kruunukartonki – Länsipahvi Oy. Prior the cup making the extrusion coated paperboard (coating weight of 18–28 g/m²) was die cut into suitable side wall blanks and bottom ribbon to form a paper cup with 2.5 dl volume (height 92 mm, bottom diameter 60 mm, rim diameter 80 mm). In the cup machine, three individual heat sealing events took place (Figure 1). Ultrasonic sealing (Figure 1A) (signal length 0.2s, signal strength 1 in

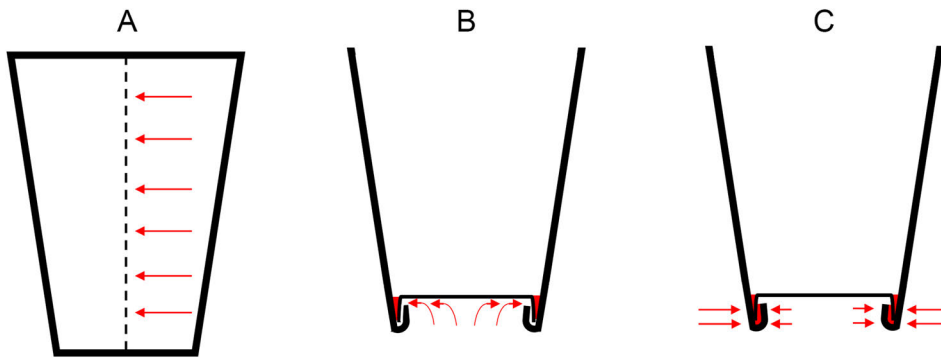


Figure 1: Heat seals in cup forming process. Red arrows illustrates the applied heat. (A) ultrasonic heat sealing of cup side seam, (B) Hot air heat seal activation of 1st bottom seal, (C) hot bar heat sealing of both bottom seals (1 and 2).

scale of 1–3) was used to seal the side seam of the cup side wall blank. Hot air heat sealing (Figure 1B) (temperature 190 °C, air pressure 6–7 bar, treating time 1.5 s) was used to activate the first seam for the bottom and hot bar heat sealing (Figure 1C) (temperature 190 °C, pressing time 1.5 s) to finalize the cup bottom. Cup formability was evaluated by testing individual heat seams with manual peeling method according to the scale presented in Table 1.

Repulpability and biodegradability

In the repulpability test of the extrusion coated paperboards, 50 g of sample was cut into 2.5 cm × 2.5 cm pieces and applied into a dish with 950 g of 23 °C of water (5 % consistency) and mixed with Diaf dissolver (model FFBH 3, n. 22727) for 17 minutes with the speed of 3000 rpm. After mixing, 500 g of the slurry is diluted (with 2 kg of water) into 1 % consistency, and mixed for 4 more minutes. 2 dl of the 1 % slurry is poured into a special blue glass tray (37.5 × 27 cm) for visual investigation of possible fiber bundles or coating pieces.

The ultimate aerobic biodegradability in compost was performed for the extrusion coated paperboard sample points with 5 wt% of filler (talc, kaolin or calcium carbonate) and the “Ref.” with neat matrix polymer coating. Test was implemented according to UNE-EN 13432:2001 and UNE-EN ISO 14855 1:2013 standards. Tests were carried out for 100 days in 2 liters biodegradation reactors under 58±2 °C/50 % RH conditions. 200 g of dry compost (COGERSA, 4 months), 50 g of inert vermiculite (Leroy Merlin), and 250–265 g of water were applied to all reactors. In addition, 30 g of dry cellulose (SigmaCell cellulose type 20, Sigma-Aldrich) was added into reference reactor, and 30 g of powdered (500 µm) dry test material was added into test sample reactor. Biodegradation degree was deter-

mined via determined total dry solids (g), total organic carbon (%), and cumulative amount of CO₂. The results are averages of three parallel measurements.

Results and discussion

Barrier properties

Water vapor resistance was improved with all the different fillers. However, not with all the filler loadings. Talc (3–4 wt%) and kaolin (1 wt%) additions increased the WVTR meaning lower water vapor resistance compared to the reference (Figure 2). Improvement with kaolin (3 wt%) was only marginal (<2%) but with talc and calcium carbonate additions clear improvements were observed. Despite the T1 sample, the water vapor resistance increased with increasing filler content. The most optimal talc additions were 1 and 5 wt% which lead to 16 % improvement in water vapor resistance, while with calcium carbonate the optimal additions were 5 and 10 wt% with 15 % improvement in water vapor resistance.

