Pilot-scale filler-reinforced biodegradable coatings for paperboard packaging

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A? **Aalto University**

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Abstract

Environmental impact and regulation of packaging materials are topics that critically influence the adoption of alternatives to fossil-based systems that are in current use. In this context, paperboards represent suitable renewable and biodegradable options that also have the advantage of recyclability. However, the nature and structure of paperboard-based products limit their use and undermine other competitive advantages. A main reason is the limited barrier properties displayed by paperboard products. Gaining control of the transport of moisture, grease, liquids and gases is the most relevant requirement for packaging materials together with heat sealability. A possible route to achieve barrier control includes consideration of biodegradable thermoplastic polymer coatings, such as poly(lactic acid) (PLA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(butylene adipate terephthalate) (PBAT). However, the application of these materials needs adjustments in the processability aspects. They also affect the interactions with the packaged goods and the overall functionality, demanding the adoption of auxiliary components, including plasticizers, nucleating agents and fillers. These subjects are complex and should be examined carefully, not only from the fundamental viewpoint but for actual deployment. This thesis discusses these topics from the perspective of scalable and deployable technologies.

The effect of mineral fillers on biodegradable polymer coatings for paperboard packaging is examined at a pilot scale. The utilized thermoplastic polymers included PLA and PLA-based blends, PHBV and PBAT. The fillers introduced to the polymer matrices included talc, kaolin and calcium carbonate. Production processes typical of the packaging industry were contemplated, such as injection and compression moulding and pilot-scale extrusion coating. The potential of the packaging materials and their combinations was evaluated from the perspective of processability to the end-of-life. The addition of fillers benefited processability in the extrusion coating process by reducing neck-in and improving adhesion formation. As a drawback, they contributed to the formation of pinholes at lower coating weights. The barrier properties of intact films and coatings were improved, whereas the introduction of the fillers did not significantly impact on the biodegradability characteristics. This thesis provides insights on the filler-reinforcement of biodegradable polymers and their utilization as coating layers. This work is expected to serve as a guide for future developments of sustainable extrusion coatings for paperboard packaging.

Tiivistelmä

Ympäristövaikutukset ja pakkausmateriaalien sääntely vaikuttavat merkittävästi pakkausmateriaalien kehitykseen ja vaihtoehtoisten materiaalien hyödyntämiseen perinteisten fossiilipohjaisten sijasta. Kartonki edustaa tyypillisesti uusiutuvaa, biohajoavaa ja helposti kierrätettävissä olevaa materiaalia. Kartonkipohjaisten tuotteiden luontaiset ominaisuudet ja rakenne saattavat kuitenkin rajoittaa niiden käyttöä. Kartongilla ei ole luontaista suojaa kosteudelle, rasvalle, nesteille tai kaasuille, mitä pakkausmateriaalit usein tarvitsevat yhdessä kuumasaumattavuuden kanssa. Biohajoavien termoplastisten polymeeripäällysteiden, kuten polylaktidin (PLA), poly(3-hydroksibutyraatti-ko-3-hydroksivaleraatin) (PHBV) ja polybutyleeni-adipaatti-tereftalaatin (PBAT) avulla kartongin toiminnallisuutta voidaan lisätä. Biohajoavien polymeerien prosessoitavuutta, toiminnallisuutta ja vuorovaikutuksia on parannettu hyödyntämällä erilaisia pehmittimiä sekä ydintämis- ja täyteaineita. Näitä aiheita tulisi tarkastella perustutkimuksen lisäksi myös käyttöönoton näkökulmasta. Tässä väitöskirjassa hyödynnetään tuotantoon skaalautuvaa teknologiaa.

Mineraalitäyteaineiden vaikutusta kartonkipakkausten biohajoaviin polymeeripinnoitteisiin tutkittiin pilottimittakaavassa. Tutkimuksessa käytetyt termoplastiset polymeerit olivat PLA ja PLA-pohjaiset seokset, PHBV sekä PBAT. Polymeerimatriiseihin lisätyt täyteaineet olivat talkki, kaoliini ja kalsiumkarbonaatti. Työssä hyödynnettiin pakkausteollisuudesta tuttuja prosesseja, kuten ruisku- ja puristusmuovausta sekä ekstruusiopäällystystä pilottimittakaavassa. Pakkausmateriaaliyhdistelmien potentiaalia arvioitiin prosessoitavuudesta aina pakkauksen elinkaaren loppuun asti. Täyteainelisäykset paransivat prosessoitavuutta alentamalla kuroumaa ja lisäten adheesiota ekstruusiopäällystysprosessissa. Lisäykset kuitenkin aiheuttivat pienten reikien muodostumisen alemmilla päällystemäärillä. Ehjien kalvojen ja päällysteiden barrier-ominaisuudet paranivat, kun taas täyteainelisäyksillä ei ollut merkittävää vaikutusta pakkausmateriaalien biohajoavuuteen. Tämä väitöskirja tarjoaa näkökulmia täyteaineen käytöstä biohajoavissa polymeereissä sekä materiaalien hyödyntämisestä päällysteenä. Työn odotetaan tukevan tulevaisuuden kestävän kehityksen mukaisten ekstruusiopäällysteiden kehitystä kartonkipakkausmateriaaleille.

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Contents

List of abbreviations and symbols

BDO	1,4-butanediol
Blend1	Ecovio® PS 1606
Blend2	Mater-Bi® EX51A0
C	Omya Smartfill® 55-OM (calcium carbonate)
K	Hydrite SB 100 (kaolin)
PBAT	poly(butylene adipate terephthalate)
PBS	poly(butylene succinate)
PCL	poly(ε-caprolactone)
PDLA	poly(D-lactide)
PDLLA	poly(DL-lactide)
PE-LD	low density polyethylene
PGA	poly(glycolic acid)
PHA	polyhydroxyalkanoate
PHB	poly(ß-hydroxybutyrate)
PHBH	poly(3-hydroxybutyrate-co-4-hydroxybutyrate)
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	poly(lactic acid)
PLLA	poly(L-lactide)
PPC	poly(propylene carbonate)
SEM	scanning electron microscopy
$Talc_1$ / T_1	Finntalc M03N (Talc)
$Talc_2$ / T_2	Finntalc M05SL (Talc)
$w_{polymer}$	weight fraction of a polymer
X_c	degree of crystallinity

ΔH_o melting enthalpy of 100 % crystalline polymer

ΔH_c crystallization enthalpy

ΔH_m melting enthalpy

List of publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

1. Helanto, Karoliina; Talja, Riku; Rojas, Orlando. 2021. Talc reinforcement of polylactide and biodegradable polyester blends via injection-molding and pilot-scale film extrusion. *Journal of Applied Polymer Science*. 138 (41). e51225. DOI: https://doi.org/10.1002/app.51225

2. Helanto, Karoliina; Talja, Riku; Rojas, Orlando. 2021. Effects of talc, kaolin and calcium carbonate as fillers in biopolymer packaging materials. *Journal of Polymer Engineering*. 41 (9). 746-758. DOI: https://doi.org/10.1515/polyeng-2021-0076

3. Helanto, Karoliina; Talja, Riku; Li, Sai; Rojas, Orlando. 2022. Effect of filler additions on pilot-scale extrusion coating of paperboard with PLA-based blends. *Nordic Pulp & Paper Research Journal*. 37(1). 108-119. DOI: https://doi.org/10.1515/npprj-2021-0070

4. Helanto, Karoliina; Talja, Riku; Rojas, Orlando. 2022. Mineral-filled bio-polyester coatings for paperboard packaging materials: barrier, sealability, convertability and biodegradability properties. *Nordic Pulp & Paper Research Journal*. 37(1). 212-221. DOI: https://doi.org/10.1515/npprj-2021-0076

Author's contribution

Publication 1: Talc reinforcement of polylactide and biodegradable polyester blends via injection-molding and pilot-scale film extrusion.

KH was responsible for planning the experiments together with RT. KH performed the main part of the experimental work, interpreted the results, and wrote the manuscript. RT assisted interpreting the results and critically reviewed and edited the manuscript. OR provide direction, discussed and critically reviewed and edited the manuscript.

Publication 2: Effects of talc, kaolin, and calcium carbonate as fillers in biopolymer packaging materials.

KH designed the experiments, carried out the majority of the experimental work, analysed the results and wrote the manuscript under the assistance and supervision of RT. RT and OR discussed and critically reviewed and edited the manuscript.

Publication 3: Effect of filler additions on pilot-scale extrusion coating of paperboard with PLA-based blends.

KH was responsible for designing the experimental work with RT. KH contributed to the experimental work, analysed the results and wrote the manuscript. SL was responsible for the pinhole-related efforts by designing, performing, analysing and writing the respective part. RT and OR discussed the work, provided guidance and critically reviewed and edited the full article.

Publication 4: Mineral-filled biopolyester coatings for paperboard packaging materials: barrier, sealability, convertability and biodegradability properties.

Experimental planning was conducted by KH and RT. KH was involved with the experimental part, analysed the results and wrote the manuscript under the supervision of RT and OR. RT and OR critically discussed, reviewed, and edited the manuscript.

1. Introduction

The packaging industry is under constant change driven by various factors, including, environmental and regulatory aspects (Cameron 2020). Significant packaging-related regulations have recently been introduced by the EU, for example, the EU Directive (EU) 2019/904 on single-used plastics (SUP) and the Regulation on Packaging and Packaging Waste (PPWR) (proposal for a revision 11/2022, including Regulation (EU) 2019/1020, Directive (EU) 2019/904 and repealing Directive 94/62/EC). The SUP directive aims to prevent and lower the environmental impacts of certain plastics, while PPWR targets the reduction of packaging waste and an increase in the recyclability and recycled content in plastic packaging. PPWR excludes compostable plastics from the mandatory inclusion of recycled content.

Paperboard, a widely utilized packaging material, represents multiple advantages from the materials point of view, such as great physical and convertability properties, and support of sustainability targets: it is renewable, recyclable, and biodegradable. However, the barrier properties and heat sealability, critical in packaging products, are subjects that are limited for paperboard. These functions can be fulfilled by treating paperboard structure with thermoplastic barrier coatings. (Rhim et al. 2007, Andersson 2008, Rastogi and Samyn 2015) Typical paperboard barrier coatings, mainly fossil-based, are applied by continuous extrusion coating, resulting in reasonably uniform coverage (Rastogi and Samyn 2015). In addition, bio-based coatings, such as poly(lactic acid) (PLA), have been investigated and introduced (Rhim et al. 2007, Lahtinen et al. 2009, Rhim and Kim 2009, Sonjui and Jiratumnukul 2014, Thitsartarn and Jinkarn 2021, Poulose et al. 2022). Common drawbacks of the bio-based and/or biodegradable polymer coatings have been cost effectiveness, availability, processability, functionality and convertability. To overcome these obstacles, biopolymers have been blended, for instance, with plasticizers, fillers, or nucleating agents. (Andersson 2008, Rastogi and Samyn 2015, Helanto et al. 2019)

The aim of this thesis was to study the effect of mineral fillers on biodegradable and/or bio-based polymers, introduced for their potential utilization in extrusion coatings in paperboard packaging. In particular, PLA and PLA-based blends, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(butylene adipate terephthalate) (PBAT) were investigated, together with talc, kaolin and surface-treated calcium carbonate.

The thesis consists of four publications. **Publication 1** explored the effect of talc addition (0-30 wt%) in PLA/ biodegradable polyester blends. Evaluations were carried out by using injection moulded specimens and pilot-scale extruded films to access the thermal, mechanical, morphological and barrier effects of the introduced blends. A more comprehensive polymer and filler comparison was performed in **Publication 2**, where PLA, PHBV and PBAT were investigated along with talc, kaolin, or surface treated calcium carbonate, added at concentrations ranging from 0 to 30 wt% . The examinations in terms of thermal, mechanical, morphological and barrier properties were performed with injection moulded specimens and compression moulded films. **Publication 3** compared the effects of three different mineral fillers (talc, kaolin, or calcium carbonate, 0-10 wt%) in PLA/ biodegradable polyester blend, when applied on top of paperboard substrates using a pilot-scale film extrusion coating unit. The comparison was made with respect to processability parameters e.g., the development of neck-in, adhesion and pinholes. **Publication 4** utilized the material produced in **Publication 3** and examined the effect of the mineral fillers regarding the end-product, convertability and end-of-life properties of the extrusion coated paperboard. The study involved barrier development, heat sealability (hot bar and hot air), cup formability, repulpability and biodegradability. The main themes of **Publication 1-4** are outlined in Figure 1.
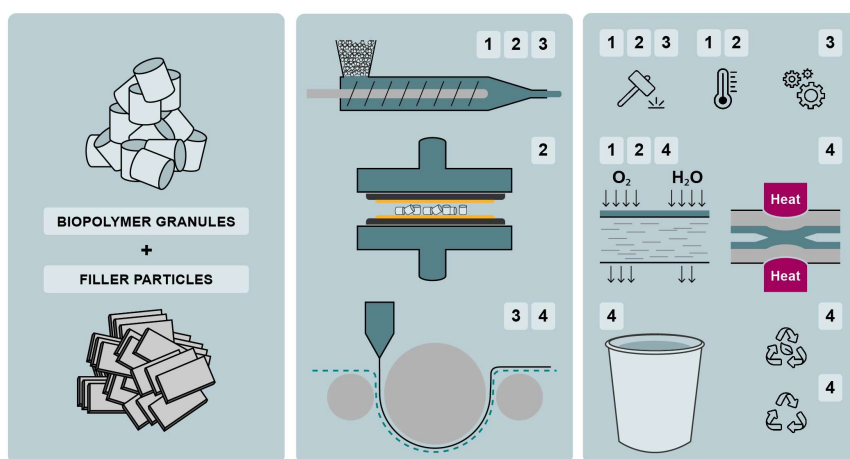

Figure 1 The outline of the main themes covered in **Publications 1** to **4**. (Left) polymer granules and filler particles that can be used in different processes, as shown in the middle. (Right) Key packaging material properties examined. (Free icons utilized from www.flaticon.com)

2. Background

This section provides an overview of the topics related to biodegradable paperboard packaging. Paperboard, biodegradable thermoplastics, and mineral fillers are reviewed together with the key requirements of a packaging material.

2.1 Paperboard as a packaging material

Paperboard is globally the most used material in packaging applications (Cameron 2020). It can be utilized as primary, secondary and tertiary packaging for various end-uses (Kirwan 2013). The use of paperboard is promoted for its cost efficiency, mechanical properties, great convertability and sustainability aspects, but also the impact of e.g., e-commerce (Kirwan 2013, Cameron 2020, Rastogi and Samyn 2015). The feedstock origin, high recycling rates and biodegradability of paperboard enable a lower carbon footprint for fossil-based packaging materials (Kirwan 2013, Kunam et al. 2022).

