Department of Physics
University of Helsinki
Report Series in Physics
D299

The effect of nanoscale structures of biowaxes on the barrier properties of polymeric dispersion coatings

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ACADEMIC DISSERTATION
To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public examination in lecture room E204, Physicum,
on 28 August 2026, at 13.00.

Helsinki 2026

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ISBN 978-952-84-3236-4 (paperback)
ISBN 978-952-84-3237-1 (PDF)
ISSN 0356-0961 (print)
ISSN 2954-3142 (PDF)

PunaMusta Oy
Joensuu 2026

Preface

After completing my degree in fibre and polymer engineering, I wanted something more. So, I did the most obvious thing, I googled options and I discovered the master's programme in materials research at the University of Helsinki. I was lucky enough to get accepted. Some of the best discussions might happen in the corridors, I had one with my Professor Simo Huotari, and Simo asked, "Why not study in our doctoral programme?" The question made sense. I was lucky again to get accepted into the programme. I am grateful for my discussion with Simo and how Simo introduced me to the world of X-rays, synchrotrons, and nanoscale structures.

I want to express my deepest gratitude to my instructor Kirsi Svedström. With Kirsi's guidance and Kirsi's enthusiastic attitude towards the work we did together, everything felt possible. Kirsi, you are the kindest and best person one can have as an instructor and a mentor. Your knowledge and the way you guided me were something special. I will remember the work we did together for the rest of my life.

I am thankful to my manager Annaleena Kokko at Kemira. The research topics Annaleena's team focused on aligned well with my university research. I also want to thank my co-author, Anneli Lepo, in the same team for contributing to all the articles in my thesis. Anneli's depth of knowledge in the field is impressive, and never-ending patience is inspiring. I am also grateful to all other members of the team for their support with the laboratory work and for sharing the fun coffee break discussions. My pre-examiners, Professor Jurkka Kuusipalo and Professor Ville Leminen, deserve big thanks for reviewing my thesis and providing constructive feedback.

Finally, special thanks to my family and Janne for their support in my life. Thank you for being there for me. To all my dearest friends, you are the ones who always know the best jokes, snacks, and places to drink coffee. You also have the best opinions on everything. Elsi, Karélia, Laura, and Pauliina, you listened the most when I talked about this project. I appreciate your patience and all the fun moments we have shared. Thank you deeply for your friendship.

Kirkkonummi, August 2026
Sai Li

Abstract

Legislative acts, environmental concerns, and increased consumer awareness have driven the transition and adaptation of using sustainable food packaging alternatives. Currently, fossil-based plastic materials are used in food packaging applications due to the lightness, versatile converting possibilities, and excellent barrier properties to preserve the food throughout the supply chain. Recyclable and renewable fibre-based packaging material is seen as an attractive option to package, preserve, deliver, and communicate the product. However, the drawbacks of fibre-based materials are the lack of barrier properties due to their hydrophilic nature and the porous structure. Some of the well-established technologies to introduce a fossil-based thermoplastic film as a barrier layer on the fibre substrate are extrusion coating and lamination methods. A promising alternative solution is to apply a water-based polymer dispersion coating layer. Typically, these materials are also fossil-based, and the barrier performance does not yet meet the level of thermoplastics. To improve the barrier properties of the water-based polymer dispersions, bio-based and renewable biowaxes are a promising material group to enhance the performance. Biowaxes are naturally hydrophobic and there are several types of raw material sources available.

This thesis aimed to study the nanoscale structures of biowaxes using wide-angle X-ray scattering method and combine the structural information with barrier properties. First, the crystalline phases and the thermal stability of commercially available biowaxes' structures were investigated. The results suggested that biowaxes having the dominant orthorhombic phase were more structurally stable alternatives. Further, the biowaxes were used as a part of the pigment-containing water-based polymer barrier coating formulations in which the goal was to introduce the renewable content to the coatings. The compatibility of biowaxes with polyacrylate and polystyrene acrylate dispersions and mineral pigments were investigated. The best barrier performance results were obtained with polyacrylate dispersion and talc pigment. Most importantly, throughout the studies, the main observation was that the industrial scalability of the findings and the results are high since the processability of the materials was promising.

Keywords: biowax, fibre-based packaging, barrier, wide-angle X-ray scattering

List of original publications

This thesis is based on the following publications:

I **Li, S.**, Svedström, K., Lepo, A (2024). Biowaxes used as a barrier formulation material in coating fibre-based substrates. Packaging Technology and Science, 37 (11), 1095 – 1105. https://doi.org/10.1002/pts.2846

II **Li, S.**, Lepo, A., Svedström, K. (2025). Towards optimized barrier performance using biowaxes and inorganic pigments in coating formulations on fibre-based substrates. Journal of Coating Technology and Research. https://doi.org/10.1007/s11998-025-01155-y

III **Li, S.**, Lepo, A., Svedström, K. Barrier properties and crystalline structure of biowax containing water-based polymer dispersions under different processing conditions. Submitted.

Author's contribution

Paper I: Biowaxes used as a barrier formulation material in coating fibre-based substrates.

S.L. conducted the WAXS experiments with K.S., and S.L. and K.S. analysed the data. S.L. and A.L. designed the experimental part for barrier tests. S.L. wrote the first version of the manuscript. S.L., K.S. and A.L. analysed and interpreted the results, and wrote the final version of the manuscript.

Paper II: Towards optimized barrier performance using biowaxes and inorganic pigments in coating formulations on fibre-based substrates.

S.L. designed the barrier tests. A.L. designed the polymers assessed. S.L. wrote the first version of the manuscript. S.L., A.L. and K.S. analysed and interpreted the results, and wrote the final version of the manuscript.

Paper III: Barrier properties of crystalline structure of biowax containing water-based polymer dispersions under different processing conditions.

S.L. designed the study and selected the biowax raw materials for the experimental part. S.L. conducted the WAXS experiments and analysed the results together with K.S. A.L. designed the polymers assessed. S.L. wrote the first version of the manuscript. S.L., K.S. and A.L. analysed and interpreted the results, and wrote the final version of the manuscript.

List of abbreviations

BSD	backscattering detection
GCC	ground calcium carbonate
IR	infrared
PCC	precipitated calcium carbonate
PFAS	per- and polyfluoroalkyl substance
SEM	scanning electron microscope
WAXS	wide-angle X-ray scattering
WBPD	water-based polymer dispersion
WVTR	water vapour transmission rate

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1 Introduction

In recent decades, the global packaging industry has been dominated by petroleum-based plastic materials (Kibria et al., 2023; Martins et al., 2024). Food packaging materials, more specifically plastics, play a significant role in production, transportation, storage, distribution, and food safety. The advantages of using plastics are durability, processability, light weight, low-cost, and excellent barrier performance. (Cordeiro et al., 2025; Seref & Cufaoglu, 2025; Wu et al., 2021) The awareness of sustainability topics, from limited raw materials to managing waste, as well as both EU and global legislative acts have been driving industrial materials development work towards circular, recyclable, and reusable alternatives. The interactions between function, material, shape, and process set the rules for material selection (Afif et al., 2022; Directive (EU) 2019/904; Dörnyei et al., 2023; Edo et al., 2025a; Edwards, 1994; Mahmud et al., 2024; Thapliyal et al., 2024).

Especially in the food sector, packaging extends the shelf life, improves food quality, protects and preserves the food product throughout the supply chain. (Chatterjee et al., 2025; Edo et al., 2025b; Norton et al., 2022; Tukenmez Emre et al., 2025; Yu et al., 2025) The relevance of packaging materials in providing the necessary barrier performance is crucial (Hussain et al., 2024; Karnwal et al., 2025). However, commonly used fibre-based materials face challenges in meeting the barrier requirements compared to plastic materials. Extrusion coating and lamination methods are well-established techniques for surface-treating paper and paperboard materials to provide superior barrier properties. Typically, a layer of fossil-based plastic film is extruded or laminated on a fibrous material substrate, and the need for plastic remains. These types of materials are composed of more than one material, and each individual material is calculated and reported separately in the EU. A material may be exempted from this requirement by the Member States if the insignificant part of the material accounts for no more than 5 %. In this case, the final material could be considered a monomaterial. Thus, there is a strong desire to develop low-weight and functional water-based dispersion barrier coatings for fibre-based materials, as the legislative acts are driving the development towards monomaterial. (Bakker, Bosveld, et al., 2022; Kumar et al., 2025; Mendes & Pedersen, 2021; Mikriukova et al., 2022; Nechita & Iana-Roman, 2020; Regulation (EU) 2025/40; Saroha et al., 2022)