Oxygen resistance showed improving trend with increasing filler additions, where sample with 3 wt% of talc acted as the only exception (Figure 2). However, not all the samples (K1 and C1) reached better oxygen resistance than the neat polymer (Ref.). Talc improved up to 32 % (with 4 wt%), kaolin up to 56 % (with 3 wt%) and calcium carbonate up to 23 % (with 10 wt%) the oxygen resistance compared to the reference sample.

The generated improvements in barrier properties are likely caused by multiple reasons. Especially talc (Jain et al. 2010, Ouchiar et al. 2015, Buzarovska et al. 2016, Helanto et al. 2021a, Helanto et al. 2021b), but also somewhat kaolin and calcium carbonate (Helanto et al. 2021a), have promoted the crystallinity of the polymer material,

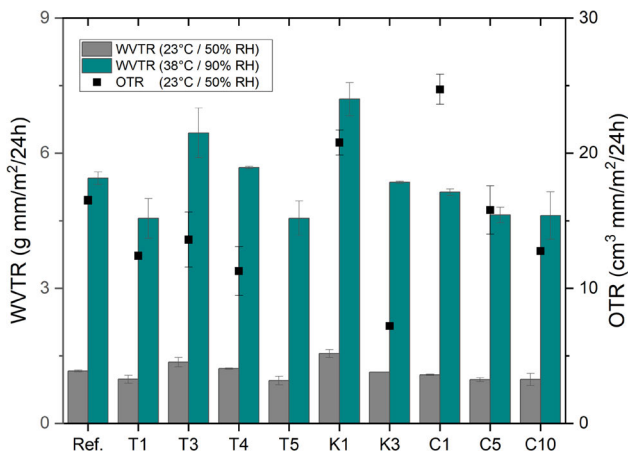


Figure 2: The results of water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of Mater-Bi coated paperboards with 1–10 wt% of talc (T), kaolin (K) and calcium carbonate (C). The results are normalized to the polymer film thicknesses.

which effect positively on the WVTR and OTR. Similarly, talc has been reported to work as compatibilizer in polymer blends (Jain et al. 2010, Helanto et al. 2021b) effecting to the both barrier properties. The hydrophobicity of the fillers plays also a role (Yu et al. 2012) as being part of a material against water vapor. As the fillers have also had negative impact on the barrier results, those could be explained by minor defects (Helanto et al. 2022) or by filler level that has not been optimal working as compatibilizer in the PLA based blend. For example, similarly increased WVTR were observed with the same Mater-Bi polymer and 3 wt% of talc compared to the 1 wt% and 4 wt% additions in our earlier study (Helanto et al. 2021b). Compatibility of Mater-Bi and talc were observed to take place >3 wt% talc additions (Helanto et al. 2021b). Improved barrier properties with talc (Jain et al. 2010, Buzarovska et al. 2016), kaolinite (Girdthep et al. 2014) or calcium carbonate (Rocha et al. 2018) in PLA based/ included systems have been reported also by other authors.

Convertability

Heat sealing

Filler additions did not have great influence on the hot bar sealing temperature resulting 100 % fiber tear (Table 2). All of the sample points sealed with 160–200 °C temperature with full fiber tear. However, improvement were seen at 140 °C, where especially talc and calcium carbonate additions seemed to improve the degree of the fiber tear. Talc additions of 3 wt% and 4 wt% seemed to be optimal in

Table 2: Hot bar heat sealing results. Scaling from 0–5 (0 = no seal, 5 = 100 % fiber tear) in fiber tear.

Samples	120 °C	140 °C	160 °C	180 °C	200 °C
Ref.	1	2	5	5	5
T1	1	3	5	5	5
T3	1	4	5	5	5
T4	1	4	5	5	5
T5	1	3	5	5	5
K1	1	2	5	5	5
K3	1	3	5	5	5
K5	1	2	5	5	5
C1	1	3	5	5	5
C5	1	3	5	5	5
C10	1	4	5	5	5

heat sealing point of view, whereas with calcium carbonate 10 wt% improved the heat sealability the most.