Paperboard typically has a multi-layered structure which can consist of different pulp types. Virgin fibre pulps can be chemical, mechanical or chemi-mehanical and either bleached or unbleached. Additionally, recycled fibres can be used. The surface of the paperboard can be pigment coated to enhance the printability. Depending on the raw material selection, a variety of different paperboards can be manufactured for multiple packaging purposes from rigid, semi-rigid to flexible packaging in a cost-efficient manner. (Kirwan 2013) The most popular packaging board types are folding box board, corrugated board, and liquid packaging board (Cameron 2020). Due to the relatively porous structure and hydrophilicity of paperboard, a barrier layer is needed when targeting resistance against water, water vapor, grease, and gases (Andersson 2008, Kirwan 2013, Rastogi and Samyn 2015). In addition to barrier properties, thermoplastic polymer coatings enable the heat sealability and can enhance the puncture, tear and rub resistance of the packaging material (Durling 2017). The demand for sustainable and protective packaging has been estimated to boost the consumption of barrier paperboards (Cameron 2020).

2.2 Biodegradable barrier materials

Biodegradable barrier polymers can be produced from renewable and/ or fossil-based resources as illustrated in Figure 2 (Vroman and Tighzert 2009). Biodegradable material degrades mainly into carbon dioxide, biomass and water, when exposed to physical, chemical, biological or thermal decomposing (European Parliament and Council Directive 94/62/EC). The end-of-life properties of the biodegradable packaging material differ from conventional materials since they do not accumulate in landfill (Vroman and Tighzert 2009). Typical challenges of biodegradable polymers are an insufficient barrier level with low physical properties and processability challenges (Jawaid and Swain 2018). The oxygen and water vapor permeabilities of typical biodegradable thermoplastics are presented in Figure 3 in comparison to low density polyethylene (PE-LD).

Paperboard as a substrate is typically biodegradable. However, the common methods to enhance barrier properties with conventional polymers or aluminium, do not support the ability. Therefore, the biodegradable barrier materials have been involved. (Kirwan 2013) Different biodegradable barriers have been introduced to paperboard, such as polyesters, polysaccharides, proteins and lipids (Kirwan 2013, Rastogi and Samyn 2015). Biopolymers have been applied onto the paperboard substrate by extrusion coating or solvent/ dispersion coating techniques. Extrusion coating represents the mainstream technology with respect to barrier coating application onto paperboard. However, the extrusion coating technique applies only to thermoplastic polymers, which are the focus of this thesis, leaving out most of the polysaccharides, proteins, and lipids. (Rastogi and Samyn 2015)

Petrochemical-based biodegradable polymers are i.e., poly(butylene adipate terephthalate) (PBAT), poly(butylene succinate) (PBS) and poly(ε-caprolactone) (PCL) and Poly(propylene carbonate) (PPC). Bio-based biodegradable polymers can be classified into natural and synthetic polymers (Figure 2). Natural polymers include i.e., cellulose, starch, chitosan, lipids and proteins, whereas synthetic polymers include polymers such as poly(lactic acid) (PLA), polyhydroxyalkanoate (PHA), poly(glycolic acid) (PGA) and bio-based PBS. (Rastogi and Samyn 2015, Helanto et al. 2019, Wu et al. 2021)

Biodegradable Polymers

Petrochemical-based
- Poly(butylene adipate terephthalate) (PBAT)
- Poly(butylene succinate) (PBS)
- Poly(ε-caprolactone) (PCL)
- Poly(propylene carbonate) (PPC)

Bio-based

SYNTHETIC
- Poly(lactic acid) (PLA)
- Polyhydroxyalkanoates (PHA)
- Poly(butylene succinate) (PBS)
- Poly(glycolic acid) (PGA)

NATURAL
- Polysaccharides (e.g. cellulose, starch)
- Lipid (e.g. wax, fatty acids)
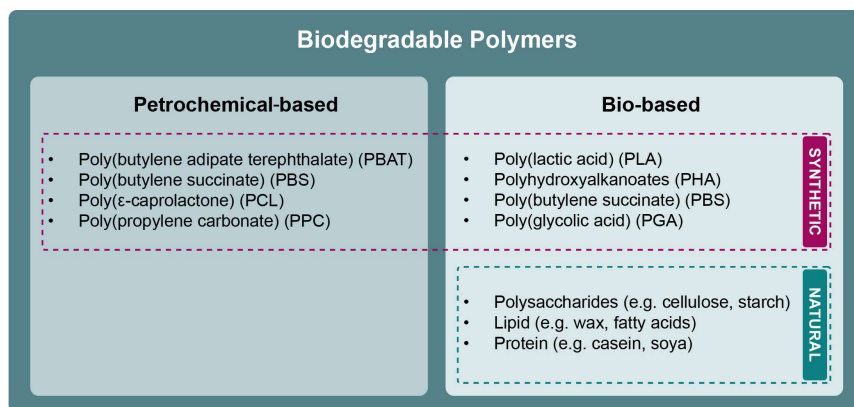- Protein (e.g. casein, soya)

Figure 2 Biodegradable polymers. (Redrawn according to Helanto et al. 2019 and Wu et al. 2021)

The global production capacity of biopolymers has been estimated to be 6.3 million tonnes in 2027, of which the 56.5 % represents biodegradable biopolymers (PLA 37.9 %, PBAT 1.6 %, starch blends 6.3 %, PHA 8.9 %, PBS 0.3 %, cellulose films 1.5 %). (European Bioplastics 2022) Not all the listed biodegradable polymer volumes are bio-based or partly bio-based (PBAT, PBS) (Döhler et al. 2022).
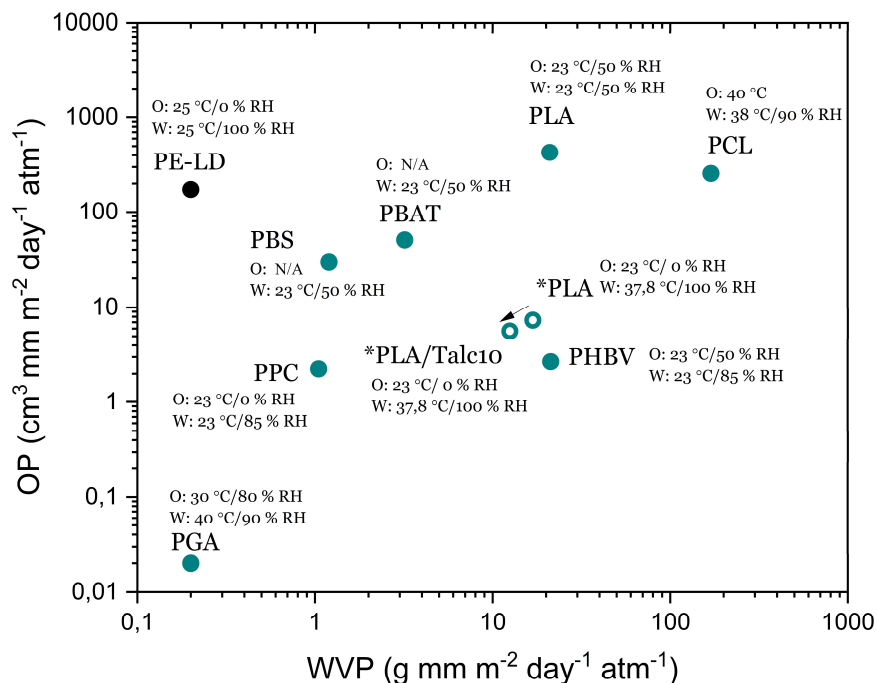
Figure 3 Oxygen permeability (OP) and water vapor permeability (WVP) of biodegradable polymers and low-density polyethylene (PE-LD). OP and WVP values have been unified by converting the original values from the publications: PE-LD (Park et al. 2010), PGA (Yamane et al. 2014), PPC (Zhai et al. 2015), PBS and PBAT (Sonchaeng et al. 2022), PHBV (Jost and Langowski 2015), PLA (Poulose et al. 2022), PCL (Ding et al. 2021), *PLA and *PLA/Talc10 (Snowdon et al. 2019), where Talc10 refers to 10 wt% talc addition into PLA.

According to European Bioplastics estimates, PLA holds the highest production capacity among all bioplastics in 2027 (European Bioplastics 2022). PLA is an aliphatic thermoplastic biopolyester which is produced from sugar-rich feedstock e.g., sugarcane, sugar beet or corn via bacterial fermentation (lactic acid) and polymerization (Rhim and Kim 2009). PLA has stereoisomers of which the most common are semicrystallized poly(L-lactide) (PLLA), amorphous poly(D-lactide) (PDLA) and poly(DL-lactide) (PDLLA) (Farah et al. 2016, Wu et al. 2021). PLLA results in a more transparent, but lower barrier film than PDLA (Wu et al. 2021). Generally, PLA has been reported to have good processability (Rhim and Kim 2009), mechanical properties (Yu et al. 2006) and moisture barrier (Liu 2006). Typical challenges of PLA have been its high brittleness, moderate thermal stability, low gas barrier (Figure 3) (Andersson 2008; Rhim and Kim 2009) and rather slow degradation rate (Farah et al. 2016). To enhance the functionality, several different polymers, fillers and additives have been in-

troduced (Bhatia et al. 2012, Gorrasi et al. 2014, Helanto et al. 2019). An example of the effect of filler addition (10 wt% of talc) into PLA is shown from the barrier perspective in Figure 3.

Poly(butylene adipate terephthalate) (PBAT) is widely utilized biodegradable and petroleum or partially bio-based aliphatic–aromatic copolyester. PBAT consists of 1,4-butanediol (BDO), adipic acid and terephthalic acid monomers. (Venkatesan et al. 2017) Flexibility, toughness and thermal properties benefit the use of PBAT, while the limiting factors are i.e., low crystallinity, tensile strength and barrier properties (Bastarrachea et al. 2010, Venkatesan et al. 2017, Qiu et al. 2021). The high toughness of PBAT has been utilized in biopolymer blends with high stiffness i.e., PLA or PHBV (Wu et al. 2021).

Polyhydroxyalkanoates (PHA) represent a group of linear thermoplastic biopolyesters which are synthesized by microorganisms via bacterial fermentation. Typically, industrial scale production of PHAs utilizes sugars as fermentation feedstock. (Bugnicourt et al. 2014) From the large variety (>150) of PHAs, the most studied polymers in packaging field are short-chain-length poly(ß-hydroxybutyrate) (PHB) and its copolymers poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (PHBH) (Bugnicourt et al. 2014, Li et al. 2016, Wu et al. 2021). PHAs have displayed good resistance to moisture, oxygen and UV-light and the biodegradability has been ranked the highest among PBS and PLA (Bugnicourt et al. 2014). PHAs have been successfully creased and heat sealed (Andersson 2008). The high cost and limitations in the physical and thermal properties of PHAs have reduced the usage (Bugnicourt et al. 2014, Li et al. 2016). PHAs have been introduced to a variety of polymers and fillers to enhance the properties and lower the cost (Yu et al. 2006, Helanto et al. 2019).

Other thermoplastic biodegradable polymers include i.e., PBS, PCL, PPC and PGA, as presented in Figure 2. Poly(butylene succinate) (PBS) is the semi-crystalline product of succinic acid and BDO, which can be produced fully or partly from renewable feedstock by fermentation (Xu and Guo 2010, Rafiqah et al. 2021). However, prevalent feedstock of BDO is yet petroleum oil (Yim et al. 2011, Rafiqah et al. 2021). PBS has been reported to be well processable, but relatively low gas barrier properties have led to incorporation of different fillers and polymers (Helanto et al. 2019, Rafiqah et al. 2021). Poly(ε-caprolactone) (PCL) is an aliphatic polyester with repeating hexanoate units (Labet and Thielemans 2009). Similar to PBAT, it is lacking high barrier properties, but offers flexibility and toughness (Wu et al. 2021). Poly(propylene carbonate) (PPC) is the product of copolymerization of propylene oxide (PO) and carbon dioxide (Luinstra and Borchardt 2012). PPC has good moisture and oxygen barrier properties, which have been utilized in blends and multi-layered structures e.g., with PLA, PBS and PBAT (Wu et al. 2021). The challenges of PPC are related to its thermal characteristics, which influence its processability and end-uses (Luinstra and Borchardt 2012). Poly(glycolic acid) (PGA) is an aliphatic polyester with great gas barrier and physical properties (Yamane et al. 2014). The industrial scale production of PGA utilizes ring-opening polymerization of glycolide (Samantaray et al. 2020). Even though the production capacity is very

limited, and the price is high, PGA has been used in multilayered and copolymer structures (Samantaray et al. 2020, Wu et al. 2021).

2.3 Mineral fillers

Inorganic mineral fillers (aka pigments) are typically utilized in paper and paperboard making. Mineral filler usage reduces the cost of the final material and benefits the paperboard properties from a physical and convertability aspect and makes a visual impact. (Chauhan and Bhardwaj 2013, Durling 2017) Similarly in the polymer industry, mineral fillers have been adapted to reduce the cost and adjust mechanical, thermal and barrier properties (Leong et al. 2004, Jain et al. 2012, Ouchiar et al. 2015). The effect of filler additions into a polymer matrix is greatly dependent on filler geometry (Leong et al. 2004) and surface properties, filler amount, filler-matrix and filler-filler interactions, filler dispersion and orientation (Jain et al. 2012).

Common mineral fillers used both in paper and polymer industries are talc, kaolin and calcium carbonate (ground and precipitated) (Leong et al. 2004, Jain et al. 2012, Chauhan and Bhardwaj 2013, Durling 2017). Talc ($Mg_3Si_4O_{10}(OH)_2$) is a three-layered, hydrophobic, neutrally charged platy mineral filler. The sandwich-like structure consists of an octahedral brucite layer in between tetrahedral silica sheets connected by weak van der Waals forces. (Jain et al. 2012, Yu et al. 2012) Silanol functions on the edge of the talc enable covalent bonding with appropriate chemical groups (Raquez et al. 2008). Talc is easily dispersed in the polymer matrix under shear forces due to its softness and composition (Jain et al. 2012, Yu et al. 2012, Shakoor and Thomas 2014). Talc has been introduced to biopolymer matrices resulting in an increased degree of crystallinity, and enhanced physical (Jain et al. 2012, Yu et al. 2012, Buzarovska et al. 2016, Ghassemi et al. 2017, Lee et al. 2020), thermal (Yu et al. 2012, Lee et al. 2020), morphological (Jain et al. 2010) and barrier properties (Jain et al. 2010, Buzarovska et al. 2016, Ghassemi et al. 2017). The most common material improving mechanisms of talc are related to the nucleability and tendency to create tortuosity in the matrix (Buzarovska et al. 2016).