A water-based polymer dispersion can be produced by emulsion polymerisation. The barrier properties are affected by the chemical composition of the coating material and the uniformity of the polymer film on the fibre substrate. Water, water vapour, and oil and grease resistance are some of the main barrier properties that are needed for food packaging. The film formation process of water-based polymer dispersion is a sequence of events including water evaporation, polymer particle deformation and coalescence, and polymer chain interdiffusion. It is challenging to obtain a completely pinhole-free film with outstanding barrier performance. Pigments are often added to improve performance and reduce costs. Other raw materials such as chitosan, starch, or proteins are widely investigated, and they have shown improved barrier and mechanical properties when used in fibre-based packaging materials. (Asua, 2004; Bakker, Aarts, et al., 2022; Hu et al., 2025; Keddie, Joseph, Routh, 2010; Lovell & Schork, 2020; Steward et al., 2000)

The barrier performance of water-based polymer dispersions may not be comparable to fossil-based plastic layers; thus, their properties and compositions are continuously evolving. One way of improving the barrier performance of water-based polymer dispersions is to add fossil-based wax or biowax components. Both fossil- and bio-based waxes are lipid compounds (e.g., long-chain fatty acids and alcohols, esters, or combinations of these) that exhibit low polarity, thereby reducing moisture permeation. Due to the crystalline structures of waxes, they may also improve water vapour resistance. Previously, the crystallinity of different polymeric materials was studied, and the results showed that the crystalline regions lowered the permeability of the diffusing molecules due to the tortuous pathways created (Duan & Thomas, 2014; Idris et al., 2021; Sundar et al., 2024; Tan & Thomas, 2017). Biowaxes belong to a group of naturally hydrophobic materials of either plant or animal origin. These biowaxes can be used in a coating formulation to improve, for example, water resistance. In addition to their performance, the ability of biowaxes to be repulped is seen as a commercial advantage in the packaging industry. (Jahangiri et al., 2025; Lyytikäinen et al., 2024)

Figure 1 illustrates the working principles in Papers **I**–**III**. The prepared coating formulations were also industrially relevant and could be scaled up to pilot or even full-scale tests.



Figure 1 The working principles in Papers **I**–**III**. Step 1: Main raw materials that were used in this research. Step 2: Wide-angle X-ray scattering characterisation of the raw materials and their dispersions. Step 3: Laboratory-scale coating of the fibre-based substrates. Step 4: Application tests and SEM imaging. (All icons are free from www.flaticon.com)

This thesis focuses on investigating how incorporating biowaxes into water-based polymer dispersions affects barrier performance, specifically by mapping their possible structure–function relationships. The nanostructures of plant-based biowaxes and their corresponding dispersions were characterised using the wide-angle X-ray scattering method. Polymer–biowax dispersion formulations were used to coat the industrially manufactured paperboard base sheets on a laboratory scale. This work was conducted with an application-driven approach, and the main barrier properties such as water, water vapour, and oil and grease resistance of the coated sheets were studied and analysed thoroughly.

2 Research goals

The main goal of this thesis was to understand the effects of biowaxes on the barrier properties of coated fibre-based substrates when formulated with water-based polymer dispersions. A significant part of the work involved characterising the nanoscale structures of plant-based biowaxes using the wide-angle X-ray scattering (WAXS) method and combining this nanoscale structural information with the barrier properties of the final coated sample sheets. This research setup is novel in the field: there are very few previous studies which combine the nanoscale characterisation of raw materials, end-use applications, and application-driven barrier testing.

First, the structural changes of the selected commercially available biowaxes during melting cycles were studied to gain information about their thermal stability during industrial-scale production. Furthermore, the nanostructures of water-based polymer dispersions were characterised both in their original liquid phase and after various drying treatments.

The aim of obtaining all this nanoscale information about different biowaxes is to select the most suitable structures for improving the barrier properties of the coatings. For example, understanding the effects of melting cycles on the structures of biowaxes can help to adjust the process so that unwanted structural changes caused by thermal events in industrial production are minimised. Overall, the WAXS results provide information on the crystalline structures, identifying the present or dominant crystalline phases in the studied polymorphic wax materials and their typical lamellar distances. Combining this structural information with the barrier test results of the actual coatings ultimately reveals information on which materials were the most favourable to obtain improved barrier performance.

After characterising the main raw materials, biowaxes and water-based polymer dispersions, the coating formulations were prepared. The goal was to use these formulations to coat industrially manufactured paperboard base sheets made from wood fibres. Subsequently, the industrially relevant barrier tests were performed. The reference samples were always the corresponding samples without any biowax components. Scanning electron microscope (SEM) imaging technique was used to observe the coating layer uniformity and coverage of both surfaces and cross-sections. The surface images also revealed the visible pinholes generated from the coating materials.

Paper **I** aimed to investigate the feasibility and the effects of adding different biowaxes to the pigment-containing polymer dispersions. It also evaluated the resulting barrier properties when industrially manufactured paperboard base sheets were coated. The four biowaxes selected for this study were commercially available grades from two different suppliers, and they were in the solid form when received. All four biowax samples were characterised as received, melted once, and melted three times by the WAXS method. The goal was to see the structural differences after melting cycles of each biowax grade. Additionally, the nanostructure of the biowax after preparing it into a dispersion form was also characterised. In this study, the first observations on the possible connections between the wax nanostructures and the barrier properties were obtained. The results demonstrated the feasibility of using biowaxes combined with polymer dispersions, encouraging further research in this area.

Paper **II** focused on formulating and optimising the commercially available biowax dispersions in two different laboratory-scale synthesised water-based polymer dispersions. The goal was to characterise the effects of biowax addition on the barrier properties of polyacrylate and polystyrene acrylate dispersions formulated with either talc or calcium carbonate pigments. All these selections were made with a focus on industrial-relevant coating formulations that can be scaled up when needed. This study revealed the compatibility of the two pigments, along with the two acrylate dispersions, with the biowaxes.

The aim of Paper **III** was to further understand how diverse ways of introducing a biowax component to a polymer system may affect structure–function relationships. In this paper, two polymer dispersions were polymerised in two distinct ways: 1) without additives, and 2) in the presence of two different biowaxes. In addition, the same biowaxes were mixed into the ready-polymerised polymer dispersions. The goal was to study the optimal way of adding biowax from both a barrier performance and a processability perspective. The nanostructures of biowaxes, polymers, biowax containing polymers, and polymer-biowax mixtures were characterised by the WAXS method, and the SEM results and barrier properties of the final coated samples were evaluated.

3 Materials

The materials used in this thesis are divided into four main categories: 1) biowaxes, 2) water-based polymer dispersions, 3) pigments, and 4) fibre-based packaging materials. Materials 1–3 were used as main components in the barrier coating formulations. The fibre-based packaging material was an industrially manufactured paperboard. Table 1 shows the raw material list used in this thesis. The fibre-based packaging material was used as the substrate on which the coating layer was applied on.

Table 1 Raw materials used in Papers **I**–**III**.

Material category	Name	Manufacturer	Paper
Biowax	Nowax CW 6096	Paramelt	I
Biowax	Nowax CW 6111	Paramelt	I
Biowax	Agri-Pure 635	Cargill	I
Biowax	Agri-Pure 660	Cargill	I
Biowax	Impermax B11	GOVI	II
Biowax	Impermax B58	GOVI	II, III
Biowax	Impermax B48P	GOVI	III
Biowax	Impermax B73	GOVI	II
Biowax	Impermax B90	GOVI	II
Polymer dispersion	Polyacrylate-based	Kemira	I, II, III
Polymer dispersion	Polystyrene acrylate-based	Kemira	I, II
Polymer dispersion	Polyacrylate-based dispersion polymerised with Impermax B58	Kemira	III
Polymer dispersion	Polyacrylate-based dispersion polymerised with Impermax B48P	Kemira	III
Pigment	Hydrocarb 60	Omya	I, II
Pigment	Finntalc C15B	Elementis	II
Fibre-based substrate	Folding boxboard	Kotkamills	I, II, III

3.1 Waxes

Waxes are a group of lipids that exist in the solids, and they are naturally water-repellent materials. They have ester bonds and long-chain alcohols in their molecules. The structural differences, such as the degree of unsaturation and branching affect wax's chemical and physical properties. Waxes are insoluble in water but can be dissolved into solvents. (Cirisano & Ferrari, 2021) Some of the well-known wax-based applications are, for example, candles, cosmetics, medicine, and coatings in packaging materials. (Khan et al., 2024; Krendlinger & Wolfmeier, 2021; Tambe et al., 2016)

The sources of waxes can be natural or synthetic. Natural waxes are divided into petroleum-based from fossil sources or bio-based from renewable sources. Petroleum-based waxes are typically mixtures of hydrocarbons including n-paraffins, branched chain paraffins and cycloparaffins. Bio-based waxes can be animal-origin waxes such as beeswax, or they can be plant-based waxes such as rice bran wax. Plant-based waxes can also be modified from vegetable oils, for example via hydrogenation or esterification, e.g., palm oil wax or soy wax. Plant-based waxes are typically mixtures of n-alkanes and oxygen-containing functional groups. Synthetic waxes are, for example, polyolefin waxes and Fischer-Tropsch waxes that are artificially synthesised. Waxes that are structurally modified from plant-based sources can also fall into the category of synthetic wax. (Cushman et al., 2025; Ensikat et al., 2006; Islam et al., 2024; Khan et al., 2024; Krendlinger & Wolfmeier, 2021; Olarte et al., 2023; Samir Soliman, 2020) Figure 2 further illustrates the classification of waxes.