Filler additions in hot air heat sealing results did effect on the degree of fiber tear in lower temperatures (Figure 3). The degree of fiber tear increased slightly with talc (Figure 3B) and kaolin (Figure 3C) additions at lower temperatures compared to the reference (Figure 3A). Calcium carbonate (Figure 3D) samples resulted biggest improvement in fiber tear (370–390 °C) in lower temperatures. However, the full fiber tear was not reached at lower temperatures compared to the reference sample with most of the filler additions. The exception was 10 wt% of calcium carbonate containing sample, which reached full fiber tear with 10 °C lower temperature than the reference material.

Based on the results gained with hot bar and hot air sealing tests, the fillers have an effect on the sealability, even though major changes to the temperatures gaining full fiber tear were not observed. In both methods, higher temperatures were beneficial for the sealing outcome. Filler particles in the polymer matrix maintained the polymer warmer during the sealing event and benefited the seam formation. Lahtinen et al. studied hot bar heat sealability of PLA coated paperboards conditioned in different temperatures from 100 to 150 °C for 2 to 40 minutes. They discovered that the heat treatment increased the crystallinity of PLA coating which increased the heat sealing temperature required for the full fiber tear (Lahtinen et al. 2009). In our earlier study (Helanto et al. 2021a), we have noticed that talc and kaolin additions increased the crystallinity of PLA more than the addition of calcium carbonate. This could explain the higher degree of fiber tear at lower temperatures gained with the calcium carbonate in hot air sealing (Figure 3D). Other learnings from the heat sealability of PLA based material have also been published (Auras et al. 2004). Solvent casted PLA coated paperboard