Kaolin is a platy clay mineral which is primarily composed of kaolinite ($Al_2Si_2O_5(OH)_4$). Hydrogen bonded tetrahedral silica and octahedral alumina sheets form the layers of kaolinite. (Segura Gonzalez et al. 2015, Wang et al. 2015) The reinforcing effect of kaolin is enabled by its high surface energy and strong interfacial interactions, which have boosted its broad usage in the polymer industry (Leong et al. 2004, Zhang et al. 2019). In a polymer matrix, both layers of kaolin, the alumina and silicate, are in contact with the polymer chains. In comparison, talc has two silicate layers involved. Strong interactions (hydrogen bonds) between biopolymer chains (PLA) and silicate layers have been reported and the stronger interactions of a talc and polymer matrix have been explained by the two silicate layers compared to the one layer of kaolin. (Ouchiar et al. 2015)

Calcium carbonate (CaCO$_3$) is commonly an irregularly formed and widely utilized filler in thermoplastics. The traditional driver of calcium carbonate addition has been the cost benefit. (Leong et al. 2004) However, enhancements in processability, compatibility, crystallinity and rheological and physical properties have been reported (Leong et al. 2004, Duangphet et al. 2017, Rocha et al. 2018). The interactions of calcium carbonate with polymer matrices have been improved by different surface treatments, such as stearic acid, phosphates or silanes (Leong et al. 2004).

2.4 Packaging material requirements

Generally, the main objective of a packaging is to provide protection for the packed good during storage, transport, sales and use, but also to protect the surrounding environment, extend the shelf life, provide information and help to sell the product in a sustainable manner. The desirable protection varies according to the packed good (Figure 4). (Andersson 2008, Verma et al. 2021) To fulfil the above mentioned functions, the packaging material must be processable, convertible and resistant to different circumstances (from freezer to oven, from dry to wet) (Kirwan 2013).
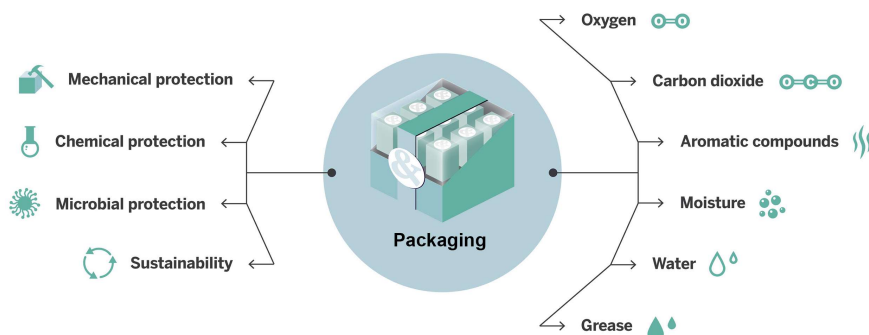
Figure 4 Examples of possible protection requirements of a package. (Adapted from Helanto et al. 2019 with permission from the *BioResources*)

2.4.1 Processability

Extrusion coating represents the mainstream of barrier coating technology for paperboard substrates. However, the technique is suitable only for thermoplastic polymers, while a variety of different dispersion coating techniques, such as bar, curtain or size press, are commonly utilized also for non-thermoplastic polymers. (Rastogi and Samyn 2015) In this chapter, processability in terms of the extrusion coating technique is reviewed.

In principle, extrusion coating is a process where polymer granules are converted into a melted polymer curtain and introduced onto a moving i.e., paperboard surface. The material combination is instantly run in between a nip roll and a chill roll to ensure the adhesion between the thermoplastic coating and the substrate. Typical process variables in the extrusion coating process are the extruder temperature profile, backpressure, die and air gap, pre-treatment of

the paperboard substrate and chill roll temperature. (Durling 2017) The extrusion coating process offers rather challenging processing conditions for biopolymers but can result in a uniform film with a continuous process on an industrial scale. Biopolymers and conventional polymers differ notably in thermal properties, such as melting and glass transition temperature, and in melt stability. (Rastogi and Samyn 2015) In extrusion coating, the melt temperature of biodegradable polymers is typically between 220 and 250 °C, comparatively lower than that of low-density polyethylene (PE-LD), 300-325 °C (Durling 2017). To adjust the processability of biodegradable polymers, various polymer blends, fillers and additives have been introduced (Rastogi and Samyn 2015, Durling 2017).

In the extrusion coating process, the narrowing (neck-in) of the polymer melt curtain in the air gap is desired to be maintained at a minimum level. Neck-in is the difference between the final coating and the die width. (Kuusipalo et al. 2008, Durling 2017) Typical neck-in values for PE-LD are 15-30 mm/edge (Kuusipalo et al. 2008), while for biodegradable polymers the value varies between 50-70 mm/edge, respectively (Durling 2017). The neck-in of branched polymers such as PE-LD decreases with an increase in the line speed due to the strain hardening effect in the melt curtain state, but for unbranched polymers the effect is opposite (Kuusipalo et al. 2008, Durling 2017).

Adhesion between the coating and the paperboard substrate is one of the most crucial properties in extrusion coating (Tuominen et al. 2008). As previously mentioned, adhesion formation is targeted when the substrate and the coating is running between the nip and chill rolls (Durling 2017). Multiple adhesion-related theories exist (Kuusipalo et al. 2008); however, the most typical ones are mechanical and chemical adhesions (Durling 2017). Mechanical adhesion is achieved when a melted polymer curtain wets the relatively rough surface of the paperboard and penetrates the surface structure. Typically, a too low polymer temperature hinders the penetration into the paperboard surface and causes poor adhesion. The chemical adhesion mechanism is based on chemical interactions between the coating and the substrate. Prior chemical adhesion formation, oxidation, and heating of the substrate surface, as well as oxidation of the polymer melt curtain in the air gap, take place. Common pre-treatments for the paperboard surface are corona, flame, or plasma treatments (Tuominen et al. 2008). Oxidation of the polymer e.g., PE-LD can be boosted to a certain limit by increasing the polymer melt temperature and increasing the air gap (Durling 2017), or by ozone treating the melt curtain (Tuominen et al. 2008). Excess oxidation can cause odour and taint issues and challenges in converting i.e., in heat seal formation. Oxidation causes crosslinking on the polymer surface, which hinders diffusion in the heat sealing event (Figure 5C). Furthermore, too big an air gap can lead to increased neck-in and cooling of the melt curtain resulting in poor adhesion. (Durling 2017) In addition, a variety of other parameters also have an effect on the adhesion, such as paperboard roughness and surface energy, polymer viscosity and density, nip pressure, chill roll temperature and line speed (Tuominen et al. 2008, Durling 2017).

Pinholes are typical defects in extrusion coatings. They are small holes that reduce the barrier properties of the material, especially in thin films (5-15 g/m²). (Kuusipalo 2000, Kuusipalo et al. 2008, Durling 2017) Pinholes can be created by gas bubbles located in the polymer melt, gels, agglomerates, impurities in the melt, upward facing fibres or the rough surface of paperboard (Kuusipalo et al. 2008, Durling 2017). Pinhole formation can take place before the contact of the polymer melt and the substrate, before the nip, at the nip, after the chill roll and all the way to the handling of the coated product (Kuusipalo et al. 2008). The tolerance of the acceptable frequency of pinholes is defined by the end-product application (Kuusipalo 2000).

2.4.2 Convertability

Paperboard as a packaging material is strong, tough and flexible (Andersson 2008, Kirwan 2013). The physical properties and the excellent convertability (i.e. printing, cutting, creasing, gluing, folding, deep drawing, pressing) of paperboard benefits its use in various packaging solutions (Kirwan 2013). However, paperboard is lacking valid packaging functionalities, such as heat sealability and barrier properties, which can be tackled e.g. by the addition of extrudable coatings (Andersson 2008). Extrusion coated paperboard is intended to maintain the great convertability level of the substrate, indicating relatively high demands for the coating.

Forming a paperboard packaging can involve multiple unit operations such as cutting, creasing, folding, side seaming and sealing (Andersson 2008). When paperboard blanks are cut, the edge is desired to be sharp and clean from loose fibres. A crease enables the folding of a paperboard blank. (Kirwan 2013) Both in cutting and creasing processes, a variety of forces are introduced to the paperboard in a relatively small area (Andersson 2008). These operations are especially challenging for biopolymer coatings with relatively high stiffness and brittleness i.e., for PLA and PHB, which can easily crack (Andersson 2008, Rastogi and Samyn 2015). Side seaming and sealing of a paperboard packaging can be conducted by heat sealing or gluing (Andersson 2008).

Heat sealing is a significant converting operation of thermoplastic polymer coated paperboards, facilitating the leakproof packaging structure and mechanical strength (Kuusipalo 2008). A proper seam is vital to avoid spoilage and physical damage of the packaged product (Andersson 2008). There are a variety of sealing technologies, of which the most widespread technique is hot bar heat sealing (Kuusipalo 2008, Yam 2009, Durling 2017). Other common sealing technologies include ultrasonic sealing and hot air sealing techniques (Kuusipalo 2008, Yam 2009). Typically, heat sealing requires the introduction of energy (heat), pressure and time (Andersson 2008, Kuusipalo 2008, Yam 2009, Durling 2017). The principle of a heat seal formation mechanism of semi-crystalline thermoplastic polymer coating is described in Figure 5. The heat is typically conducted from outside in by one or two heated bars, which simultaneously press the two surfaces together to enable proper contact for seal formation. (Yam 2009, Durling 2017)
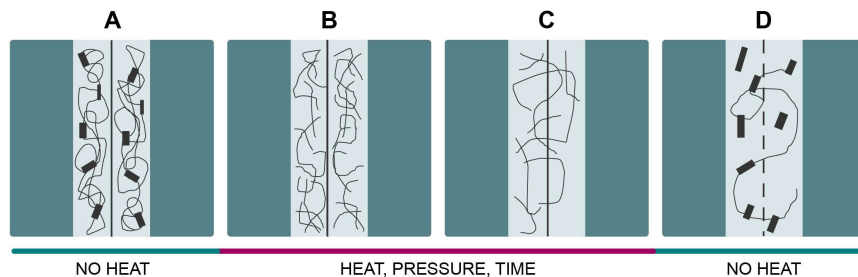
Figure 5 The principle of seal formation at the molecular level (redrawn according to Durling 2017). A) two extrusion coated paperboard surfaces are in contact, B) heat and pressure is applied followed by melting of polymer crystals and wetting, C) diffusion and entanglement of polymer chains, D) re-crystallization after heat source removal.

Ultrasonic sealing is based on mechanical vibration at high ultrasonic frequencies (20-40 kHz), which converts to heat via friction and viscoelastic response. The heat melts the surface and enables seal formation. (Yam 2009, Durling 2017) The advantage of ultrasonic sealing is the sealing speed (Durling 2017), low temperature tooling and suitability for thicker materials, like coated paperboards (Yam 2009). Similarly, the hot air sealing technique is beneficial for thicker materials that resist conduction. The hot air is blown directly on to the surfaces to be sealed. A typical application utilizing hot air sealing is liquid paperboard packaging. (Yam 2009)

Optimally heat sealable thermoplastic coatings have a low melting temperature and melt viscosity, a wide sealing temperature window, good hot-tack and seal strength (Andersson 2008, Durling 2017). PE-LD results in good seal strength and it is widely used for sealed paperboard applications. However, it results in rather low hot-tack strength, meaning low seal strength in a short time after the sealing event, due to its branched structure. The hot-tack strength plays a vital role in packaging, especially when recently formed heat seals are exposed to external forces e.g., packaging being filled shortly after the sealing process. (Durling 2017) PLA has achieved strong seals close to its melting point (PLLA, 110 °C) (Auras et al. 2004) and increased crystallinity has been reported to increase the required sealing temperature (Lahtinen et al. 2009). The seal strength of PLA has been increased by blending with other polymers i.e., PHA. PHA was reported to hinder the crystallinity of the blend therefore improving the seal strength (Diaz et al. 2016). The heat sealing temperature of PHBV coated paper and paperboards has been reported to vary between 185 -228 °C among the substrate thickness (higher thickness – higher temperature) and the counter sealing surface (PHBV-PHBV or PHBV- substrate), where polymer-polymer sealing resulted in lower sealing temperatures (Kuusipalo 2000). Similar to PLA, the heat sealing temperature of PBAT has been shown to be dependent on its crystallinity. When the crystalline structure of PBAT was removed by thermal treatment, the sealing temperature dropped ~20 °C and required force increased ~50 %. The amorphous nature of PBAT enabled chain mobility and higher diffusion leading to more optimal conditions for chain entanglement. (Tabasi and Ajji 2017)

2.4.3 Barrier properties

Wasting food causes major environmental impacts (Williams et al. 2012, Närvä-nen et al. 2020) and there is a global interest in food waste reduction (Närvänen et al. 2020). One way to extend the shelf life of a package is to have proper barrier properties (Zhang et al. 2019, Kunam et al. 2022). The nature and surrounding circumstances of the packed product specify the needed barrier level to meet the targeted shelf life. Paperboard packaging material is treated to gain protection against water, moisture, grease, gases or volatiles. Examples of goods or products demanding barriers include chocolate (grease, odour, flavour, light), coffee (moisture, grease, oxygen, odour, flavour, aroma, light) and powder detergent (moisture, grease, aroma). (Kirwan 2013)

The permeating mechanism of molecules through barrier coatings include molecule absorption onto the coating surface, diffusion of the molecule through the coating structure and desorption of the molecule when exiting the coating layer (Lagaron et al. 2004, Wu et al. 2021). However, defects, such as pinholes, pores, or cracks, can facilitate the penetration of the molecule through the barrier layer (Auvinen and Lahtinen 2008). Barrier properties are influenced significantly by the surrounding conditions (temperature, relative humidity) and the nature of the permeating molecule (size, polarity) and the barrier film (thickness, crystallinity, polarity, orientation, tortuosity, miscibility) (Auvinen and Lahtinen 2008, Jain et al. 2010, Wu et al. 2021). When the permeating molecule is soluble to the barrier material and cohesive energy in between is low, transmission can occur (Auvinen and Lahtinen 2008). Meanwhile, an increased film crystallinity is known to hinder the diffusion of molecules, improving the barrier properties (Buzarovska et al. 2016). Filler addition has been shown to improve the barrier properties by different mechanisms, for example by creating more tortuous diffusion paths for the permeating molecules (Jain et al. 2010), enhancing the hydrophobicity of the barrier (Yu et al. 2012) or by increasing the crystallinity (Buzarovska et al. 2016).

The barrier properties of thermoplastic biodegradable polymers have been reviewed in Figure 3. Compared to the widely utilized PE-LD, most of the reviewed biodegradable polymers exhibit a weaker moisture barrier, but a better oxygen barrier. Note that the surrounding conditions (temperature / relative humidity) and the film thicknesses (20-500 um) affect the OP and WVP (Figure 3), which are factors to be considered for any comparison.