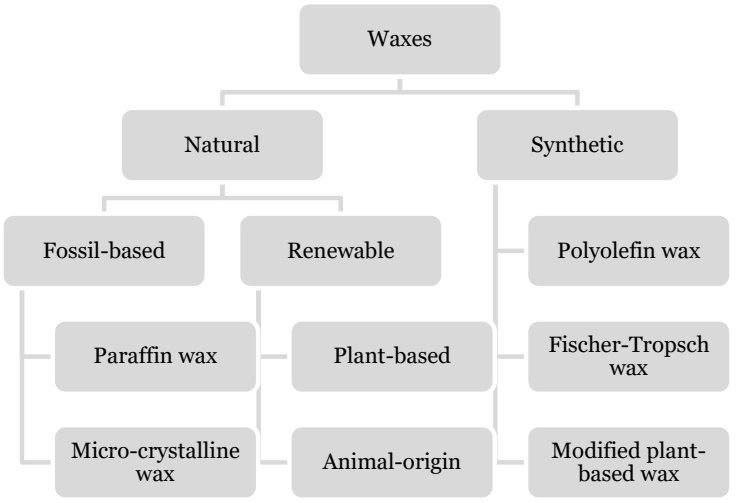

Figure 2 Wax classification. Adapted from Natural and Synthetic Waxes: Origin, Production, Technology and Applications. (Krendlinger & Wolfmeier, 2021)

3.1.1 Fossil-based waxes

Petroleum-based waxes from fossil sources are the oldest types of waxes derived from ancient fossilised organic materials. The wax-forming alkanes have typically low carbon numbers (C_{20}-C_{50}). The branching tendency is higher with heavier molecules and is less likely to enter the solid state. Thus, solid waxes are mainly composed of C_{20}-C_{50} alkanes. The wax formation occurs when the temperature drops to the wax appearance temperature and molecules begin to precipitate out from the fluid, they aggregate and crystallise with the further temperature drops. (Kiyingi et al., 2022; Krendlinger & Wolfmeier, 2021; Pal et al., 2025)

3.1.2 Bio-based waxes

Some examples of renewable waxes are beeswax, candelilla wax, carnauba wax, rice bran wax and soy wax (Calovi & Rossi, 2024; Günal-Köroğlu & Capanoglu, 2024; Jahangiri et al., 2025; D. Zhang et al., 2016). Candelilla wax is obtained from the leaves of the plant *E. antisyphilitica Zuccarini*, carnauba wax is sourced from the Brazilian palm tree and rice bran wax is found in rice husks as a by-product. (Pashova, 2023) Plant-based waxes can function as gas, moisture, oxygen, and light barriers in their natural contexts. These properties are widely used in the food industry to extend the shelf life of fruits and vegetables and preserve them during storage. (Günal-Köroğlu & Capanoglu, 2024; Pashova, 2023) Vegetable oils are also a source for plant-based waxes. Partial or full hydrogenation methods are used to obtain waxes from vegetable oils. The desired functional groups are introduced into vegetable oils to change the properties (e.g., hardness, cohesiveness, melting temperature, viscosity, and optical properties) needed for the intended end-use applications. (Fei & Wang, 2017) This thesis focuses on investigating the biowax grades obtained via hydrogenation of different vegetable oils. The biowaxes were either prepared into stable water-based dispersions or received as ready-made water-based dispersions.

3.1.3 Synthetic waxes

Synthetic waxes are wax grades that are obtained via different synthesis routes. Polymerisation, Fischer-Tropsch and chemical modifications are some of the common routes to synthesise waxes. The synthesis process enables the modification of molecular weight, polarity, and other properties to meet the application requirements. Depending on the selected raw materials, these synthetic waxes can be bio-based. (Caputo et al., 2019; Fei et al., 2020; Fei & Wang, 2017; Wang et al., 2024; Yadav et al., 2024; L. Zhang & Song, 2023)

3.1.4 Applications

Waxes are known for their use in, for example, foods, cosmetics, and packaging industry. In the food industry, oil and fats contribute flavour, texture, and mouthfeel. Solid fats are preferred over liquid fats due to their processability. One application is to use waxes as oleogelators to solidify liquid oil. The cosmetics industry uses waxes in various products including skin and lip care cosmetics. Waxes are well tolerated by the skin, they have strong protection and cleaning performance, and they are available in different viscosities. Wax materials are also interesting in coating applications due to their superhydrophobic nature. (Aranda-Ledesma et al., 2022; Deemoonmang et al., 2025; Petry et al., 2017; Thakur et al., 2023; Wettlaufer & Flöter, 2022)

In paper applications, waxes and wax mixtures are used as surface treatment materials to improve the barrier properties. (W. Zhang et al., 2014) The main goals of this study were to characterise the nanostructures of biowaxes and to test different biowaxes obtained via the hydrogenation of vegetable oils as components in polymeric barrier coating formulations for fibre-based food packaging applications. The intention was to study solutions that are industrially applicable and scalable. The hypothesis is that the hydrophobic nature of a biowax combined with its unique crystalline structure improves the barrier properties of a common water-based polymer dispersion.

3.2 Water-based polymer dispersions

In this study, the polymer dispersions were produced by emulsion polymerisation, a widely used method to produce water-based polymer dispersions. The method allows to produce low-viscous, high-molecular-weight polymers at a high rate. When water is used as a continuous phase, the heat removal is efficient. The produced emulsion contains small particles between 0.05 to 5 μm. The final product is a stable latex, and its typical applications require film formation with sufficient cohesive properties. (Brown, 1956; Han, 1983; Ravve, 2012; Richard & Maquet, 1992)

The main components of emulsion polymerisation are one or several monomers, a surface-active agent (surfactant), an initiator, and water. Figure 3 illustrates the main components and basic principles of emulsion polymerisation.

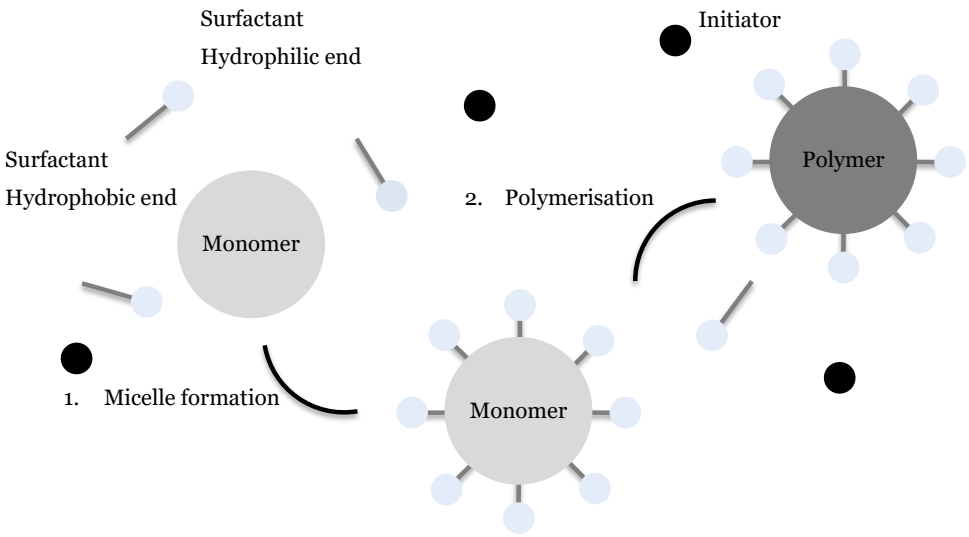

Figure 3 Simplified illustration of emulsion polymerisation. Adapted from Principles of Polymer Systems and Principles of Polymer Chemistry. (Han, 1983; Ravve, 2012)

The surfactant molecules shown in Figure 3 can exist in three different loci: 1) as a solute in the continuous water phase; 2) within micelles; and 3) at the interface between the monomer droplet and the water. The surfactant molecules can begin to form micelles at a relatively low critical micelle concentration with the hydrophobic ends facing inward and the hydrophilic ends outward. This is also the point when the surface tension of the continuous water phase stops decreasing rapidly. Next, the monomers are introduced to the system, where they also exist in three different loci: 1) solubilised in the micelles; 2) as emulsified monomer droplets; and 3) individual molecules dissolved in the water. The monomer molecules will then swell and polymerise as the emulsion polymerisation proceeds. The concentrations of surfactant and initiator affect the total number of particles per litre. (Han, 1983; Ravve, 2012)

3.2.1 Film formation

One essential aspect of using latex as a barrier coating material is the film formation process. It occurs when discrete polymer particles experience various stages of transformation including application of the water-based polymer dispersion on the substrate, water evaporation, particle deformation, and interdiffusion to form a continuous material. The evaporation phase begins to restrict particle motion, and water-air tension drives the packing of the particles. (Keddie, 1997; Moorhead & Francis, 2025; Vanderhoff, 1970) When water evaporates, the polymer particle

centres move closer to each other, and they remain deflocculated until they are forced into contact. These particles are packed densely due to the loss of water. During the process, the polymer will resist the deformation during the period when capillary pressure is present, and for some time water evaporates without particle coalescence. (Brown, 1956) Figure 4 shows the film formation of a water-based polymer dispersion in four steps: 1) applying the polymer emulsion onto the substrate surface; 2) evaporating the water in the polymer dispersion; 3) deforming the polymer particles; and 4) forming a continuous film on the substrate.