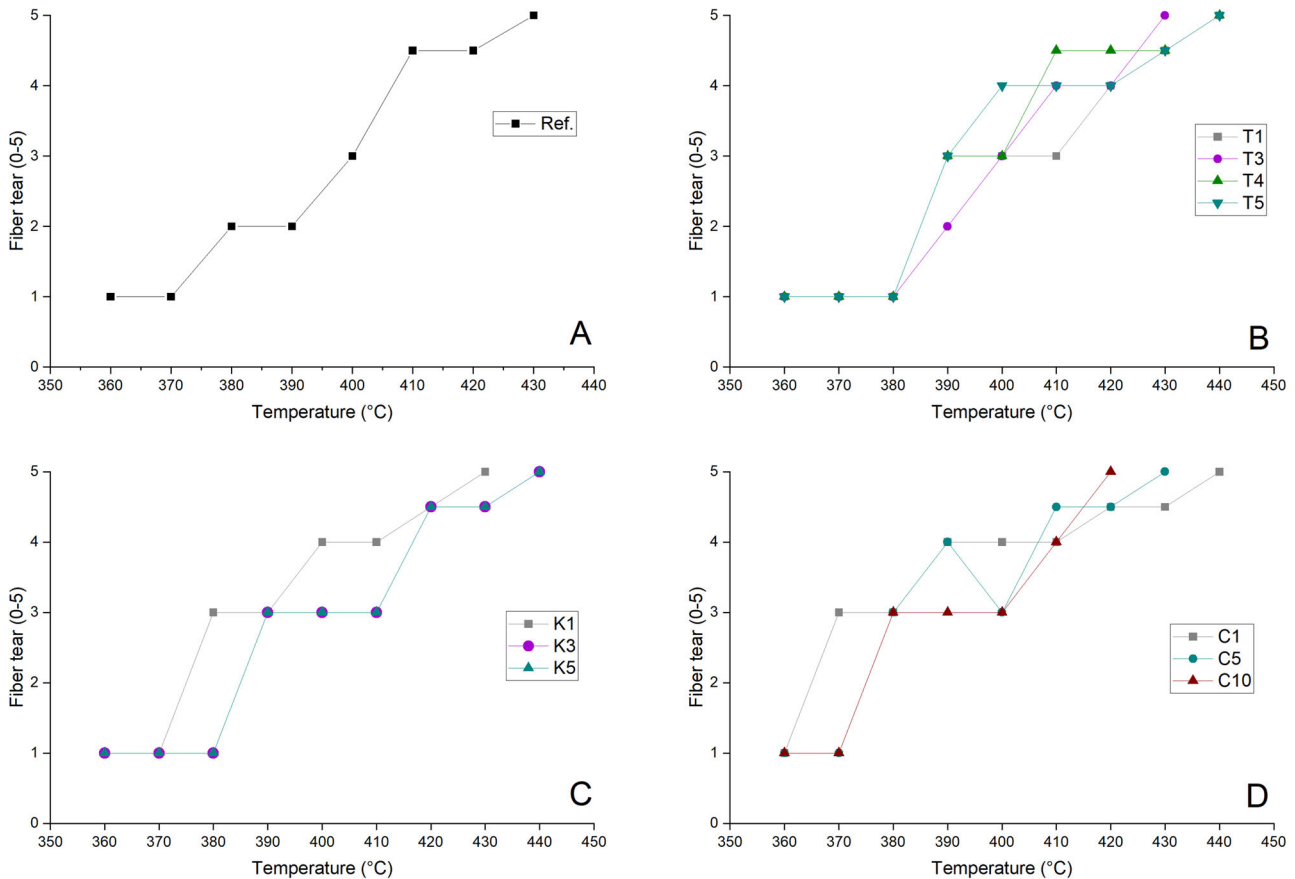


Figure 3: Hot air heat sealing results. (A) neat Mater-Bi coated paperboard, (B) Mater-Bi coated paperboard with 1–5 wt% of talc (T), (C) Mater-Bi coated paperboard with 1–5 wt% of kaolin (K), (D) Mater-Bi coated paperboard with 1–10 wt% of calcium carbonate (C). The heat seal has been evaluated based on fiber tear, scaling from 0–5 (0 = no seal, 5 = 100 % fiber tear).

was heat sealed with hot bar heat sealer and different concentrations (0.25–5 w/v%) of PLA was compared. The highest heat sealing strength was reached with 4 and 5 w/v% of PLA, while < 1 w/v% of PLA did not seal at all (Rhim and Kim 2009). Heat sealability with hot bar sealer was studied from PLA/PBAT-based films with different ratio of PLA and PBAT. PBAT was discovered to form stronger seals than PLA, but the combination of PLA and PBAT resulted higher seal strength than the neat polymers. Highest sealing strength was reached with PLA 40 %: PBAT 60 % ratio (Ai et al. 2019).

Cup forming

Filler additions did not seem to effect on the cup formability in heat sealing point of view (Table 3). Hot air heat sealing did not improve with filler additions, but other heat sealing events resulted good seals with and without fillers. Since the 2nd seams of the bottoms were well heat sealed, the resulted cups were leakproof despite the 1st seam quality. To ensure two perfect seams on the cup bottom, two

Table 3: Cup forming of extrusion coated paperboard with 3–10 wt% of talc (T), kaolin (K), or calcium carbonate (C). Scaling from 0–5 (0 = no seal, 5 = 100 % fiber tear) in fiber tear.

Sample	Coating weight g/m ²	Side seam ultrasonic	Bottom seam	
			1 hot air 190 °C	2 hot bar 190 °C
Ref.	18.0	5	1–2	5
T4	27.9	5	1–2	5
K3	22.5	5	1–2	5
C10	17.8	5	2	5

side coated bottom material would have helped. The overall cup machine runnability of these materials could have been improved by the usage of a thicker and more moist paperboard grade with both side coating.

Cups produced from paperboard coated with PLA based polymer has been investigated also by Cheng et al. (2015). They used gelatin modified PLA in the extrusion coatings and produced paper cups which stand refilling

with hot beverages such as coffee or tea without causing a leakage (Cheng et al. 2015). In another study, a solution casted PLA coated paperboards were tested in terms of e. g. barrier properties and heat sealability to evaluate the suitability for paper cup end-use. Based on the results, it was noticed that PLA coated paperboard could be used for paper cups, when the PLA concentration was higher than 1 w/v%, in order to ensure proper heat seal and reach the level suitable for cup forming (Rhim and Kim 2009).

Repulpability and biodegradability

In the repulpability tests, the fiber matrix of the sample points were well dispersed but the extruded coating layer without and with fillers were not. When the 1% consistency mixtures were investigated on the special blue glass tray, big and obvious coating flakes were observed (Figure 4). The behavior of different sample points did not differ from each other with different fillers, filler loadings or even when no filler was added.