2.4.4 End-of-life properties

Paperboard itself offers a variety of end-of-life options, since the substrate is generally recyclable, biodegradable/compostable and combustible (Kirwan 2013). However, the end-of-life options of the packaging material depend on the final composition, including surface treatments, inks, adhesives (Andersson 2008, Kirwan 2013), food contaminants (Thurber and Curtzwiler 2020) or waste management infrastructure (Andersson 2008).

Recycling fundamentally involves reusing a given material to regenerate a similar material (Höke and Schabel 2010). In general, recycling is a way to decrease environmental impacts by saving resources and energy with less pollution (Geueke et al. 2018). In the recycling process, paperboard packaging material must be repulpable in aqueous conditions (Höke and Schabel 2010). Fibres are separated from other materials by screening, centrifugal cleaning, flotation, washing and fractionation processes. The separation utilizes different particle characteristics e.g. density, size, form or surface properties. (Andersson 2008, Höke and Schabel 2010) After the separation processes, the recovered pulp can be used as a raw material in paper or board mill (4evergreen 2022). Cellulose fibres in paperboard lose length in recycling processes and can therefore be recycled from 5 to 10 times depending on the fibre type (Kirwan 2013).

The recycling rate of paper and board was 73,9 % in 2020 in Europe (European Paper Recycling Council 2022), while the corresponding number for plastic packaging waste was 38 % in EU in 2020 (Eurostat 2022). The recycling rate for paper and board is rather high and it represents well the circularity of the value chain (Cepi 2022). The European Commission published a proposal for a regulation on packaging and packaging waste (PPWR) 11/2022. The aim of PPWR is to reduce packaging waste and to make all packaging reusable or recyclable by 2030. For paperboards, the regulation supports i.e., the development of lightweight packaging materials and further increasing the already high recycling rate. In terms of plastic packaging, PPWR targets an increase of recycled content in plastic packaging. For example, contact sensitive packaging, such as food packaging made of plastic should have 10 % recycled content by 2030 and 50 % by 2040. However, if the plastic packaging is compostable, recycled content is not required. (European commission 2022)

There are multiple test methods for the evaluation of recyclability of fibre-based materials. A harmonized recyclability has been recently published by Cepi. In the Cepi recyclability laboratory test method (version 2), the number of rejects, visual impurities and sheet adhesion are evaluated. As an example, <20 % of total reject is acceptable to be recycled in a standard mill, if no visual impurities or sheet adhesion issues are detected. (Cepi 2022)

Not all paperboard packaging is feasibly recyclable e.g. due to food contamination. Biodegradability and compostability of packaging waste offer a sustainable route to prevent waste accumulation in landfills (Thurber and Curtzwiler 2020) and help to maintain cleaner recyclable waste streams (Markevičiūtė and Varžinskas 2022).

Biodegradability and compostability have been standardized by international and national standardization bodies (Ebnesajjad 2012) and multiple standards are available of which the European standard EN 13432 is widely utilized (Philp et al. 2013, Helanto et al. 2019). In principle, biodegradable packaging waste should be convertible mainly into carbon dioxide, biomass and water under physical, chemical, thermal or biological decomposition according to the European Parliament and Council Directive 94/62/EC. Biodegradation processes can be rather complex and therefore choosing a suitable biodegradability test is

crucial considering the packaging application and expected end-of-life environment (i.e., compost, soil, marine, water) (Philp et al. 2013). Compostable material is also biodegradable, but not necessarily vice versa due to more demanding requirements (Song et al. 2009). The compostability test (European standard EN 13432) includes chemical characterization, biodegradability, disintegration, ecotoxity and compost quality tests. International standards cover industrial composting methods (higher composting temperatures and shorter time), while various national standards cover home compostability test methods with varying testing conditions. Commonly, the testing time is longer, and the temperature is lower in home compostability tests compared to industrial ones. Home compostability certifications are offered e.g., by TÜV AUSTRIA and DIN CERTO. (European Bioplastics 2018)

2.5 Ideal packaging material and the research questions

Reducing material usage has been a trend in the packaging industry. Light weighting is beneficial from the environmental and cost points of view. However, an ambitious reduction of material weight might impair the material properties and further lead to spoilage or damage of the packed good. (Emblem and Emblem 2012) Another common topic raised by the industry is extended shelf life and thus food waste reduction. By using sufficient packaging material and barrier choices, shelf life can be extended, and major environmental impacts caused by food waste can be decreased (Williams et al. 2012, Närvänen et al. 2020, Kunam et al. 2022). Biodegradability is valuable when there is a risk of landfill accumulation (Vroman and Tighzert 2009).

Ideal biodegradable packaging material would have good processability properties with existing processing equipment. Material performance from a mechanical, thermal and barrier perspective would answer the needs of the industry while in light-weight form. Ideally, the material would originate from renewable resources and would enable reusability, recyclability and compostability depending on the packaging application. All of the above-mentioned properties should be gained in a sustainable and economically reasonable manner. The wish list for ideal biodegradable packaging material is long and there exists room for further development work in terms of material and scale-up. This thesis aims to cover these questions:

1. Can mineral filler additions enhance the processability of biodegradable polymers in the extrusion coating process?
2. How do mineral fillers affect the biopolymer material characteristics and performance?
3. What is the role of mineral filler additions on the convertability of biopolymer coated paperboard?
4. Can mineral filler utilization promote recyclability and/ or biodegradability?
5. Do some of the utilized fillers or biopolymers stand out from the perspective of the question raised above?

These questions are covered by the Results and Discussion and Concluding Remarks parts of this thesis, but also separately in the publications. Question 1 is discussed in **Publication 3**, question 2 is covered by **Publication 1** and **2**. **Publication 4** covers the topics of question 3 and 4, while question 5 is discussed in all the publications, but most noticeably in **Publication 2**.

3. Experimental

This section presents the materials used, such as the biodegradable polymers and the inorganic fillers. In addition, most of the applied methods and analyses from **Publication 1-4**, are described.

3.1   Materials

Materials used in this thesis are listed in Table 1. In addition to the polymers and fillers, an uncoated 200 g/m², 275 μm folding boxboard (Metsä Board Oyj) was used as a baseboard in **publication 3** and **4**.

Table 1 Polymers and fillers used in this thesis.

Material	Company	Details	Publication	Abbreviation
Ecovio® PS 1606	BASF	PLA-based blend, 1.24-1.26 g/cm³ (ISO 1183)	1	Blend1
Ecoworld 009	Jinhui Zhaolong High Technology Co., Ltd.	PBAT, 1.26 g/cm³ (ISO 1183)	2	PBAT
ENMAT Y1000P	TianAn Biologic Materials Co., Ltd.	PHBV, specific gravity 1.25	2	PHBV
Ingeo 4032D	NatureWorks	PLA, 1.24 g/cm3 (ASTM D1505)	2	PLA
Mater-Bi® EX51A0	Novamont S.p.A.	PLA-based blend, 1.24 g/cm³ (ASTM D792)	1, 3, 4	Blend2
Finntalc M03N	Elementis (formerly Mondo Minerals)	Talc, median particle size 1 μm	1	$Talc_1$ /T_1
Finntalc M05SL	Elementis (formerly Mondo Minerals)	Talc, median particle size 2.2 μm	2, 3, 4	$Talc_2$ /T_2
Hydrite SB 100	Imerys	Kaolin, particle size 1 μm (min 40%)	2, 3, 4	Kaolin / K
Omya Smartfill® 55-OM	Omya	Modified calcium carbonate, particles <2 μm (55%)	2, 3, 4	Calcium carbonate / C

3.2   Methods

This part includes the description of the utilized polymer processing methods followed by the polymer, extrusion coating and packaging-related analyses.

3.2.1 Melt compounding

Two types of melt compounding processes were adopted. In **Publication 1**, **3** and **4**, melt compounding of masterbatches (30 wt% of filler/ 70 wt% of polymer) were conducted with a 25 mm Coperion ZSK 26 Mc (32 L/D ratio) counter-rotating twin-screw extruder with K-Tron gravimetric feeder K-ML-KT20. In **Publication 1**, the applied temperature profile of the extruder was 195/195/185/180/175/170/165/160 °C (feeding to die zone) with screw speed, and mass flow rate of 350 rpm and 30 kg/h, respectively. In **Publication 3** and 4, the adopted temperature profile, screw speed and yield were 195/195/185/180/175/170/165/160 °C, 400 rpm, and 20 kg/h, respectively. After melt compounding, the extruded filaments were cooled in water and ambient air, and pelletized. Melt compounding of masterbatches used in **Publication 2**, were prepared to the same filler/polymer ratio (30/70 %), as in other publications, but using a Brabender Plasti-Corder PLE 651 twin screw extruder. The applied temperature zones from the feeding die zone varied among the polymers: 230/210/210 °C (PLA), 230/230/230 °C (PBAT), and 170/170/190 °C (PHBV), respectively. Similarly, the extruded filaments were cooled in water and air, and pelletized.

3.2.2 Injection moulding

Injection moulded specimens (with and without mineral fillers) were prepared in **Publication 1** and **2**. The specimens were prepared by Engel ES 200/40 injection moulding machine (D=25 mm). In **Publication 1** and **2**, standard tensile strength test specimens (ISO 527-2/1A) were prepared, in addition to **Publication 1**, where impact strength test specimens (ISO 179-1/1e) were prepared. Temperature profiles of the barrel are presented in Table 2. The applied packing pressure and time were 30 bar and 20 seconds, respectively, for all the sample points. Injection distances varied from 70 to 95 mm, but injection speed was set to 150 mm/s. The used mould temperature was 30 °C, and the cooling time was from 30 to 60 seconds.

Table 2 Injection moulding temperature zones from feeding to die zone.

Polymer	Temperature zones (°C)	Publication
Blend1	185/200/210/220 °C	1
Blend2	185/200/210/220 °C	1
PBAT	210/210/210/210 °C	2
PHBV	180/180/180/180 °C	2
PLA	185/230/230/230 °C	2

3.2.3 Compression moulding

In **Publication 2**, films were prepared with a Fontijne Vlaardingen Hollad (model TP400) table press. Sample materials (granules or pieces of injection moulded specimens) were laid in between two PET films or greaseproof paper sheets and further between two metal plates. This "sandwich" was pre-heated

surrounded by heated plates without pressure in 210 °C for 30 seconds. After pre-heating, a 140 kN load was applied for 1.5 minutes. Films were cooled in between two 25 °C plates for 2 minutes. The resulting films were 112 to 328 µm thick.

3.2.4 Pilot-scale extrusion coating

Extrusion coating was performed at a pilot extrusion coating line (D=60 mm, L/D=30, T-die) presented in Figure 6. The technology was utilized in **Publication 1**, **3**, and **4**. The neat polymers and masterbatches (filler content 30 wt%) were pre-dried (45-50 °C / 20 h) and mixed in a container to targeted filler concentrations (0-5 wt% in **Publication 1**, 0-10 wt% in **Publication 3** and **4**). The corresponding extruder temperature profiles used for Blend1 PS 1606 was 170/195/210/230 °C (**Publication 1**), and for Blend2 EX51A0 219-220/240/255/265 °C (**Publication 1**, **3** and **4**). The applied back pressure, screw rotation speed, air gap, nip pressure, and line speed were 87–108 bar, 80 rpm, 160 mm, 6 bar, and 40-140 m/min. The paperboard substrate was pre-treated with flame in **Publication 3** and **4**. In **Publication 1** and **3**, silicon paper sheets were place on top of the paperboard substrate prior to the extrusion coating to avoid adhesion and enable plain polymer films. The chill roll temperature was 20 °C, and the type was glossy in **Publication 1**, and matte in **Publication 3** and **4**.
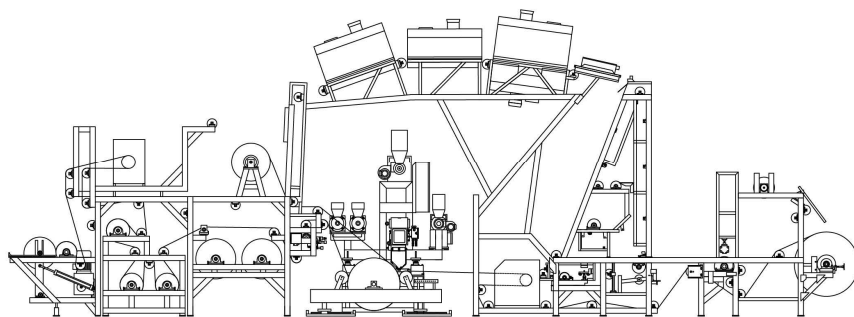

Figure 6 Pilot-scale extrusion coating line utilized in this work. Unwinding is located on the right, extruders (4) are in the centre and rewinding on the left. Adapted with permission from KCL.

3.2.5 Analyses

Morphology
Morphology was investigated from scanning electron microscope (SEM, Jeol JCL-6000Plus) images. SEM images were taken from fractured injection moulded specimens (**Publication 1**), a cross section of compression moulded films (**Publication 2**), and a cross-section of extrusion coated paperboards (Publication 3). All the samples were sputtered with a fine layer of gold prior to SEM imaging. Imaging was carried out under low-vacuum (**Publication 1-2**), and under high-vacuum (**Publication 2-3**), with a secondary electron detector (SED) (**Publication 1-2**), and with a backscatter detector (BED-C) (**Publication 3**).

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Thermal characteristics

Thermal characteristics were determined from granules (neat and masterbatch), and injection moulded specimens with differential scanning calorimetry (Thermal Analyzer, DSC Q2000) equipment in **Publication 1** and **2**. The analysis was carried out on samples of 2-10 mg under nitrogen atmosphere at a flow rate of 50 ml/min. In both publications, the samples were hermetically sealed in aluminium pans, and the first heating cycles were performed with a constant heating rate (10 °C/min) from 20 °C to 200 °C, with 2 minutes hold on at 200 °C. The cooling cycles were run with a constant cooling rate (20 °C/min) down to 20 °C (**Publication 1**), or to -70 °C (**Publication 2**). The second heating cycles were performed similarly to the first one (up to 200 °C at 10 °C/min). The glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures were gained from the DSC thermograms. The degree of crystallinity (X_c) was defined by applying the Equation 1.

$$X_c = 100 \frac{(\Delta H_m - \Delta H_c)}{\Delta H_0 \, w_{polymer}} \qquad (1)$$

,where ΔH_m, ΔH_c , ΔH_o, and $w_{polymer}$ stand for the melting enthalpy, the crystallization enthalpy during heating, the melting enthalpy of 100 % crystalline polymer, and the weight fraction of the polymer in the specimen. The melting enthalpies (ΔH_o) were assumed to be: 93 J/g for PLA and PLA-based blends (**Publication 1-2**) (Khuenkeao et al. 2016, Jain et al. 2012), 114 J/g for PBAT (Chivrac et al. 2006), and 146.6 J/g for PHBV (Carli et al. 2011, Shan et al. 2011) (**Publication 2**).