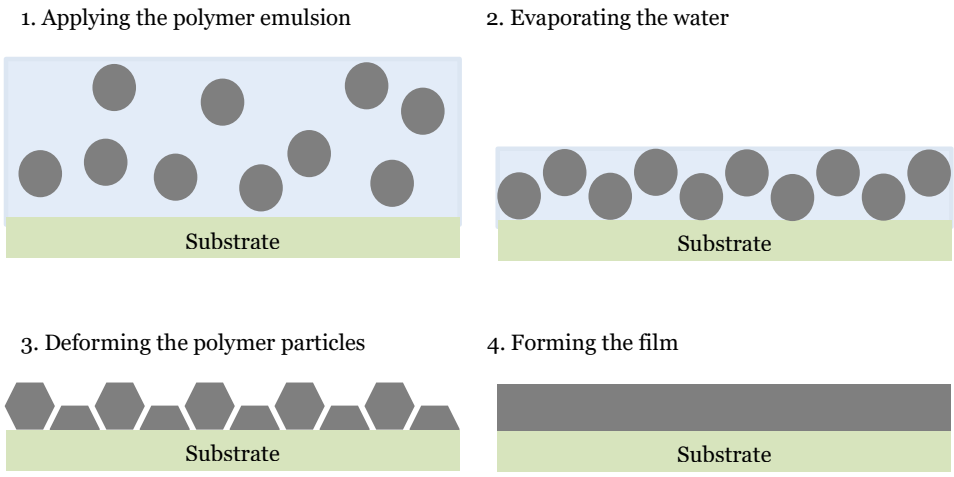

Figure 4 The mechanism of film formation in four steps. Adapted from Formation of films from polymer dispersions. (Brown, 1956)

The mechanism of film formation of polymer dispersions is affected by the particle size, the rheological properties and the surface tension of the emulsion, the temperature at which the film formation occurs, and the rate of water evaporation. (Brown, 1956) The goal of this study was to achieve a continuous film without pinholes or any other defects on the substrate. To observe the film formation phenomenon, scanning electron microscope images were acquired of the surfaces and cross-sections of the coated samples in Paper **II** and Paper **III**. The number of visible pinholes on the surface images indicates the coating layer quality, while the cross-sectional images show layer continuity.

3.2.2 Polymer dispersions as coating materials

Water-based polymer dispersions, e.g., acrylic polymer dispersions, are produced in massive quantities for multiple industrial end-uses. In paper coatings, styrene-butadiene and styrene acrylate latexes are commonly used. Acrylic polymers include acrylates and methacrylates. Low glass transition temperature acrylates are

esters derived from acrylic acid. Methacrylic acid-derived methacrylates have a higher glass transition temperature. The selection of monomers can alter the behaviour and properties of the polymerised dispersions, including rigidity, hardness, elasticity, and chemical resistance. (Kwon et al., 2020; Solera-Sendra et al., 2025) Also, the degree of cross-linking, glass transition temperature and degree of carboxylation are characteristics that affect the end-use properties of the polymer dispersion. Previously, these synthetic latexes were commonly used to bind pigments to fibre-based materials. Due to the demand for more sustainable packaging materials with sufficient barrier properties, these latexes have gained interest as barrier coating materials. These materials are easier to recycle, repulp, and compost after use. (Morits et al., 2025; Schuman et al., 2004) This study investigated the compatibility and the use of water-based polystyrene acrylate and polyacrylate dispersions together with biowaxes. The strategies for introducing biowaxes to the polymer systems in this study were the following: 1) mixing biowax dispersions into polymer dispersions; and 2) polymerising the polymer dispersions in the presence of biowaxes.

3.3 Pigments

Pigments are a group of materials that can be natural or synthetic. In industrial applications, pigments are often used as filler materials that can be engineered to meet the end-use requirements. Natural pigments include inorganic mineral fillers that can improve, for example, print quality, gloss, brightness, and opacity in conventional paper coating applications. Talc, kaolin, and calcium carbonate are some of the common alternatives in the paper industry. From the sustainability point of view, the use of pigments may also improve repulpability. (Buyondo et al., 2025; Schuman et al., 2005; Zhao et al., 2014; Zou et al., 2007) These inorganic filler materials have gained popularity in coating applications for food packaging materials due to their ability to improve barrier properties and lower the overall cost of the coating layer applied. (Bollström et al., 2012; Cho & Lee, 2015; Devisetti et al., 2023; Ouchiar et al., 2015; Uchefuna et al., 2024; Zhu et al., 2019, 2022) Synthetic filler materials can be silica, barium sulphate, or polymer-based alternatives (Buyondo et al., 2025).

In this study, two pigments, talc and calcium carbonate, were included to assess their compatibility with biowaxes.

3.3.1 Talc

Talc pigment is chemically a magnesium layer sandwiched between silicate layers, and its chemical formula is $Mg_3Si_4O_{10}(OH)_2$. (Ouchiar et al., 2015) This naturally occurring mineral has shown to improve water vapour barrier properties when used

in paper coating. (Li et al., 2025; Morris et al., 2002; Saroha et al., 2022; Schuman et al., 2005) Structurally, talc is a trioctahedral phyllosilicate, and it does not have a layer charge. When talc is present in most of the organic solvents, the charge is negative and when talc is present in a non-polar solvent, the charge becomes positive. Additionally, talc contains both acidic and basic groups. The material itself is macroscopically hydrophobic and floats. When outgassed between 100 and 400 ◦C, a strong affinity towards water molecules is exhibited. (Mälhammar, 1990; Michot et al., 1994)

The possible mechanisms by which talc and polymer surfaces interact are speculated to be chemical, electrostatic, hydrogen and hydrophobic bonding. (Morris et al., 2002) Talc also has a platelet structure with a large specific surface area and laminar morphology. Depending on the genesis of the talc, the microcrystalline talc contains heterogeneous stacks of irregular platelets, and macrocrystalline talc has well-stacked platelets. (L. A. Castillo & Barbosa, 2020) The talc pigment has been studied widely with nanocelluloses, biodegradable polymers, and starches to improve barrier properties (L. Castillo et al., 2013; Feranc et al., 2025; Liimatainen et al., 2013; G. Lin et al., 2023; Long et al., 2021; Scharnowski et al., 2022) Previously, the use of talc with waxes in a polymer system has also been studied and has shown improvements in water vapour transmission rate. (Mesic et al., 2019; Schuman et al., 2005)

3.3.2 Calcium carbonate

Calcium carbonate pigments have low solubility, and they can be divided into two types: ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). (Brečević & Kralj, 2007; Santos & Velho, 2004) From an industrial point of view, PCC is more attractive compared to GCC since PCC has higher purity and it is customisable in particle size and morphology. The production of GCC involves crushing limestone, whereas PCC is produced by calcining limestone and precipitating the hydrated lime. (Zide et al., 2026)

3.4 Fibre-based packaging materials

Packaging is an essential part of consumer goods, especially in food, beverages, and pharmaceutical products. The primary packaging protects the product from mechanical stress, reduces waste, and preserves the product by extending the shelf life, and carries the product throughout the supply chain. (Pulikkalparambil et al., 2023; Yadav et al., 2025) Fibre-based packaging materials are made from lignocellulosic raw materials that are abundant and low-cost. In addition, increased consumer awareness, corporate sustainability targets, and regulatory activities in restricting the use of plastic materials and packaging waste management are

favouring the development of fibre-based materials. (Directive (EU) 2019/904; Regulation (EU) 2025/40; Kathuria & Zhang, 2022; J. Lin et al., 2025; Niero, 2023; Sonck-Rautio et al., 2024)

The drawbacks of using fibre-based materials, especially in food packaging are water absorption, permeability to gases and water vapour, and low resistance to oil and grease. (Arrieta et al., 2017; Korumilli et al., 2024; Vinitskaia et al., 2025) To improve these properties, a barrier layer is typically applied to the fibre surface. Fossil-based polymeric materials, per- and polyfluoroalkyl substances (PFAS), and waxes are some of the commonly used coating materials in food packaging. However, these materials are challenging to recycle and PFAS have recently emerged as a risk for both human and environmental health. To mitigate these problems, the research focuses more on utilising bio-based, renewable, and recyclable alternatives. (Chandarana et al., 2025; Kathuria & Zhang, 2022; Lev et al., 2025; Minet et al., 2022; Murugesan & Li, 2026) In this study, industrially manufactured paperboard material was used as a substrate for testing different barrier coating formulations. The goal is to explore how biowaxes can be used as a component and replacement material in a water-based polymer dispersion system to increase the renewable content while improving the barrier performance.