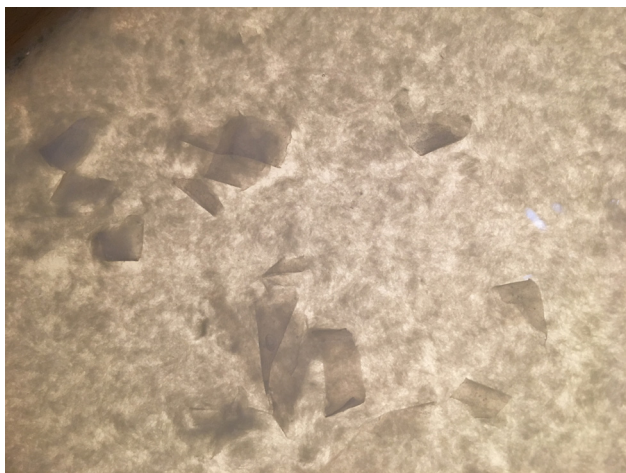


Figure 4: Image after repulpability test in 1% consistency. Example image is from Mater-Bi coated paperboard with 3 wt% of talc in the coating (T3 sample). Image size is 37.5 × 27 cm.

A test procedure of the recyclability of paper-based packaging has been described e. g. in PTS-RH 021/97 (Cat. II) method. Repulpability test resulting <20% of reject is acceptable, meaning also the materials used in this study could be rated as recyclable. Conventional PE coated paperboard could be recycled by utilizing heated water-based bath for separation of the fibers and the coating. Since the density of PE is $<1\text{ g/cm}^3$, a flotation technique can be used. The density of the neat Mater-Bi biopolymer

coating was $>1\text{ g/cm}^3$ (1.24 g/cm^3) meaning it would not float in water system like PE. This feature might cause challenges in the separation process (Schoukens et al. 2014). Repulpability of different barrier coated materials have been tested (Abhijit 2015, Glasenapp et al. 2018, Ojanen et al. 2021). Traditional PE coated paperboard have resulted very similar polymer flakes as seen in our study in the repulpability test (Abhijit 2015, Ojanen et al. 2021). Recyclability of paper where 10–20 wt% of PLA has been introduced were studied by repulping method. Recyclability of PLA containing virgin fiber paper was achieved with up to 10 wt% of PLA (Glasenapp et al. 2018). In another study, PLA coated ($10\text{--}12\text{ g/m}^2$) paperboard was repulped, and notable amount of coating flakes were visible indicating the unsuitability of PLA coated paperboard for conventional broke handling processes present at paper mills (Abhijit 2015).

Biodegradability after 100 days of the extrusion coated paperboards were not considerably affected by the 5 wt% filler additions (Table 4). However, when looking at the cumulative biodegradation degree in Figure 5, differences can be seen in time period ~10 to 60 days. Biodegradability of the neat Mater-Bi coated paperboard and the reference material (cellulose) were more likely equal, while in filled sample points, talc seemed to have the lowest biodegradation rate. After the 60 days of time, neat Mater-Bi coated sample reached the highest biodegradability compared to the reference material and filler containing samples. The reference material biodegradation degree were little bit lower than of talc and calcium carbonate, and basically even with kaolin containing sample. According to the EN 13432 standard, the biodegradation degree (%) respect to the reference material must be higher than 90% to be considered as biodegradable material, and this was reached with all the sample points.

Similar biodegradation study for PLA based filler containing products were conducted by Ozkoc and Kemalglu. PLA and plasticized PLA were introduced up to 5 wt% of organoclay (Cloisite 30B), and the biodegradability was studied. It was noticed that the organoclay increased the crystallinity and decreased the biodegradability compared to neat PLA and plasticized PLA (Ozkoc and Kemalglu 2009). Similar trend was seen in our cumulative biodegradation degree results within the 30–60 days of time period (Figure 5). Neat Mater-Bi coated paperboard reached the highest cumulative biodegradation degree, followed by calcium carbonate, kaolin and finally talc containing samples. The same order has been seen in crystallinity development in PLA, where talc has increased it the most and calcium carbonate the least (Helanto et al. 2021a). The unfavorable effect of the increased crystallinity of PLA on

Table 4: Biodegradation test results after 100.5 days of Mater-Bi coated paperboards with 5 wt% of talc (T5), kaolin (K5), and calcium carbonate (C5). Neat Mater-Bi coated paperboard is referred as (Ref.).