Mechanical properties

Mechanical properties of injection moulded specimens and films (compression moulded or extruded) were determined in **Publication 1-3**. Tensile and elongational properties of preconditioned samples (at least 88 h, 23 °C/ 50 % RH) were analysed with a Zwick Roell Z010 material tester (max. load 10kN) in accordance with ISO 527-2:2012 under 23 ± 2 °C and 50 ± 10 % RH conditions. Test specimens were prepared to the shape of ISO 527-2/1A. The applied preliminary crosshead separation and speed were 110 mm and 5 mm/min, respectively. The average result of five replicates was reported.

Barrier characteristics

Water vapor and oxygen barrier properties were investigated from films or extrusion coated paperboards in **Publication 1**, **2** and **4**. A modified ISO 2528 standard was used to determine the water vapor transmission rate (WVTR), where the weight change of a desiccant (anhydrous $CaCl_2$) containing measurement cup covered with the sample, was observed as a function of time. The analysis was conducted in an alternating climate chamber (BINDER, model KMF

240) under two conditions (23 °C /50 %RH and 38 °C / 90 %RH). The oxygen transmission rate (OTR) based on the ASTM D3985-05 standard was implemented with an OTR analyser (MOCON, Ox-Tran 2/21 MH/SS) under 23 °C and 50 %RH conditions. The results of the WVTR and OTR analyses were the average of two replicates with a few exceptions described in **Publication 1**. Samples were normalized by the film/ coating thicknesses.

Neck-in

Neck-in was determined in **Publication 3**. The neck-in was observed by the difference of the applied deckles (570 mm and 590 mm) and resulted coating width (mm) on the coated paperboard sheet. The reported value was the average of three replicates.

Adhesion

Adhesion between the extrusion coating and the paperboard substrate was determined in **Publication 3**. The extrusion coating was carefully cut (X-shape) with a sharp knife, and manually peeled to the machine direction, and to the opposite. Adhesion was evaluated visually from the degree of fibre tear and scaled from 0 to 5 (0= no adhesion, 5= 100 % fibre tear).

Pinhole analysis

The pinholes of the extrusion coated paperboards were studied in **Publication 3**. A red water-based solution (500 ml of water, 5.34 g of Triton X-100, 5 g of beetroot colour) was applied on top of the extrusion coating to expose pinholes. Coloured and dried samples were photographed (NIKON D5200, 6000 x 4000 pixels, 300 dpi) under 254 nm UV light. Matlab software was used for further analysis of the images. The original images were extracted by the blue colour channel, and the inspected area selected (Matlab function imcrop). The pinhole rich area was pre-defined (2670 x 3530 pixels), extracted, and binarized (Matlab function imbinarize with adaptive method). Random white pixels were removed from the edges of the image by defining a new target size (2650 x 3510 pixels) and binarizing it. In the resulting image, the number of connected white pixel areas represented the number of pinholes, which were found by a Matlab function bwconncomp.

Heat sealing

Heat sealability of extrusion coated paperboards was studied in **Publication 4**. Heat sealability was examined with one side heated hot bar sealing equipment (GL Instruments, 010806A, UK). Sealing force, pressure and pressing time were set to 300 N, 3 bar and 3 seconds, respectively. Temperature range varied from 120 to 200 °C. Hot air sealability tests took place at Tampere University with hot air sealing machine (Lahti et al. 2017). The used sealing force, network pressure, heating -, open -, and pressing time were: 400 N, 6 bar, 1.24

seconds, 0 seconds, and 1.9 seconds, respectively. The applied sealing temperatures were 350-440 °C. Both in hot bar and hot air sealing tests, the samples were cooled down to room temperature after sealing and teared manually. Evaluation was made visually and scaled based on the degree of fibre tear (0= no seal, 1= weak adhesion, 2= adhesion but no fibre tear, 3= <50 % fibre tear, 4= >50 % fibre tear, 4.5= >90 % fibre tear, 5= 100 % fibre tear).

Cup forming

Cup formability was investigated in **Publication 4**. Cup forming tests were implemented with a cup forming machine of 50 cups/min maximum speed. The cup side wall blanks were die cut, and bottom ribbon cut prior to the cup making. The targeted paper cup dimensions were height 92 mm, bottom diameter 60 mm, rim diameter 80 mm, resulting in a cup with 2.5 dl volume. The cup forming process included three individual sealing events (Figure 7), 1) ultrasonic sealing of the cup side wall (signal length 0.2 s, signal strength 1 in scale of 1-3), 2) hot air sealing to activate the 1st seam of the cup bottom (temperature 190 °C, air pressure 6-7 bar, heating time 1.5 s), and 3) hot bar sealing to seal the 1st and 2nd bottom seams (temperature 190 °C, pressing time 1.5 s). Evaluation was executed from the individual seams with a manual peeling method, and the degree of fibre tear was scaled from 0-5.
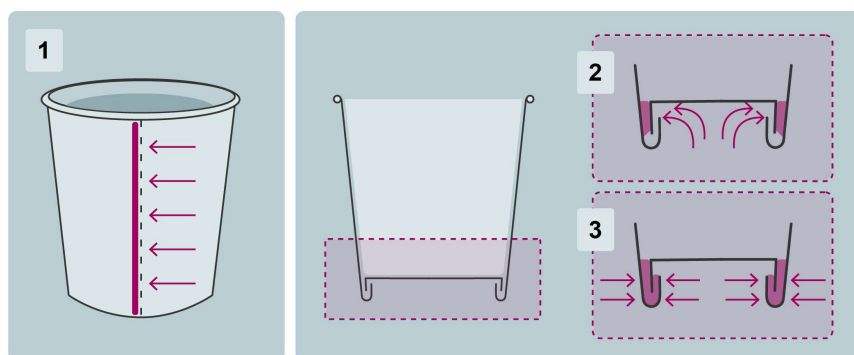

Figure 7 Heat sealing events of the paper cup (redrawn from **Publication 4**). The arrows present the applied heat and the red area the formed seals. 1) Cup side seam with ultrasonic sealing, 2) 1st bottom seal activation with hot air, 3) 1st and 2nd bottom seal heat sealing with hot bar.

Repulpability

Repulpability of extrusion coated paperboards was evaluated in **Publication 4**, where 50 g of pre-cut (2.5 cm x 2.5 cm) samples were mixed (Diaf dissolver, model FFBH 3, n. 22727) with 950 g of water (23 °C) for 17 minutes at 3000 rpm speed. Hereafter, the resulting slurry was diluted into 1 % consistency, and mixed for 4 minutes. Visual inspection for potential fibre bundles and coating pieces of 2 dl of the 1 % slurry was made on a special blue glass tray (37.5 x 27 cm).

Biodegradability

The ultimate aerobic biodegradability in compost (100 days, 58±2 °C / 50 %RH) was studied in **Publication 4** from extrusion coated paperboards according to UNE-EN 13432:2001 and UNE-EN ISO 14855 1:2013 standards. The test was implemented in biodegradation reactors (2 L) including: dry compost (200 g, COGERSA, 4 months), inert vermiculite (50 g, Leroy Merlin), and water (250-265 g). Additionally, the reference reactor included dry cellulose (30 g, Sigmacell cellulose type 20, Sigma-Aldrich), and the test sample reactor dry test material (30 g in 500 μm powder form). The biodegradation degree was defined from the obtained values of total dry solids (g), total organic carbon (%), and cumulative amount of CO_2. The results are averages of three replicates.

4. Results and discussion

The most important results of this work are presented in this section. The discussion of **Publication 1-4** has been used in such a manner to develop a comparison and to reach key conclusions about the ultimate effect of filler additions. Most of the results are from films or coatings. The mineral filler effect on the characteristics of the biodegradable polymer materials, such as on thermal, mechanical and morphological properties, is discussed first. Then, a discussion is offered about the impact on the processability, product, convertability and end-of-life properties. A more detailed evaluation of each topic is presented in the Publications.

4.1 Material characteristics

The material characteristics of the explored polymer-filler systems are reviewed from morphological, thermal and mechanical points of view. The examined samples were injection moulded, compression moulded, film extruded, or extrusion coated. Injection and compression moulding were employed for laboratory-scale experiments, whereas extrusion coating was utilized for pilot-scale trials.

4.1.1 Morphology

The morphology of injection and compression moulded specimens, and extruded films/ coatings was studied from SEM images in **Publication 1-3**. The $talc_1$ addition to the PLA-based polymer blends (Blend1 and Blend2) was observed to reduce the size of the polyester domains in injection moulded specimens and therefore improved the miscibility when $talc_1$ content was higher than 2 wt% (Blend1) and 3 wt% (Blend2) in **Publication 1**. An SEM image of a fractured injection moulded specimen (Blend1) with 1 and 4 wt% of $talc_1$ is presented in Figure 8. The polyester domains are visible in Figure 8A after 1 wt% of $talc_1$ addition, whereas the domains were no longer visible in Figure 8B with 4 wt% of $talc_1$. $Talc_1$ particles were tightly embedded and settled in the mould fill direction relatively uniformly throughout the injection moulded specimen (Figure 8B). Immiscible blends of PLA and PBAT have been investigated by other authors. Presented phase-separated structures were similarly visible in their SEM images than in this work and explained by the weak interfacial adhesion of the two polymers. (Kumar et al. 2010, Teamsinsungvon et al. 2013, Correa et al. 2016)

The compatibilizing effect of nano- and micro-sized talc in immiscible polymer blends has been compared. Both filler types improved the miscibility of the blend, but with different techniques. Micro-sized talc, like the talc used in this work, were proposed to reduce the domain size by Zhu´s mechanism. (Yousfi et al. 2014) Zhu's mechanism is based on the cutting effect caused by shear of the filler particles during mixing (Zhu et al. 2008, Yousfi et al. 2014).
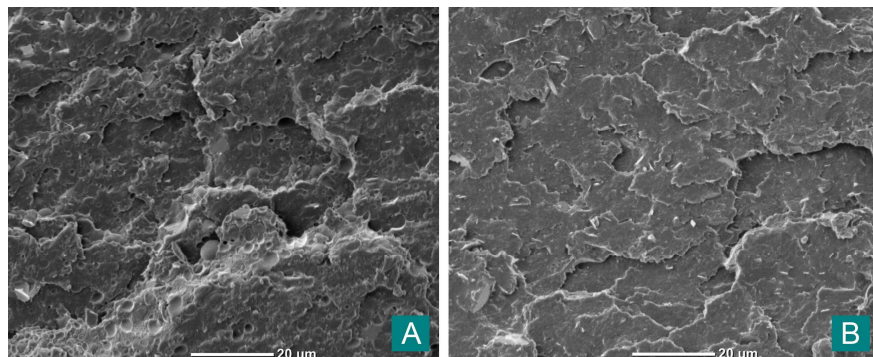

Figure 8 Cross section SEM images of fractured injection moulded specimen. A) Blend1 with 1 wt% of talc, B) Blend1 with 4 wt% of talc.

Blend1 (>3 wt% of $talc_1$) and Blend2 (>4 wt% of $talc_1$) generated few pinholes when film extruded in **Publication 1**, and an example is presented in Figure 9A. Similarly in **Publication 3**, pinholes were generated into the extrusion coating with $talc_2$, kaolin and calcium carbonate especially when coating weight decreased. Likewise, to our observations, filler additions have been reported to have an effect on the pinhole formations e.g. as a result of filler agglomerates (Krook et al. 2005). In the compression moulded films of PLA, PBAT, and PHBV, the fillers ($talc_2$, kaolin and calcium carbonate) were mainly dispersed rather uniformly into the polymer matrices (Figure 9B). However, due to the lack of mixing during the film formation some agglomerates were present in kaolin containing films. $Talc_2$ and kaolin were tightly surrounded by the polymer matrices, whereas calcium carbonate generated small cavities around the fillers, as shown in Figure 9B. Well embedded filler particles have been considered to have good polymer-filler interactions (Leong et al. 2004), whereas cavities surrounding the filler particles indicated poor polymer-filler interactions (Sitthi et al. 2017, Aliotta et al. 2019). Calcium carbonate has been reported to result in cavities i.e., in PLA (Aliotta et al. 2019), PBAT (Nunes et al. 2017), and in PHBV (Sitthi et al. 2017) matrices, which correlates to our observations in **Publication 3**. Commonly utilized surface treatment (stearic acid) lowers the surface energy of calcium carbonate and hinders the filler-matrix adhesion while improving the dispersion of the fillers (Aliotta et al. 2019). Untreated calcium carbonates have a higher agglomeration tendency (Aliotta et al. 2019) and agglomerates can promote the formation of large cavities (Nunes et al. 2017).
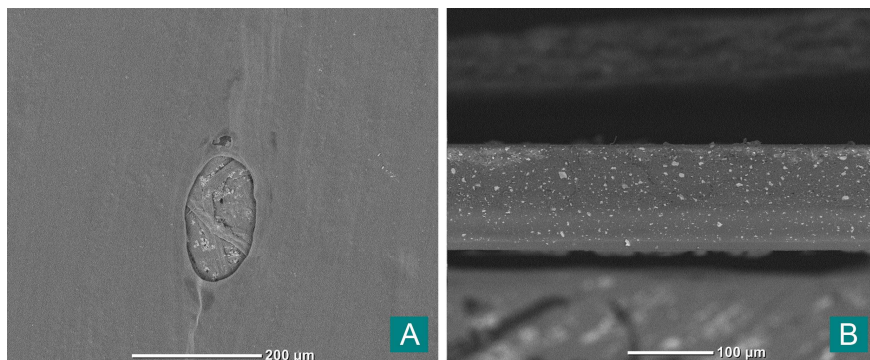
Figure 9 SEM images of A) a pinhole in extruded Blend1 film with 5 wt% $talc_1$ (related to **Publication 1**), B) a cross section of compression moulded PLA film with 10 wt% of calcium carbonate (related to **Publication 2**)

The morphology of extrusion coatings (Blend2 with $talc_2$, kaolin or calcium carbonate) were studied in **Publication 3**. Filler particles seemed to be settled relatively uniformly into the coating when investigated from top (Figure 10A) and cross section (Figure 10B) SEM images. Also, the platy fillers seemed to be aligned mainly parallel to the film surface. These results correlate with samples produced through injection and compression moulding. Utilization of typical production processes used for packaging materials have been reported to result in parallel orientation of talc to the film surface, which is beneficial e.g., from a barrier point of view (Castillo et al. 2013). From the cross-section SEM images a good adhesion between the coating and the paperboard was able to be confirmed from the lack of air in between of the coating and paperboard substrate (Figure 10B).
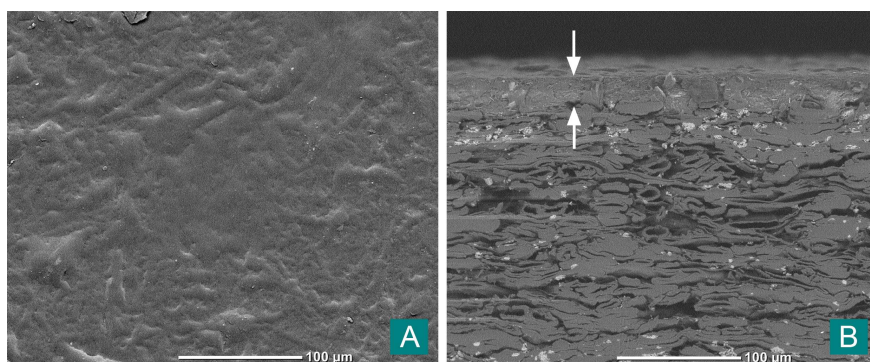

Figure 10 SEM images related to **Publication 3** of Blend2 with 4 wt% of $talc_2$ extrusion coated paperboard. A) top image, B) Cross section image, where the coating layer has been marked with arrows.