4 Methods

This section lists all the methods used in Papers **I**–**III**. The descriptions of the preparation of the biowax dispersion, laboratory-scale rod coating, barrier properties characterisation, wide-angle X-ray scattering measurement and scanning electron microscope imaging methods are specified in more detail.

4.1 Biowax dispersion preparation

In Paper **I**, the biowax raw material was received in the solid state. Before using the biowax, it was prepared into a stable water-based dispersion. Figure 5 illustrates the main steps of the preparation of the water-based biowax dispersion.



Figure 5 Preparation steps of water-based biowax dispersion. (All icons are free from www.flaticon.com)

First, the melting temperature of the solid biowax was determined using an electrothermal method. This varied depending on the biowax raw materials. After the melting temperature was determined, the solid wax was brought to a molten state (step 1 in Figure 5). Second, a commercially available, highly cationic starch was selected to be used as a stabiliser for the dispersion, and it was dispersed into cold water at 5.75 % solids before cooking it on the hotplate (step 2 in Figure 5). After the starch solution reached 95 °C, it was cooked for at least 45 minutes until it became transparent. The aim was to use it when it was still hot. The cooked starch solution was poured into a conventional kitchen blender. A commercially available surfactant Surfaron was added at a dosing level of 0.28 % to the starch solution. While blending the surfactant into the starch solution, the melted wax was poured gradually into the mixture as the blender was mixing everything together (step 3 in

Figure 5). The wax content was approximately 15 %. After all the wax was added, the mixture was blended for one minute and finally the prepared dispersion was passed through a homogeniser under 200 bar pressure to stabilise it (step 4 in Figure 5). The visual appearance of the final dispersion was milky white and stable. Phase separation was not visually observed.

4.2 Laboratory-scale rod coating

In Papers **I**, **II**, and **III**, the barrier properties were determined from the coated paperboard base sheets. All samples were coated using a laboratory-scale rod coater with an infrared (IR) drying lamp above the coater. Industrially manufactured A4-sized paperboard base sheets were used as substrates. All base sheets were kept in a rack in the standard conditioning room (23 °C and 50 % relative humidity) for at least 4 hours. This enabled thorough ventilation of base sheets. After ventilating the base sheets, they were weighed individually before the coating process, which allowed for the determination of the coat weight. In Papers **I** and **II**, the aim was to apply two coating layers, a pre-coat without biowax materials and a topcoat with biowax materials. The target coat weight for the pre-coat layer was between 8 and 10 g/m^2, and that for the topcoat layer was between 6 and 8 g/m^2. In Paper **III**, only a single coating layer was applied. After applying each coating layer, an IR lamp above the rod coater was used to dry the layer for 60 s. In Papers **I** and **II**, the pre-coat layer was dried before applying the topcoat layer, and the topcoat layer was also dried for 60 s. In Paper **III**, the single layer was dried for 60 s. After each coating layer was applied, the sheets were cut and weighed to determine the coat weight. To adjust the coat weights, the size of the rod and the coating speed were used to control the amount of dispersion applied.

4.3 Characterising barrier properties

The barrier properties were characterised in Papers **I**–**III**. The ethanol stain test was used to detect pinholes in the coating layer, and the olive oil test (ASTM F119 – 82) was used to determine the oil resistance at 40 ◦C. For the ethanol stain and olive oil tests, the samples were both creased and folded. A laboratory-scale creasing machine was used to create the crease lines in both the machine and cross directions. The folding was done using the roller for the Cobb water test along the creased lines. The modified water vapour transmission rate (WVTR) test (ASTM F-1249, ISO 15105-2:2003, ISO 15106-3:2003 and DIN 53122-2 standards) was used to determine the water vapour transmission; the Cobb water resistance test was done according to ISO 535 standard, and the KIT test followed TAPPI UM 559 standard.

4.4 Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) and X-ray diffraction are measurement techniques used to determine the structures of materials at the atomic level up to the nanoscale. Scattering is one of the fundamental interactions between incident radiation and a sample (X-rays interact with the electrons of the atom); diffraction is a special case of the elastic scattering phenomenon from a crystalline material. Thus, the scattering/diffraction pattern is produced when the incident rays interact with the sample, by the interference of (monochromatic) X-rays incident on the sample. (Als-Nielsen & McMorrow, 2011) The technique can be utilised in various fields for the determination of the crystalline structure of the sample by analysing the diffraction maxima, i.e., Bragg peaks. (Nozue et al., 2007; Podorov et al., 2006; Ray & Banerjee, 2023; Romo-Uribe & Maranzano, 2025; Stribeck, 2007; Tian et al., 2024) Bragg's law ($n\lambda=2d\sin\theta$) gives the condition for the constructive interference: n is the diffraction order, d is the spacing between the atomic planes; λ is the radiation wavelength; and θ is the angle between the atomic planes and the incident rays.

The WAXS measurements for the wax in the solid phase, wax dispersion, polymer dispersion, and wax-containing polymer dispersion samples in Papers **I** and **III** were conducted at the X-ray Laboratory at the University of Helsinki. The WAXS measurement setup is presented schematically in Figure 6.

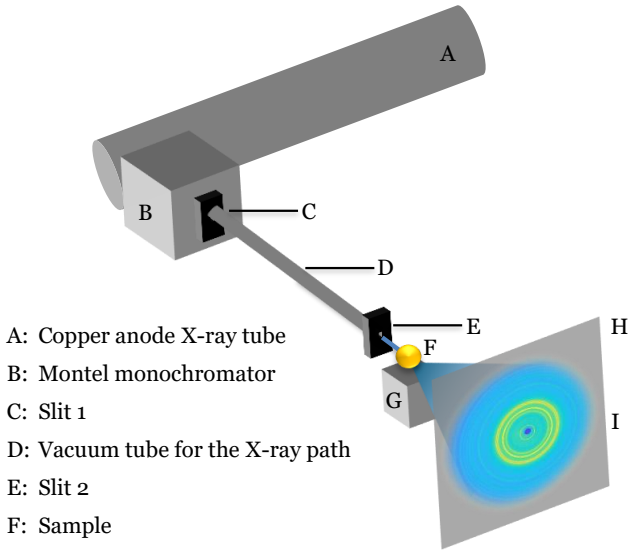

Figure 6 The schematical WAXS setup used in this thesis.

A Cu-anode tube and a Seifert generator (voltage 36 kV, current of 25 mA) were used to produce X-rays. A Montel multilayer monochromator (Incoatec) was used to select Cu Kα radiation with the wavelength (λ) of 1.541 Å. A mar345 image plate detector (marXperts) was used to collect the scattering patterns using perpendicular transmission geometry. Lanthanum hexaboride (LaB6) was used for the calibration of the scattering angle (2θ) scale before the actual samples were measured.

All the measurements were conducted at room temperature. The wet dispersions were measured in washers between two Mylar foils for 60 to 120 min, and dry samples were measured as such for 30 min. The data were integrated (using around 80 degree-wide sector) from the 2D scattering patterns, and the background scattering pattern due to air scattering and the Mylar foils (for the wet dispersions) was subtracted from the data. Furthermore, polarisation, absorption and geometrical corrections were applied.

From the integrated WAXS data, the positions of the diffraction peaks were analysed, and the corresponding lattice distances (d-values) were computed by using the relation: $d = n\lambda/(2\sin\theta)$. MATLAB was used for the data analysis. Based on the lattice distances observed and the relative heights of the corresponding diffraction peaks, information on the crystalline phases of the samples was obtained.

4.4.1 Crystal structures of waxes

Crystal structures represent an arrangement of atoms distributed in space in a certain way, where the atoms occupy their equilibrium positions. These structures are further divided into one-, two-, or three-dimensional crystal structures. In the three-dimensional lattice system, there are fourteen lattice types (Bravais lattices). The lattice types are further divided into seven crystal systems: monoclinic, orthorhombic, tetragonal, cubic, triclinic, trigonal, and hexagonal. The lattices belonging to a certain group have the same point symmetry. (Gonzalez Szwacki & Szwacka, 2010). Ensikat et al. concluded that most of the waxes exhibit orthorhombic structures due to the aliphatic compounds in the waxes. The existence of a triclinic phase is mainly attributed to the secondary alcohols. (Ensikat et al., 2006)

The biowax materials analysed in this thesis represented three-dimensional crystal lattices; more specifically, crystalline reflections related to the orthorhombic and triclinic crystal lattices were detected from the WAXS patterns. These two crystalline phases are typical of waxes and other lipids (Ensikat et al., 2006; Seilert et al., 2025). In addition, a hexagonal crystal phase is common in waxes, and all these three crystalline phases have been observed, e.g., in plant epicuticular waxes (Ensikat et al., 2006).