Sample	Thickness μm (Mean \pm SD)	Volatile solids % (Mean \pm SD)	Total organic carbon %* (Mean \pm SD)	Cumulative biodegradation degree % (Mean)	Biodegradation degree* % (Mean)
Ref.	288.9 \pm 8.4	95.46 \pm 0.13	40.99 \pm 0.57	90.73	102.19
T5	300.23 \pm 5.13	95.39 \pm 0.13	41.33 \pm 1.08	89.26	100.53
K5	293.13 \pm 7.62	94.91 \pm 0.02	40.66 \pm 0.45	88.70	99.90
C5	297.8 \pm 7.8	94.83 \pm 0.01	41.07 \pm 0.29	88.94	100.17

*Biodegradation degree respect to the reference material (cellulose), cumulative biodegradation degree of the reference material 88.79% (100.5 days).

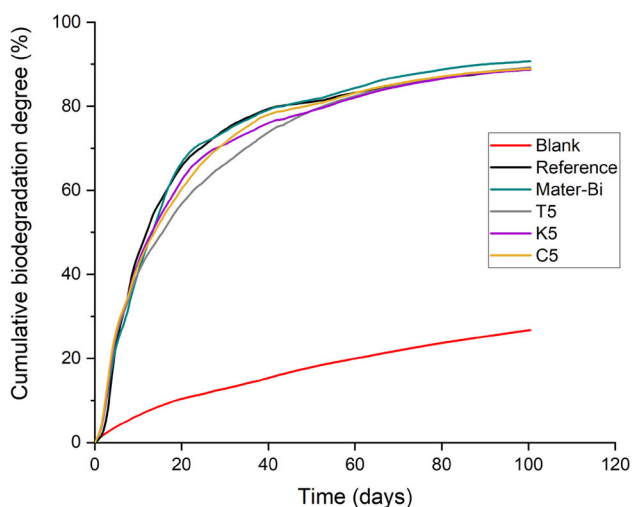


Figure 5: Mean cumulative biodegradation degree as a function of time of Mater-Bi coated paperboards with 5 wt% of talc (T5), kaolin (K5), and calcium carbonate (C5). Neat Mater-Bi coated paperboard is referred as (Mater-Bi). Reference material is cellulose.

the biodegradation has also been reported by several others (Auras et al. 2004, Kale et al. 2006, Tokiwa and Calabia 2006, Pantani and Sorrentino 2013, Musioł et al. 2016, Yu et al. 2020).

Conclusions

New material combinations could solve the challenges of PLA-based coatings for paperboard packaging materials. The effect of different concentrations (0–10 wt%) of talc, kaolin and calcium carbonate were studied regarding crucial packaging material properties. The water vapor transmission rate was decreased, by up to 16 % with talc (1 and 5 wt% loading) and calcium carbonate (5 and 10 wt% loading). Meanwhile, such reduction was limited to <2% for kaolin (3 wt%). The oxygen transmission rate decreased extensively with kaolin (up to 56 %, 3 wt% loading) and

with talc (up to 32 %, 4 wt% loading) and calcium carbonate (up to 23 %, 10 wt% loading). The barrier development improved with increasing filler content, which can be explained by the increased crystallinity, tortuosity and hydrophobicity of the coating. Heat sealability was good and resulted in full fiber tear, with both hot bar and hot air sealing. The impact of the filler additions was seen in the fiber tear development of the seams at low temperatures. However, the filler addition did not influence the temperatures that resulted in full fiber tear. Leakproof paper cups were formed with a cup machine equipped with ultrasound, hot air and hot bar sealers. The bottom of the cup was formed by 2 seams, one of which was strong, with full fiber tear. As a result, no leakages were detected from the cups. Differences among the filler-containing and unfilled samples were not observed. The repulpability test at 1 % consistency showed that the extrusion-coated samples resulted in dispersed fiber matrix and major polymer coating flakes. No differences were detected within the sample points. The fillers slightly slowed down the biodegradability of the samples, most likely due to the crystallinity development caused by filler addition, in the first half of the test compared to the neat polymer coated paperboard. However, after a 100-day biodegradability tests, the differences were very small, and all the samples fitted the definition of a biodegradable material. Based on our results, we conclude that filler addition offer potential benefits to improve the functional properties of paperboard packaging materials.

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