4.1.2 Degree of crystallinity

Thermal characteristics were studied with DSC in **Publication 1** and **2** from granules, masterbatches and injection moulded specimens. The development in the degree of crystallinity is presented in Figure 11. In general, the higher degree of crystallinity promotes the barrier properties due to the strong linkage of crystalline and amorphous regions and harder molecule penetration through more

tortuous crystalline areas (Delpouve et al. 2012). As expected, $talc_1$ behaved as a nucleating agent for crystal formation in the PLA-based polymer blends (Blend1 and Blend2), as well as $talc_2$ in PLA and PHBV sample points. The nucleating effect of talc on PLA-based systems has also been discovered by several others (Battegazzore et al. 2011, Jain et al. 2012, Qin et al. 2014, Ouchiar et al. 2015, Buzarovska et al. 2016, Khuenkeao et al. 2016, Phetwarotai and Aht-Ong 2016, Ghassemi et al. 2017). Talc has been reported to indirectly affect the crystallization of PHB/PHBV polymers by reacting with the molten polymer chains, acting as a chemical reagent. The actual nucleating agent was reported to be the reaction product instead of talc. (Kai et al. 2005) The observed exception in this work was PBAT, where no such a behaviour was seen with $talc_2$. The filler addition in general decreased the crystallinity of PBAT. Similarly, in our results, the crystallinity of PBAT has been observed to decrease with filler additions. Chivrac et al. assumed nanofillers (mineral clays) hindered the crystallite growth of PBAT and similarly Bastarrachea et al. observed nisin addition decreasing the crystallinity of PBAT (Chivrac et al. 2006, Bastarrachea et al. 2010). However, examples with similar fillers used in this work were lacking.

Kaolin along with $talc_2$, worked as a nucleating agent in PLA and PHBV matrices. However, the nucleating effect in PLA matrix was significantly lower than with $talc_2$, whereas in PHBV matrix kaolin containing sample resulted in the highest crystallinity among all the sample points. Similar to our work, kaolinite has been observed to nucleate PLA, but compared to talc, the nucleating effect has been very limited (Ouchiar et al. 2015, Ouchiar et al. 2016). The difference has been explained by Ouchiar et al. 2016 by the absence of crystallographic interactions between the kaolin and PLA crystal structure. In addition, a moderately increased crystallinity has been observed with halloysite, which belongs to the kaolin group of clay minerals, in PHBV matrix (Carli et al. 2011). In this work, kaolin, among other fillers, reduced the crystallinity of PBAT. However, the reduction with kaolin was the biggest, and could partly explain the poor oxygen barrier of kaolin containing PBAT-film in **Publication 2**.

Calcium carbonate was observed to decrease the crystallinity in PLA and PBAT matrices, while increasing it in PHBV matrix. The efficiency of calcium carbonate as a nucleating agent has been reported to be dependent on the particle size, purity and surface properties when introduced in syndiotactic poly(propylene). Surface treated (stearic acid and paraffin) calcium carbonate was noticed to hinder the nucleability of the filler, whereas small particle size (higher surface area) appeared beneficial. According to the proposed theory, the rough surface of the filler enabled the syndiotactic poly(propylene) crystallites to become entrapped and further promoted the crystallization. The surface treated fillers were lacking the optimal surface and therefore hindering the crystallite entrapment. (Supaphol et al. 2004) Nano-sized calcium carbonate has been reported both to increase and decrease the crystallinity of PLA matrix (Sabzi et al. 2013, Piekarska et al. 2017). Typically, higher loadings of nanofillers can hinder the crystallinity development (Piekarska et al. 2017), e.g., by physically limiting the mobility of polymer chains to form crystals (Tjong 2006). However, opposite results have also been reported. Lower nano-sized calcium carbonate loadings

(<10 wt%) have been observed to hinder the crystallite growth in the PLA matrix, while higher loadings (>10 wt%) have increased it due to the filler agglomeration, and therefore, lowered the confinement of the nanofillers. (Sabzi et al. 2013) Crystallinity in the PHBV matrix has been observed to increase with lower calcium carbonate concentrations and decrease with high concentrations. The major cause for the hindered crystallinity development with a high concentration of calcium carbonate was the agglomeration of the fillers (Sitthi et al. 2017). In this work, the likely explanation of the limited nucleability of calcium carbonate is the surface modification of the filler rather than the relatively high filler content. This is because no significant aggregates were detected in the SEM images containing calcium carbonate. Thus, cavities, which indicated low polymer-filler adhesion could play a role if the surface of the filler were not optimal for crystallites to be entrapped.
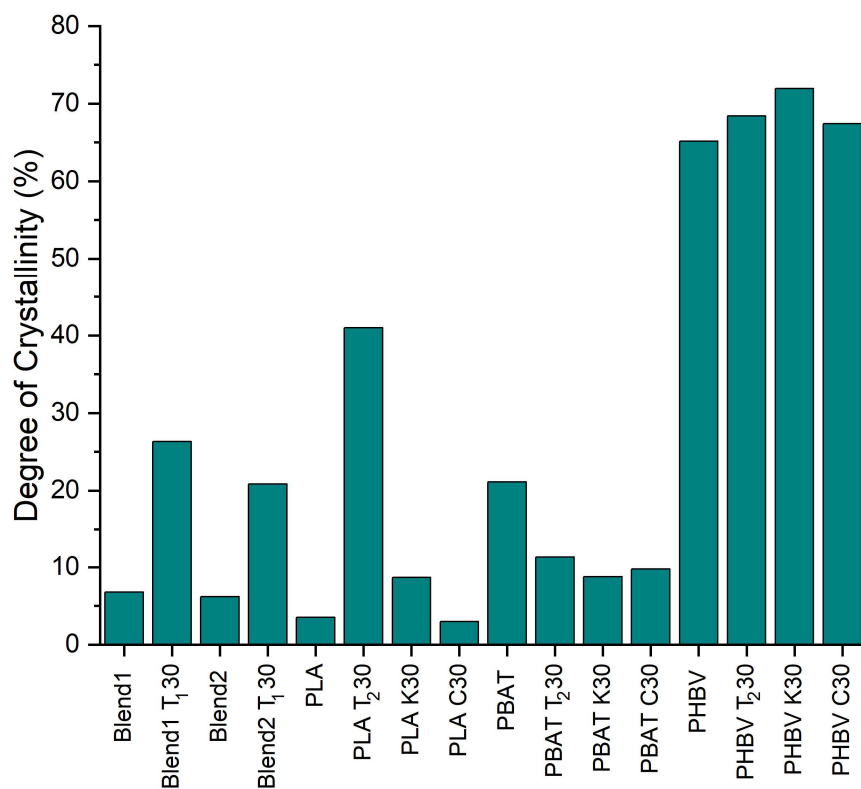

Figure 11 The degree of crystallinity determined from granules (neat and masterbatch) and injection-moulded specimens (**Publication 1-2**). T_1= talc$_1$ (particle size 1 µm), T_2= talc$_2$ (particle size 2,2 µm), K=kaolin, C= calcium carbonate, and the number after the letter stands for the filler content (wt%).

In **Publication 1**, it was discovered that the crystallinity development of the used PLA-based polymer blends (Blend1 and Blend2) was influenced also by the miscibility change of the blends. Blend1 and Blend2 changed from immiscible to miscible due to the talc$_1$ addition. Before the observed miscibility change, the crystallinity increased alongside the increasing talc1 content. However, in the

range of the change, the degree of crystallinity dropped, but continued to increase after the change. The decreased droplet size has been observed to decrease the crystallinity in immiscible blends. The phenomenon has been explained by the fractionated crystallization of immiscible blends, where crystallizations take place at different, lowered temperatures leading to imperfect crystals and further decreased crystallinity. (Tol et al. 2005)

4.1.3 Mechanical characteristics

Mechanical characteristics were studied in **Publication 1- 3**. Tensile strength development after 4-5 wt% of filler additions in films (compression moulded or film extruded) has been presented in Figure 12. The results showed a decrease in tensile strength with the addition of 4-5 wt% fillers except for PLA with 5 wt% of talc$_2$, which was an exception. The most favourable filler in terms of tensile strength varied among different polymer matrices. Talc$_2$ was the most favourable filler for PLA, kaolin for PBAT, and calcium carbonate for PHBV and Blend2 (in **Publication 3**). When comparing the fillers, talc has been reported to form stronger polymer-filler interactions with PLA chains compared to kaolin. This has been explained by the chemical differences of these fillers, talc having two silicate layers for PLA chains to form hydrogen bonds, while kaolin has only one silicate layer. (Ouchiar et al. 2015) Furthermore, kaolin often appears as aggregates rather than individual particles in polymer matrix which can cause reduction in strength (Leong et al. 2004). Calcium carbonate with and without stearic acid surface treatment has been observed to result in poor polymer-filler interactions with PLA (Aliotta et al. 2019). Overall, the highest tensile strength obtained in this work, was with PLA and its composites, then for PHBV and the blends, while the lowest tensile strengths obtained were with PBAT samples. Generally, in terms of mechanical characteristics, micro-sized fillers have been reported to be generally rather unbeneficial due to their ability to form stress concentrators in biopolymer matrices (Castillo et al. 2013). However, filler additions generally increased the crystallinity of the blends and the PLA and PHBV samples. In theory, increased crystallinity could lead to increased strength due to stronger intermolecular bonding in the crystalline phase (Balani et al. 2015). In addition to the crystallinity development, several other factors affect the tensile strength of polymer-filler systems. Other authors have observed the effect of the filler distribution in the matrix, polymer-filler and filler-filler interactions and blend compatibility on the tensile strength (Chow et al. 2004). Furthermore, the preparation technique of the films plays a role. For example, in film extrusion, the orientation of the films is influenced e.g., by the draw ratio, air gap, machine speed, and cooling conditions, which further affect the mechanical properties (Toft and Rigdahl 2004). While in compression moulded films the polymers are randomly oriented and therefore comparison with extruded films needs to be done with caution.
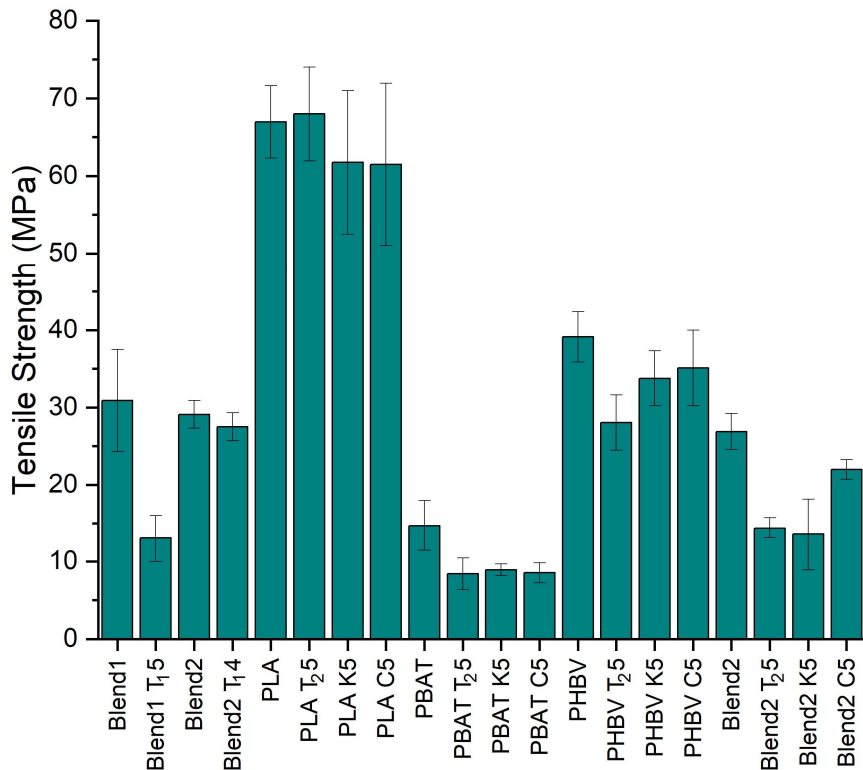
Figure 12 Tensile strength of 4-5 wt% filler-reinforced biodegradable polymer films manufactured by film extrusion (Blend1 and Blend2) or compression moulding (PLA, PBAT, PHBV) in **Publication 1-3**. T_1= talc$_1$ (particle size 1 μm), T_2= talc$_2$ (particle size 2,2 μm), K=kaolin, C= calcium carbonate and the number after the letter stands for the filler content (wt%).