4.5 Scanning electron microscope imaging

Scanning electron microscope (SEM) images were taken using Jeol JSM 7900-F, Feg FESEM and analysed by Oxford Instruments EDS with AZtec software in both Papers **II** and **III**. Both surface and cross-sectional SEM images were acquired. The surface SEM images were acquired using low-energy secondary electrons. The cross-sectional SEM images were acquired using the backscattering detection (BSD) method. For cross-sectional images, the samples were cut with a sharp razor blade. The samples for both surface and cross-sectional images were coated with Pt/Pd using a Leica EM ACE600 high-vacuum coater. The surface SEM images reveal the smoothness of the coating layer and the number of pinholes. The cross-sectional images show the continuity of the film. These two types of images complement each other when analysing the film quality visually.

5 Results and discussion

This section highlights the most noteworthy results and observations from Papers **I**–**III**. First, the raw material characteristics and the nanostructures are discussed as studied in Paper **I**. Second, the barrier performance is covered in detail. In particular, the nanoscale structures of biowaxes and the incorporation method for biowax to the polymer dispersions are analysed. Lastly, the processability and industrial relevance are covered. A structural understanding of biowaxes was established before further studying their use as a barrier coating formulation component in an application-focused manner. To conclude the study, the biowax incorporation strategies were compared to fully maximise the benefit of adding biowaxes and improve the barrier properties.

5.1 Raw material characteristics

In Papers **I** and **III**, the raw materials were characterised using WAXS. Paper **I** focused on the nanoscale structures of four commercially available biowax raw materials, which were hydrogenated vegetable oils. These materials were in the solid state when received. Material processing in an industrial environment typically involves several thermal cycles where the materials are heated, cooled, and reheated. The melting temperature of the four tested biowaxes differed, and the results are presented in Table 2.

Table 2 Melting temperatures of the characterised biowax raw materials from Paper **I**.

Biowax	Melting temperature [◦C] ± 1 ◦C
1	70
2	59
3	60
4	71

The melting temperatures presented in Table 2 are within the same range as the biowax melting temperatures presented in the research conducted by Jahangiri et al. (Jahangiri et al., 2025). Factors affecting the thermal behaviour of biowaxes can be, for example, the number of polar groups, number of carbon atoms, molecular

weight, degree of saturation and crystallinity (Buchwald et al., 2008; Samyn & Rastogi, 2022; Seilert et al., 2025).

The WAXS patterns of the four biowaxes in Paper **I** are presented in Figure 7. The reflections of the crystalline phases are interpreted from the WAXS data.

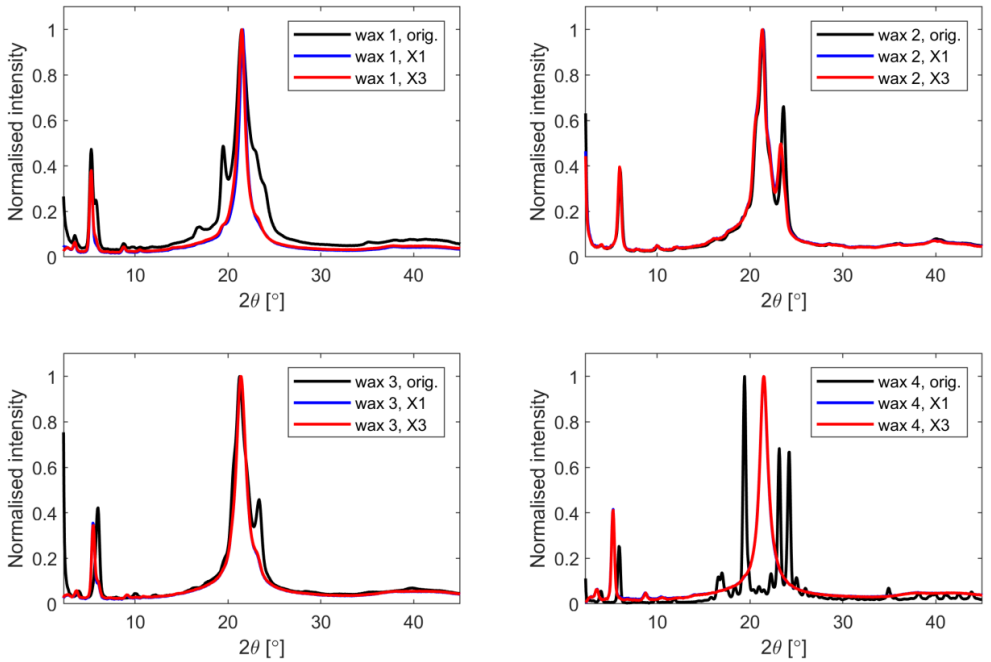

Figure 7 Melting series of biowaxes 1–4 (orig. = original sample as received, X1 = melted once, and X3 = melted three times). The WAXS intensities are normalised.

Based on the results presented in Figure 7, all the studied biowax materials have a high level of crystallinity. Biowax 1 shows both orthorhombic and triclinic crystal phases in its original state. However, after the melting procedure, only the main reflections of the orthorhombic phase are observed. Biowax 4 probably has the highest crystallinity among the tested biowaxes due to the high number, and particularly the narrowness of the detected diffraction peaks. The common behaviour of all these four biowaxes is the stability of their crystal structure after being melted once, compared to the data obtained after melting the samples three times. Both the X1 (melted once) and X3 (melted three times) data of all four biowaxes in Figure 7 seem to overlap, indicating similarity in the crystalline structures. From an industrial-scale processing aspect, stable structures and the predictability of raw material behaviour are preferred. Additionally, all four tested biowaxes have lamellar structures observed from the diffraction peaks at the low scattering angles (below 10◦). Based on the results of Paper **I**, both the crystalline phases present in the biowax and the nature and order of the lamellar structure may

affect the barrier performance of the coatings. It was also concluded in Paper **III** that the well-preserved lamellar order in combination with the orthorhombic crystalline phase might be the most favourable structure for barrier performance.

Paper **I** aimed to understand the structures of biowaxes as raw materials. However, biowaxes were not used in their solid state when applied as coating materials. In this thesis, biowaxes were studied as one component in water-based polymer dispersions (WBPDs). More specifically, WBPDs were polymerised in the presence of biowaxes, or the two materials were mechanically mixed with each other. In addition, the drying method of WBPD was critical for the film formation. Thus, it was relevant to understand the structural changes in the coating materials when they are dried differently. Paper **III** studied biowax containing WBPDs where biowaxes were incorporated into the WBPDs with different strategies. Figure 8 shows the structures of WBPDs with the biowax incorporated and dried differently.

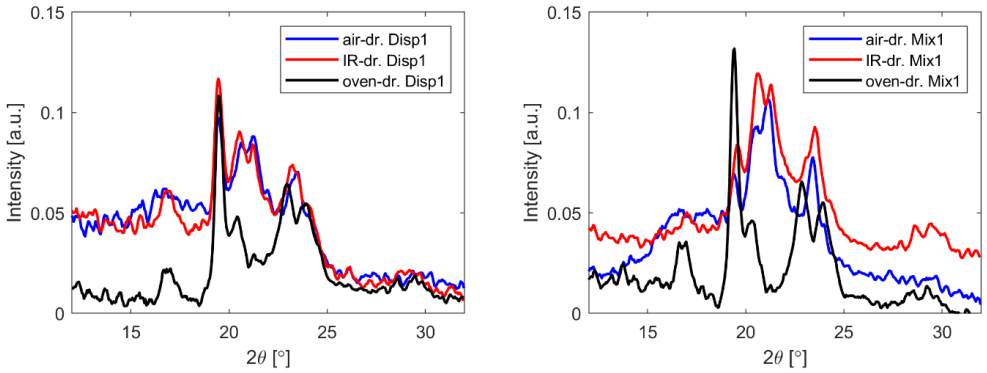

Figure 8 Structural differences of WBPDs under different drying methods. WAXS intensities of Dispersion 1 where the WBPD was polymerised in the presence of a biowax (left), and Mixture 1 where the WBPD having the same monomer composition and the same biowax as it is in Dispersion 1 is mixed (right).

As seen in Figure 8, the WAXS data are quite similar between different biowax addition strategies. One notable difference is the dominant contribution of the orthorhombic crystalline phase in Mixture 1 (right) compared to Dispersion 1 when the sample was IR-dried. Both water and water vapour resistance were improved for Mixture 1 compared to Dispersion 1 (Paper **III**). In Paper **I**, it was also observed that the orthorhombic phase was as a beneficial factor for barrier properties. Thus, to have the orthorhombic phase as the dominant phase in the coating wax materials is one of the preferred structural properties. Leyva-Gutierrez & Wang studied the effect of crystallinity of natural wax constituents (n-alkanes, alcohols, aldehydes, and fatty acids) on water vapour permeability. They concluded that the water vapour permeability decreased due to the formation of orthorhombic lattices of aldehydes, which possessed the longest chain length among the tested constituents.

(Leyva-Gutierrez & Wang, 2021) Thus, they explained the improved water vapour permeability of the orthorhombic lattice by its larger lattice cell volume, which led to a more space-filling structure. This does not apply to the oven-dried Mixture 1 and Dispersion 1 samples, which both showed reflections corresponding to a triclinic crystalline lattice. However, it can be noted that the IR drying method is attractive when considering industrial-scale production, as it is a well-established method to dry coating materials.

5.2 Barrier performance

The barrier performance of different coating formulations was studied in Papers **I**–**III**. The approach in Paper **I** was to prepare dispersions of the biowaxes before adding them to the WBPDs. Two distinct types of WBPDs were selected: polyacrylate and polystyrene acrylate dispersions. Calcium carbonate pigment was used. Paper **I** results provided knowledge to select the materials for Paper **II**, where the focus was on testing commercially available biowaxes together with both polyacrylate and polystyrene acrylate polymer dispersions, as well as with calcium carbonate and talc pigments. The materials evaluated in Paper **III** were narrowed down to the polyacrylate dispersion, two commercially available biowaxes, and talc pigment based on the results of Paper **I** and Paper **II**. The effect of biowax incorporation methods on barrier performance was the focus of Paper **III**.

5.2.1 Quantitative barrier performance results

Table 3 and Table 4 present the barrier performance results related to water and water vapour permeability from Paper **II,** which gives an overview of the barrier properties of the polyacrylate, and polystyrene acrylate dispersions mixed with different biowaxes. Additionally, the effects of the selected pigments are shown in the results.

Table 3 Barrier performance results of polyacrylate dispersions. Ref 1 contains no biowax, and S1–S4 use all different commercially available biowaxes. All Ref1 and S1–S4 samples have calcium carbonate pigment. Ref 2 contains no biowax, and S5–S8 samples use all different commercially available biowaxes. All Ref2 and S5–S8 samples have talc pigment.

	Ref 1	**S 1**	**S 2**	**S 3**	**S 4**	**Ref 2**	**S 5**	**S 6**	**S 7**	**S 8**
Coat weight [g/m²]	14.8 ±0.2	13.7 ±0.2	14.5 ±0.2	14.1 ±0.5	15.2 ±0.2	12.4 ±0.1	13.4 ±0.2	13.3 ±0.2	13.2 ±0.3	12.5 ±0.3
WVTR [g/m²/d]	48 ±5	62 ±6	55 ±6	63 ±6	54 ±5	50.8 ±5	45.2 ±5	44.8 ±4	43.2 ±4	43.3 ±4

Cobb 300 s [g/m²]	4 ±2	4 ±2	3 ±2	5 ±2	4 ±2	3 ±2	3 ±2	3 ±2	4 ±2	4 ±2
Cobb 1800 s [g/m²]	24 ±2	14 ±2	18 ±2	14 ±2	17 ±2	18 ±2	14 ±2	11 ±2	14 ±2	17 ±2

Table 4 Barrier performance results of the polystyrene acrylate dispersions. Ref3 contains no biowax, and S9–S12 samples use all different commercially available biowaxes. All Ref 3 and S9–S12 samples have calcium carbonate pigment. Ref4 sample contains no biowax, and S13–S16 samples use all different commercially available biowaxes. All Ref 4 and S13–S16 samples have talc pigment.

	Ref 3	**S 9**	**S 10**	**S 11**	**S 12**	**Ref 4**	**S 13**	**S 14**	**S 15**	**S 16**
Coat weight [g/m²]	15.8 ±0.3	14.5 ±0.5	14.8 ±0.2	15.5 ±0.1	17.6 ±0.2	12.6 ±0.2	14.2 ±0.3	13.9 ±0.4	14 ±0.3	14.1 ±0.1
WVTR [g/m²/d]	65 ±7	93.5 ±9	73.6 ±7	80.2 ±8	76.5 ±8	64 ±6	48.7 ±5	52 ±5	59 ±6	59.6 ±6
Cobb 300 s [g/m²]	45 ±2	46 ±2	45 ±2	50 ±2	48 ±2	56 ±2	53 ±2	52 ±2	56 ±2	54 ±2

Overall, the barrier properties measured in the WVTR and Cobb water tests are better with the polyacrylate dispersions than with the polystyrene acrylate dispersions (Paper **II**). An interesting observation of the WVTR results is that the addition of the biowax combined with the calcium carbonate pigment (S1–S4 and S9–S12) led to higher WVTR values (meaning worse water vapour resistance) with both the polyacrylate and the polystyrene acrylate dispersions compared to Ref1 and Ref3. The WVTR results of the biowaxes when combined with the talc pigment (S5–S8 and S13–S16) improved with both the polyacrylate and polystyrene acrylate dispersions compared to Ref2 and Ref4. Furthermore, the compatibility of the biowaxes and talc pigment was thus better than that of the calcium carbonate pigment.

The Cobb water 300 s results in Table 3 for the polyacrylate dispersion did not show major changes with the addition of the biowaxes. Generally, the polystyrene acrylate dispersion had significantly higher Cobb water 300 s results (Table 4) compared to the polyacrylate dispersion, and the use of the biowaxes did not improve these values. For samples Ref1, Ref2 and S1–S8, the Cobb water 1800 s test was performed. With both calcium carbonate and talc pigments and all the tested biowaxes, the Cobb water 1800 s values of S1–S4 and S5–S8 were better compared to their reference samples, Ref1 and Ref2, respectively. This indicates that the addition of biowaxes may improve the water resistance when the material is exposed to liquid water for longer periods of time. From a practical point of view, this means that moist or liquid food can be kept on the material for longer without leakage. The KIT results of the polyacrylate dispersion formulations were measured in Paper **II**; the addition of the biowaxes seemed to improve the values when the

calcium carbonate pigment was used. The KIT results of the polystyrene acrylate dispersion formulation were all good when evaluated in both flat and creased states in Paper **II**. The addition of the biowaxes improved most of the creased and folded samples.

The results from Paper **II** encouraged further study of polyacrylate dispersions combined with biowaxes. When scaling the process to an industrial scale, the method applied for the unit process is highly relevant. This directly affects the efficiency of the entire process. Thus, the incorporation method of the biowax dispersion into the polymer dispersion was investigated in Paper **III**. Table 5 presents the barrier performance results from Paper **III**.

Table 5 Barrier performance results of six different dispersions. RefA and RefB are both polyacrylate dispersions with solids contents of approximately 40 % and 50 %, respectively. A.1 dispersion has the same monomer composition as RefA but was polymerised in the presence of biowax. A.2 dispersion is RefA mixed with the same biowax in A.1. B.1 dispersion has the same monomer composition as RefB but was polymerised in the presence of biowax. B.2 dispersion is RefB mixed with the same biowax in B.1.

	Ref A	**S A.1**	**S A.2**	**Ref B**	**S B.1**	**S B.2**
Coat weight [g/m²]	7.4 ±0.2	8.3 ±0.3	8.9 ±0.2	8.6 ±0.3	8.6 ±0.5	8.6 ±0.3
WVTR [g/m²/d]	109.0 ±11	72.2 ±7	48.4 ±5	90.5 ±9	80.0 ±8	56.4 ±6
Cobb 300 s [g/m²]	3 ±2	2 ±2	1 ±2	2 ±2	3 ±2	1 ±2
Cobb 1800 s [g/m²]	17 ±2	11 ±2	9 ±2	12 ±2	16 ±2	4 ±2

The results of RefA and RefB in Table 5 differ significantly, and the only difference is the solids content of the dispersions. One factor that may affect the results is coat weight which is lower in the RefA sample compared to RefB. A.1 and B.1 samples are RefA and RefB dispersions polymerised in the presence of biowax. A.2 and B.2 samples are RefA and RefB samples mixed directly with biowaxes. The WVTR results follow a clear decreasing pattern in both the A and B sets, meaning that the addition of biowaxes improved the water vapour resistance. The Cobb water absorption at 300 s and 1800 s results are also lower when the biowaxes are mixed into the polymer dispersions. These observations suggest that the tested biowax dispersions should be mixed with the polymer dispersions rather than polymerising the dispersions with them. The significant benefit of the direct mixing method is that the amount of biowax can be adjusted and optimised before the coating process.

5.2.2 Visual barrier performance results

To support the interpretation of the barrier performance results, some of the methods used are based on visual interpretation. In this study, ethanol stain, olive oil tests, and SEM imaging results are interpreted based on the visual appearance of the images in Papers **I**–**III**. Figure 9 highlights the ethanol stain and olive oil test results of four samples in Paper **II**.