Similar to tensile strength, also elongation at break was weakened due to the filler additions (Figure 13). Calcium carbonate was the least unfavourable filler in terms of elongation. PLA, PHBV, and the Blend1 and Blend2 were rather brittle with low elongation, whereas PBAT was very flexible, as expected. As earlier mentioned, fillers can function as stress concentrators in the polymer films leading to cracking and weakened elongation. This phenomenon is caused by weak polymer-filler interactions which prevent the stress transfer between the filler and the polymer matrix. (Fu et al. 2008) Moreover, the increased crystallinity of the films limits the elongation (Petchwattana et al. 2014). Examples of decreased elongation because of filler addition have been reported for many polymer-filler combinations (Raquez et al. 2008, Carli et al. 2011, Ouchiar et al. 2015, Nunes et al. 2017, Aliotta et al. 2019).
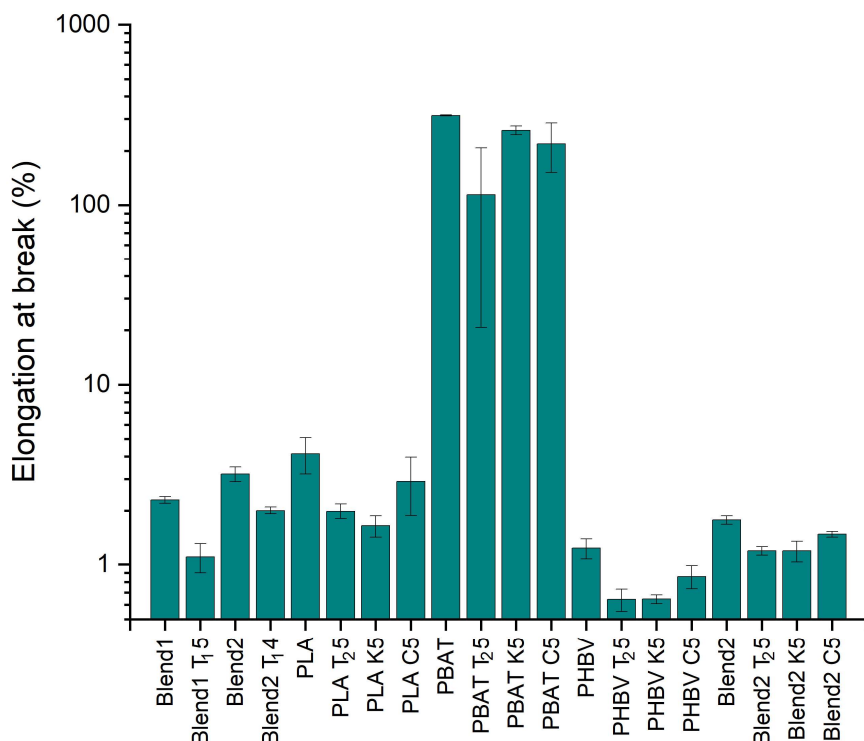
Figure 13 Elongation at break of 4-5 wt% filler-reinforced biodegradable polymer films manufactured by film extrusion (Blend1 and Blend2) or compression moulding (PLA, PBAT, PHBV) in **Publication 1-3**. T_1= talc1 (particle size 1 μm), T_2= talc2 (particle size 2,2 μm), K=kaolin, C= calcium carbonate and the number after the letter stands for the filler content (wt%).

The effect of filler additions on the elastic modulus is presented in Figure 14. The elastic modulus was increased in PLA and PHBV specimens, but in PBAT and the blends (Blend1 and Blend2), a decrease was observed. However, the decreased elastic modulus of Blend1 and Blend2 is likely the outcome of a stress concentration failure caused by the fillers in the relatively thin extruded films. The elastic modulus correlated with the development of the crystallinity degree, except in the extruded films. The elastic modulus typically correlates with crystallinity trends, increasing as crystallinity increases (Humbert et al. 2011). Talc$_2$ stood out as the most favourable filler in terms of the elastic modulus in the PLA matrix, while kaolin was most favourable in PHBV. Talc$_2$ and kaolin decreased the elastic modulus of the PBAT matrix to a similar extent, which was less than the decrease caused by calcium carbonate. An increased elastic modulus of polymer-filler systems has been reported for many polymer-filler combinations e.g., for PLA/talc (5 vol%) (Deetuam et al. 2020), PLA/talc and PLA/kaolinite (5-30 wt%) (Ouchiar et al. 2015), PBAT/CaCO$_3$ (20-30 wt%) (Nunes et al. 2017), PHBV/ halloysite (1-5 wt%) (Carli et al. 2011) composites. Among the other mechanical properties, the increased elastic modulus and, overall, the stiffness of a polymer-filler system have been reported to be increased due to the ability of the filler to transfer the stress from the polymer matrix to itself (Deetuam et al. 2020, Lee et al. 2020).
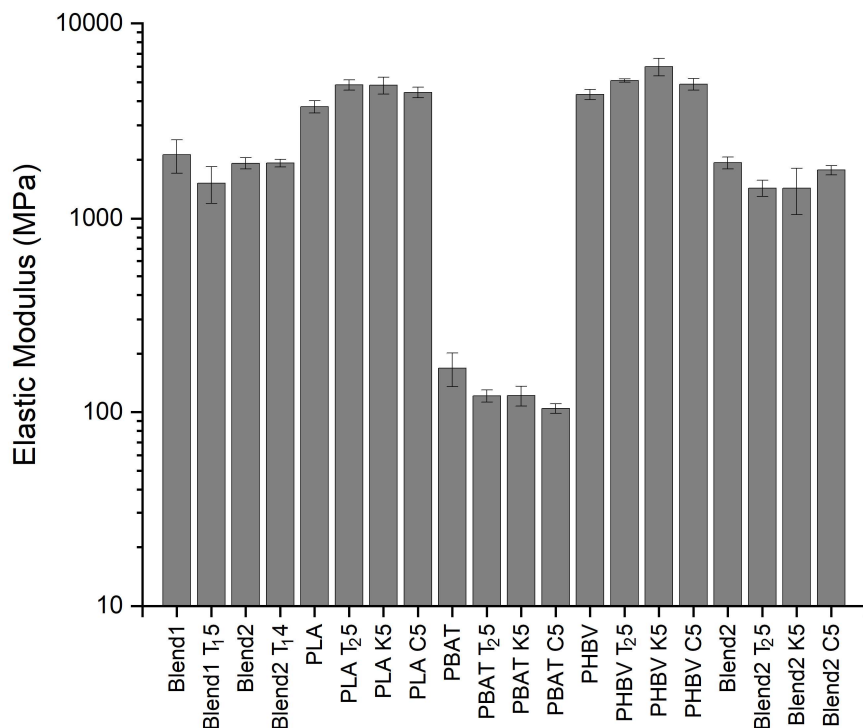
Figure 14 Elastic modulus of 4-5 wt% filler-reinforced biodegradable polymer films manufactured by film extrusion (Blend1, Blend2) or compression moulding (PLA, PBAT, PHBV) in **Publication 1-3**. T_1= talc$_1$ (particle size 1 µm), T_2= talc$_2$ (particle size 2,2 µm), K=kaolin, C= calcium carbonate and the number after the letter stands for the filler content (wt%).

4.2 Processability, end-product and end-of-life properties

In this section, the main results of every category are presented. Processability-related analyses were conducted in **Publication 3**. Barrier properties were studied in **Publication 1**, **2** and **4**. Heat sealability and Biodegradability properties were investigated in **Publication 4**.

4.2.1 Processability

Neck-in

Processability-related analyses were studied in **Publication 3**. Neck-in stands for the polymer film width reduction in the air gap. It is targeted to a minimum to optimise the material efficiency. (Shiromoto et al. 2010) The neck-in results of the 5 wt% filler containing sample points are presented in Figure 15. All the fillers at 5 wt% decreased the neck-in compared to the reference sample. With the filler content of 5 wt%, kaolin decreased the most and calcium carbonate the least. The neck-in reducing impact of high aspect ratio fillers has been reported by others. High aspect ratio fillers (clay) were reported to increase the storage modulus, complex viscosity, polymer melt tension, drawability and thus reduce the neck-in in contrast to low aspect ratio fillers (clay). (Wang et al. 2001) In this work, the lowest neck-in reduction obtained with calcium carbonate could be explained by the lower aspect ratio compared to platy talc and kaolin (Leong

et al. 2004). Reduced neck-in caused by filler additions has been observed in PLA-based systems also by other authors. Explanations for the phenomena have been e.g., increased elasticity (Khajeheian et al. 2018), increased molecular weight and an increased level of crosslinking or branching (Dhar et al. 2017). However, a reduction of molecular weight during extrusion is more typical with inorganic fillers than an increase (Dhar et al. 2017). Crosslinking or branching is also an unlikely outcome caused by the fillers utilized in this work. Neck-in could have decreased by the increased elasticity of the melt. On the other hand, the mechanism behind the reduced neck-in could have been the enhanced network structure created by the polymers and the fillers, which had the ability to resist neck-in. Similar strain hardening behaviour is known for branched polymers during neck-in (Durling 2017).

Pinholes

Filler additions affected the pinhole formation, as seen in **Publication 3**. However, the pinhole formation was more influenced by the resulting coating weight than the increasing filler amount. Also, there were differences between the filler types, as seen in the Figure 15, where no pinholes were formed in the reference sample, nor in the 5 wt% calcium carbonate containing sample. However, at 5 wt% of talc$_2$ or kaolin content, pinholes were formed at extrusion line speed of 60 m/min at coating weights 20-22 g/m^2. Kaolin generated more pinholes than talc$_2$. Calcium carbonate used in this study was seen to form cavities in compression moulded films (Figure 9B), and kaolin and talc$_2$ were found to be embedded more tightly into the polymer matrices. Despite the observations in **Publication 2**, calcium carbonate must have resulted in relatively good polymer-filler interactions to remain pinhole free in the extrusion coating process. Even though correlation was mainly observed between the decreased coating weight and pinhole formation, rather than between filler content and pinhole amount, other authors have reported such a dependency. Pinholes were increased by increasing filler content in PE-LD/ montmorillonite nanocomposite, where the possible cause of the increased pinholes was filler agglomerates (Krook et al. 2005).
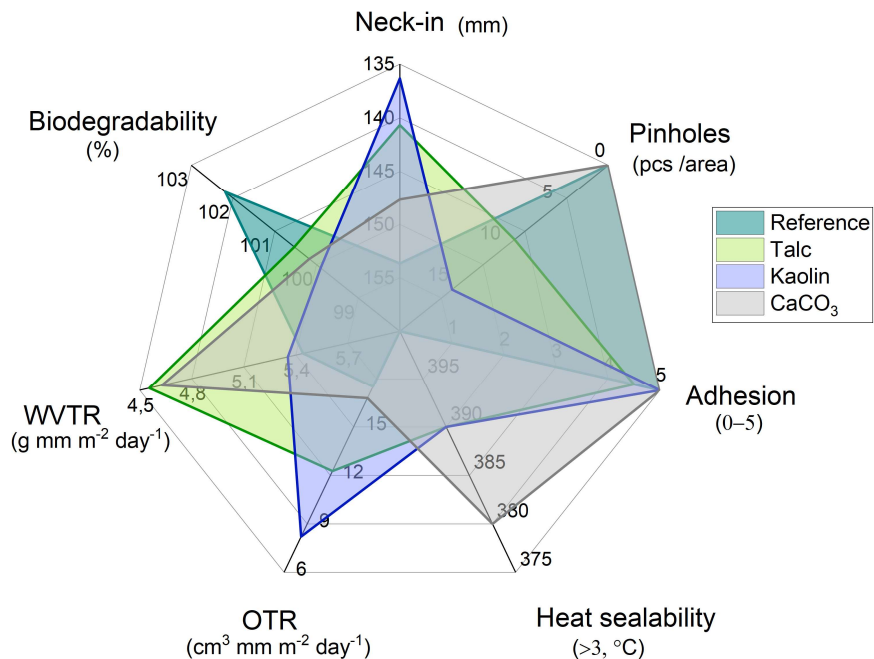
Figure 15 Processability, end-product properties and biodegradability of the extruded biode-gradable polymer (Blend2)/ filler paperboard coatings (**Publication 3**-**4**). Neck-in was measured at polymer temperature 270 °C, air gap of 160 mm and line speed of 80 m/min with 5 wt% filler content. Pinholes and adhesion were analysed from sample points extruded with 60 m/min line speed and 5 wt% filler content. The size of the analysed area for pinholes was 2650 × 3510 pixels (Matlab). Hot air sealability was measured top vs. back side from samples with 5 wt% filler content. OTR was analysed in 23 °C and 50 %RH, with 4 wt% of talc, 3 wt% of kaolin or 5 wt% of $CaCO_3$. WVTR was analysed in 38 °C and 90 %RH, with 5 wt% of talc, 3 wt% of kaolin or 5 wt% of $CaCO_3$. Biodegradability was analysed for 100 days from samples containing 5 wt% fillers.

Adhesion

Adhesion between extrusion coating and paperboard was positively affected by the filler addition as described in detail in **Publication 3**. Compared to the reference sample, lower coating weights with good adhesion were achieved with all the filler types. As expected, a dependency was seen with the coating weight and the adhesion level in general, even though fillers somewhat changed it and helped the adhesion development at lower coating weights. The adhesions of the coatings including 5 wt% of fillers are presented in Figure 15. With all the fillers, the adhesion was 4.5/ 5, meaning over 90 % fibre tear. Despite the positive development of adhesion, the low coating weights included pinholes. Calcium carbonate (1 wt% and 5 wt%) containing samples reached lower coating weight compared to the reference without any pinholes. A higher coating weight coolis more slowly, and therefore benefits the coating penetration into the substrate (Morris 2008). With a similar logic, fillers might have maintained the heat of the coating a bit longer, and further helped the penetration of the coating. Adhesion is generally obtained by wetting the melted polymer onto the substrate, and by chemical bonds and/or mechanical interlockings (Durling 2017). Opposite to our results, decreased adhesions gained after filler additions had been reported. The main reason has been the increased viscosity caused by the fillers,

therefore lowering the degree of penetration into the substrate. (Krook et al. 2005, Khajeheian et al. 2018)

4.2.2 Barrier performance

Barrier properties were studied from extruded (**Publication 1**) and compression moulded (**Publication 2**) films, as well as extrusion coated paperboards (**Publication 4**). The results of water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) are presented in Figure 16 and Figure 17, respectively. Sample points presented in the figures were selected based on the best obtained barrier result (lowest value) with every studied polymer/filler combination. Improved WVTR results compared to the neat polymer were achieved with all the fillers except in compression moulded PBAT films with calcium carbonate. In terms of OTR, improved oxygen barrier properties were achieved excluding PLA, PBAT, and PHBV with calcium carbonate, and PBAT also with kaolin. All the presented results are normalized to the film thicknesses.

Among all the studied polymer matrices, talc was observed to be the most favourable filler by decreasing the WVTR level the most compared to the neat polymer. Kaolin was the second most favourable filler, except in extrusion coated paperboard with Blend2 and 3 wt% of kaolin, which improved the water vapor barrier the least. According to our results, calcium carbonate was the least favourable filler for improving the water vapor barrier properties. The biggest impact of the filler addition was observed in PLA, and PHBV films. WVTR (23 °C/50 %RH) decreased with 30 wt% of $talc_2$ addition in PLA films up to 68 %. Whereas the improvement in PHBV films with 5 wt% of $talc_2$ was up to 47 %. Similarly, talc addition enhanced the moisture barrier of other polymer films and coatings up to 18-37 % compared to the neat polymer. Examples from other authors of improved water or water vapor barrier properties with similar fillers (talc (Jain et al. 2010, Cipriano et al. 2014, Qin et al. 2014), halloysite or silver loaded kaolinite (Girdthep et al. 2014, Gorrasi et al. 2014), calcium carbonate (Rocha et al. 2018)) can be found, especially when PLA or PLA involved matrix have been used.
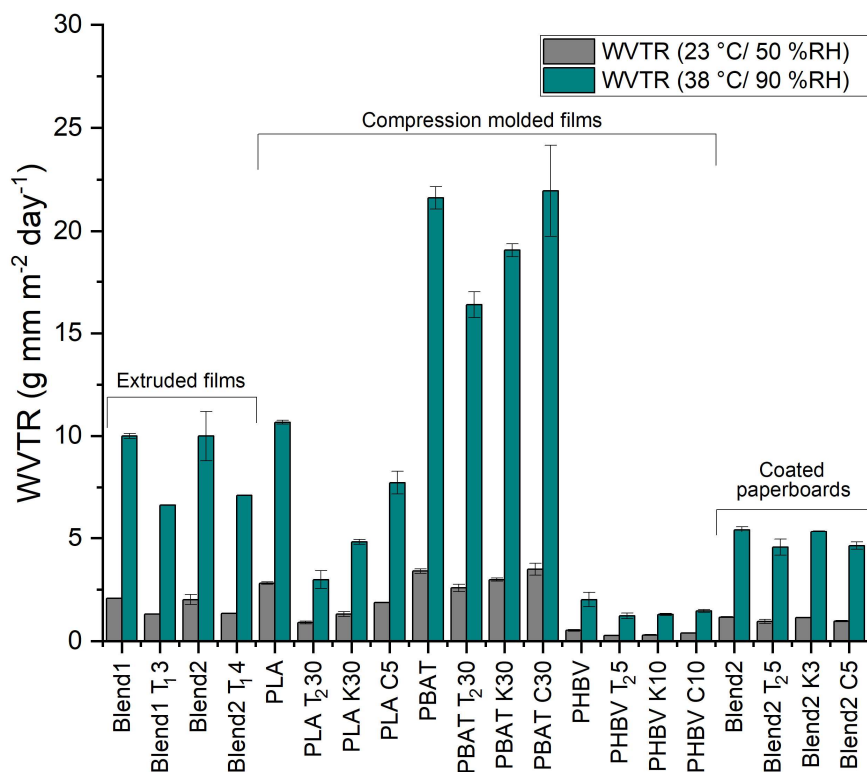
Figure 16 WVTR of filler-reinforced biodegradable polymer films, manufactured by film extrusion (Blend1, Blend2) or compression moulding (PLA, PBAT, PHBV), and extrusion coated paperboards (*Blend2). T_1= talc$_1$ (particle size 1 µm), T_2= talc$_2$ (particle size 2.2 µm), K=kaolin, C= calcium carbonate and the number after the letter stands for the filler content (wt%). (**Publication 1**, **2**, **4**)

Notable improvement in oxygen resistance was achieved with filler additions. The biggest impact on the positive barrier development was reached with talc and kaolin additions. Talc$_2$ improved the oxygen resistance by 72 % in PHBV, and by 62 % in PLA matrices. In contrast, kaolin improved the oxygen barrier up to 58 % in PHBV, and up to 56 % in Blend2 coatings. Enhancements were accomplished also with other combinations (Figure 17). As mentioned earlier, also weakened oxygen resistance of the films was obtained. Two significantly reduced oxygen barrier levels were gained with kaolin (30 wt%) in PBAT film, and with calcium carbonate (30 wt%) in PHBV films. The other two weakened results (PLA and PBAT with 30 wt% of calcium carbonate) were more minor. Examples from the literature, where OTR was improved with similar fillers, were found from PLA-based systems with talc (Jain et al. 2010, Qin et al. 2014, Ghassemi et al. 2017), and PHBV systems with kaolinite (da Costa et al. 2020), and calcium carbonate (Kirboga and Öner 2020).
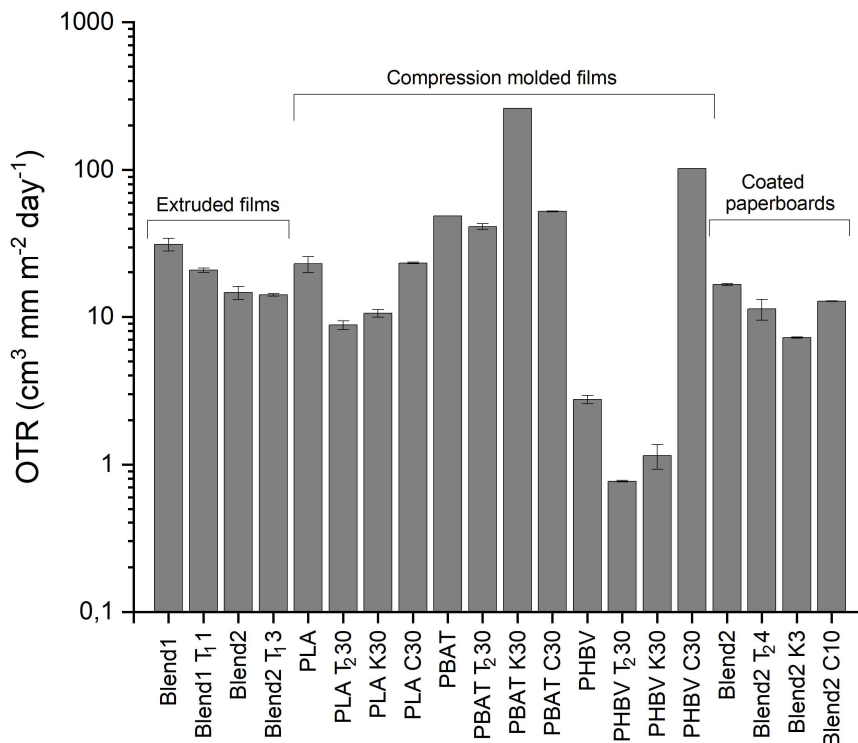
Figure 17 OTR of filler-reinforced biodegradable polymer films, manufactured by film extrusion (Blend1, Blend2) or compression moulding (PLA, PBAT, PHBV), and extrusion coated paperboards (*Blend2). T_1= talc$_1$ (particle size 1 μm), T_2= talc$_2$ (particle size 2,2 μm), K=kaolin, C= calcium carbonate and the number after the letter stands for the filler content (wt%). (**Publication 1**, **2**, **4**)

In polymer-filler systems, several aspects are needed to be considered when evaluating the effect on the barrier properties. In this study, differently shaped fillers were utilized. Where talc and kaolin are plate-like fillers, calcium carbonate represents a more irregularly shaped filler type. Platy fillers have been reported to effectively create the tortuosity in the matrix thereby hindering the diffusion of the permeating molecules (Jain et al. 2010). In addition to different filler shapes, other important factors include hydrophobicity (Qin et al. 2014), the filler amount, the aspect ratio and the way the fillers have been distributed and oriented in the matrix matters (Evstatiev et al. 2013). As also seen in this work, the filler addition can affect the compatibility and crystallinity of the matrix, but also the matrix density, which all influence the permeability properties (Evstatiev et al. 2013). In addition to the above-mentioned aspects, the solubility of the oxygen and water molecules in the polymer's matrix, their size and polarity (Evstatiev et al. 2013), together with possible defects in the film or coating (e.g. voids and pinholes) (Massey 2002) makes a difference.

4.2.3 Heat sealability

Heat sealability was studied in **Publication 4**, where different sealing techniques were evaluated. The results of hot air sealability from samples with 5 wt% of fillers are presented in Figure 15. The results are for fibre tear level 3/5, to

illustrate the development in lower temperatures caused by the filler additions. Talc$_2$ and kaolin reached a 10 °C, and calcium carbonate a 20 °C difference compared to the unfilled reference sample. Despite the obtained lower sealing temperatures, the full fibre tear (5/5) did not reach significantly lower temperatures with the fillers. The higher sealing temperature required by the platy fillers compared to calcium carbonate could be explained by their nucleating effect, since increased crystallinity will increase the required sealing temperature (Lahtinen et al. 2009). As described earlier (Figure 11), talc and kaolin have been noticed to work as nucleating agents in PLA matrix more effectively than calcium carbonate. Despite the possible increased crystallinity, the heat sealability at lower temperatures was improved, and this could be due to the ability of the fillers to keep the temperature higher for a longer time, and therefore improve the sealing event. Even though these effects were seen in hot bar, and hot air sealing techniques in **Publication 4**, in the cup forming study these effects were not visible.

Three heat sealing events (ultrasonic, hot air and hot bar), presented in Figure 6, took place in the cup forming process. With all the sample points, ultrasonic sealing (Figure 7, 1) and hot bar heat sealing (Figure 7, 3) formed perfect heat seals, while hot air activation of the first bottom seam (Figure 7, 2) resulted only in modest adhesion. It seemed that the amount of filler did not influence the paper cup formability. A higher hot air sealing temperature or two side coated material for the cup bottom could have benefitted the adhesion in the 1st bottom seam (Figure 7, 2). Nevertheless, no leakage was detected from the cups owing to two perfectly sealed seams.

4.2.4 Biodegradability and repulpability

The effect of 5 wt% filler additions were investigated from the perspective of biodegradability in **Publication 4**. The 100-day test showed that the reference material and the filler containing materials reached the biodegradability according to the EN 13432 standard. However, the reference material reached a slightly higher degree of biodegradability (102.2 %), than the filler containing samples (99.9-100.5 %). The most interesting effect of the fillers were seen in the beginning half of the test (10-60 days), where they were more notably degrading more slowly compared to the reference sample without any fillers. Talc$_2$ degraded the slowest and kaolin and calcium carbonate were degrading little bit faster to talc$_2$. A similar effect has been reported in the literature, which was caused by the nucleating effect of the filler addition and therefore resulted in a decreased biodegradability level (Ozkoc and Kemaloglu 2009). Also, many others have reported the negative effect of the crystallinity development on the biodegradation of PLA (Kale et al. 2006, Tokiwa and Calabia 2006, Pantani and Sorrentino 2013, Yu et al. 2020). Crystalline and more dense PLA structure hinder the enzymatic attack and oligomer diffusion which decelerates the biodegradation (Pantani and Sorrentino 2013).

The impact of filler addition on repulpability was studied in **Publication 4**. It was discovered that all the sample points resulted in a similar outcome. The

pa-paperboard substrate was uniformly dispersed in the 1 % consistency mixture, whereas the bits of coatings appeared as notable flakes (e.g. in Figure 4 in **Publication 4**). The effect of filler addition and filler type was not observable in respect of flake size, even though fillers could have acted as stress concentrators in the coating and repulped into smaller flakes. Recyclability of paperboard-based packaging materials are essential to meet the sustainability and recyclability targets. Repulpability plays a major role when recyclability of paperboard-based packaging material is evaluated. According to the harmonized recyclability test method (Cepi 2022), the material can be recyclable e.g., if the amount of reject is less than 20 %. Based on the accepted reject level, the coated paperboards used in this work could be ranked as recyclable.

5. Concluding remarks

The effect of mineral filler addition on biodegradable paperboard polymer coatings was studied by utilizing processes relevant to the packaging industry. Talc, kaolin and calcium carbonate were used as fillers for PLA, PLA-based blends, PHBV and PBAT, which were the polymer matrices.

Extrusion coating processability was examined in pilot-scale facilities. Filler addition showed a reduced neck-in, as desired. Platy fillers (those with high aspect ratio) were more beneficial in reducing the neck-in than the filler of low aspect ratio (calcium carbonate). Besides neck-in phenomena, adhesion was promoted by the filler when using low coating weights. However, samples with low coating weight showed pinholes. The lowest coating weight (7.5 g/m^2) with good adhesion (but showed pinholes) was obtained with 5 wt% of talc$_2$. Adhesion improvement by the fillers was likely related to the ability of the fillers to store heat and promote wetting of the polymer on the paperboard surface. Fillers contributed to the formation of pinholes, especially at low coating weight. The layers with 5 wt% calcium carbonate were pinhole-free, while talc and kaolin generated pinholes.

The fillers influenced the characteristics of the polymers. Filler particles were generally well embedded in the polymer matrices, indicating good polymer-filler interactions, with favourable filler orientation (e.g., parallel to the film surface). Nonetheless, calcium carbonate exhibited small cavities around the particles, associated with weak polymer-filler interactions. Overall, talc and kaolin acted as nucleating agents promoting crystallinity in the different polymer matrices except those based on PBAT. In such cases filler addition reduced the crystallinity. Compared to the platy fillers, calcium carbonate increased PHBV crystallinity, but produced the opposite effect on the other polymers. Based on the cavities observed in the SEM images, the surface of the modified calcium carbonate was not optimal to entrap the crystallites. In addition to its nucleation effect, talc$_1$ was found to improve the miscibility of the polymer blends, presumably based on Zhu´s mechanism, where talc particles cause a cutting effect under the shear of mixing.

The performance of biodegradable polymers was improved as a result of filler-reinforcement. Improved moisture and oxygen barrier properties were achieved with all the studied fillers though some variability exists depending on the sample point. In terms of the barrier properties, talc was found to be most effective, followed by kaolin (calcium carbonate was the one with the lowest perfor-

mance). It can be stated that except for the (PLA 5 wt% of talc) system, the addition of micro-sized mineral fillers reduced the tensile strength and elongation of the films. The elastic modulus of the compression-moulded films (PLA, PBAT, PHBV) correlated with the crystallinity development (increased for PLA and PHBV and reduced for PBAT samples). The elastic modulus of the thin extruded films (Blend1, Blend2) decreased because of filler addition, which was explained by the effect of stress concentration.

Heat sealing is one of the most critical converting operations in extrusion coated paperboard packaging. Heat sealing was influenced by filler addition. The heat sealing temperature was reduced when fillers were introduced. Calcium carbonate exerted the strongest effect compared to the reference sample, followed by talc$_2$ and kaolin. The effect of fillers on sealing at low temperatures likely obeys similar reasons as those related to adhesion phenomena, e.g., related to heat storage and the promotion of seal formation. The reason for the minor improvement observed for talc$_2$ and kaolin over that of calcium carbonate can be ascribed to the nucleating effect, since an increased crystallinity requires higher sealing temperature.

Repulpability and biodegradability were not significantly affected by the filler reinforcement. Repulping of the extrusion coated paperboards resulted in dispersed fibres with coating flakes indicating that the material did not decompose completely. However, the addition of filler did not affect the outcome. In the biodegradability tests (EN 13432 standard), all the samples reached the required level of biodegradability although the degradation appeared to be slower for the filler containing samples. The result can be explained by the nucleating effect of the fillers.

This work highlighted the potential benefits, as well as the gaps, that should be considered in future developments related to the introduction of fillers in biodegradable paperboard coatings applied by the extrusion technique. Since extrusion coating represents the mainstream technology for barrier coating of paperboard, the optimization of processability and performance of biodegradable coatings is crucial. Future investigations should concentrate on the prevention of pinhole formation, especially in filler-reinforced biodegradable coatings used in extrusion coating. This would further advance the efforts to reduce the coating weight and would result in feasible packaging materials with sound environmental and cost benefits.

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