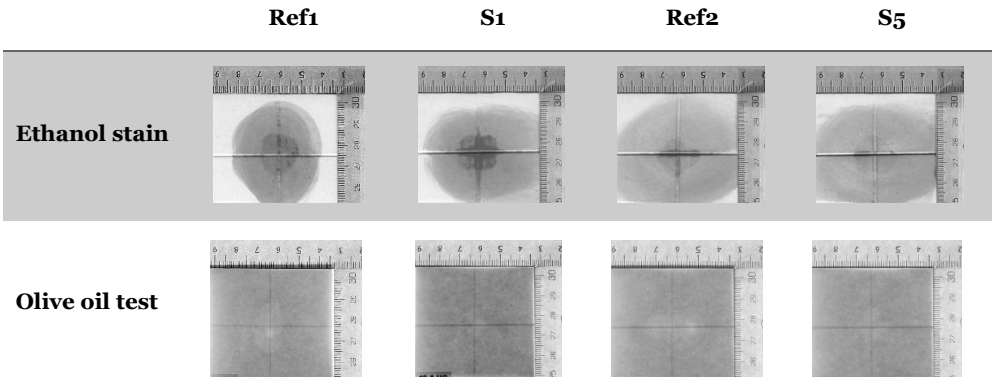

Figure 9 Visual barrier performance results from ethanol stain and olive oil tests. Ref1 and Ref2 samples contain the same polyacrylate dispersion with calcium carbonate (Ref1) and talc (Ref2) pigment. S1 and S5 samples contain the same polyacrylate dispersion and biowax, formulated with calcium carbonate (S1) and talc pigment (S5). The units of the scale in the images are in cm.

The tested samples in Figure 9 were all creased and folded. This was done since the converting process of paperboard materials typically requires creasing and folding. When the test mimics the industrial process, the interpretations and conclusions are more accurate. The addition of the biowax to Ref1 (polyacrylate dispersion containing calcium carbonate) seems to weaken the film, making it more brittle. This is seen in the ethanol stain images of Ref1 and S1 in Figure 9. At the intersection of the creased and folded lines, the ethanol solution spreads to a wider area. The mechanical treatment of creasing and folding breaks the continuity of the film. However, the addition of biowax to Ref2 sample containing talc pigment seems to improve the flexibility of the film. The intersection point of the creased and folded line is cleaner, and the ethanol solution did not stain the lines as much as in the Ref2 sample. The olive oil test results look similar for all samples in Figure 9. The samples do not have major oil stains. This will appear as translucent shades in the images.

SEM images were acquired from surfaces and cross-sections in Papers **II** and **III**. Figure 10 shows the surface of the coated fibre substrate when calcium carbonate and talc pigments were used, and the results are from Paper **II**.

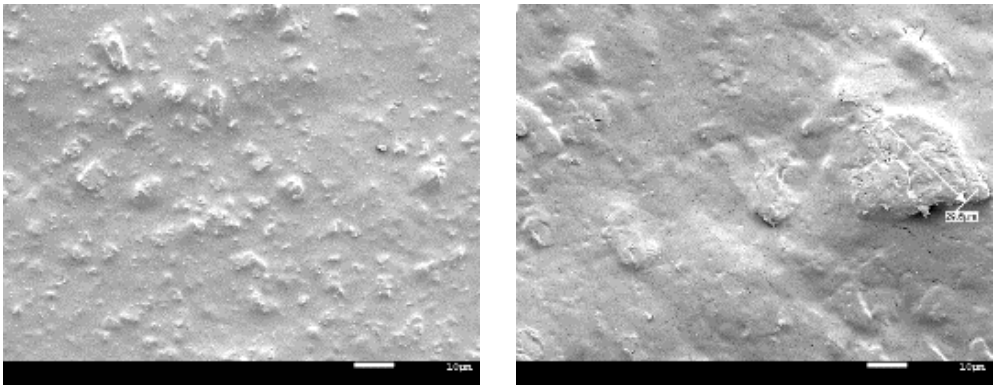

Figure 10 Surface SEM images of coatings made with polyacrylate dispersion mixed with calcium carbonate (left) and talc (right). The length of the white scale bar is 10 µm.

The calcium carbonate containing coating formulation shows grainy surface (Figure 10, left) whereas talc shows smoother surface (Figure 10, right). Also, the characteristic platelet structure of talc is visible in the right image in Figure 10. Similar platy and three-layer structure were also observed by Long et al. and Ohenoja et al. in their research (Long et al., 2021; Ohenoja & Illikainen, 2015). The platy morphology of the talc allows the pigment plates to align and overlap on the fibre surface. Consequently, permeants such as water vapour or oxygen gas face a tortuous pathway. The morphology of the talc pigment might partly explain both why talc is more compatible with biowaxes and thus provides improved barrier performance. Figure 11 presents the surface and cross-sectional SEM images from Paper **III**. Surface images visually show the coverage of the fibre substrate when the dispersion is applied. Cross-sectional images show the continuity of the film formed on the fibre substrate.

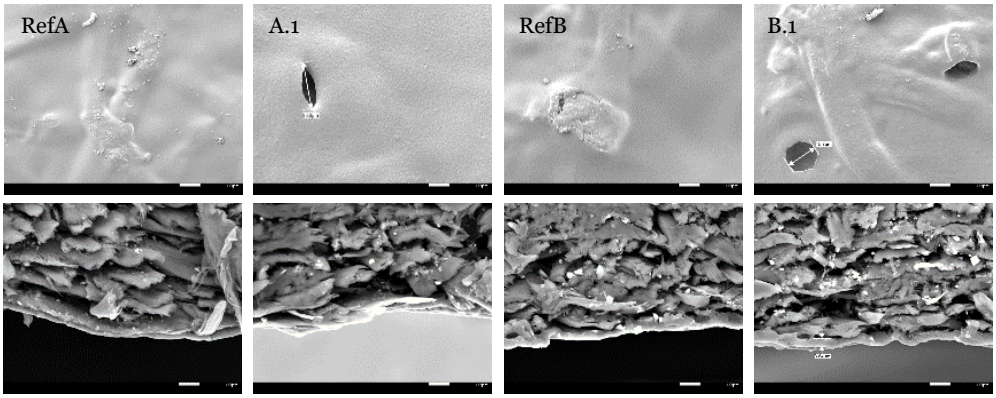

Figure 11 Surface and cross-sectional SEM images of RefA and RefB. Both are coated with polyacrylate dispersions with solids contents of approximately 40 % and 50 %, respectively. A.1 and B.1 samples are coated with dispersions polymerised in the presence of biowaxes. The top row presents surface images. The bottom row presents cross-sectional images of the samples from the first row. The length of the white scale bar is 10 μm.

In Figure 11, the RefA and RefB surface images do not show visible pinholes whereas the A.1 and B.1 images clearly show pinholes. The pinholes do not seem to affect the water vapour resistance of the coating layers. From the cross-sectional images (second row in Figure 11), it can be observed that the coating layer covers the fibre substrate well, since there are no fibres sticking out. The film formation of the tested dispersion is adequate. One important aspect of film formation is that the coating layer stays on the surface of the fibre substrate. The cross-sectional images show that the formed film is on the surface. The role of rapid drying is significant, and it allows the water to evaporate from the dispersion quickly, leaving the barrier film. The longer the dispersion stays in the wet state, the more time it will have to penetrate through the fibre structure in the z-direction. Rapid drying using, for example, an IR-based method is favourable and industrially viable.

6 Conclusions and prospects

The use of biowaxes as a barrier coating formulation component in water-based polymer dispersions was studied on a laboratory scale. In conclusion, the addition of biowax components into the coatings was feasible from an industrial point of view. This is important because introducing biowax to a coating formulation and, thus, increasing the renewable share of raw materials meets the current market demand for more sustainable packaging material solutions in the food industry. Furthermore, the effects and compatibility of the other components in these barrier coating dispersions were systematically studied with the following variations: calcium carbonate and talc pigments were used as fillers, and polyacrylate and polystyrene acrylate as polymer dispersions were investigated.

The nanoscale structures of the biowaxes were characterised in Paper **I**. It was found from the study that the biowaxes having an orthorhombic phase were the most structurally stable, meaning no significant structural changes occurred during the thermal cycles. This finding is crucial when coating is done on an industrial scale where the materials are likely to undergo several thermal cycles.

Paper **II** studied both polyacrylate and polystyrene acrylate polymer dispersions and the compatibility of pigments (calcium carbonate and talc) in the biowax containing barrier coating formulations. The addition of the biowax dispersion did not affect the preparation of the barrier coating formulation in the high shear mixer. The scale-up can be expected to be done without major challenges from the laboratory to the industrial scale. The best barrier performance was observed when biowaxes were combined with the polyacrylate dispersion and the talc pigment. The Cobb water 1800 s values decreased by 10 to 40 % and the WVTR values decreased by 11 to 15 % compared to the polyacrylate dispersion itself. The use of calcium carbonate pigment was not favourable. Also, the polystyrene acrylate dispersion did not perform as well as the polyacrylate dispersion. By combining the findings from both Paper **I** and Paper **II**, the optimal crystalline phase for the biowax can be selected and mixed with polyacrylate and talc pigment.

Based on the results in Paper **I** and Paper **II**, it was clear to continue studying polyacrylate dispersions in more detail. In Paper **III**, two polyacrylate dispersions were polymerised at different solids contents. The results suggested that higher solids content is preferred when aiming for better barrier performance. In addition,

different biowax incorporation strategies were evaluated. One way was to polymerise the polymer dispersion in the presence of biowax, and the other way was to mix the wax-free polyacrylate dispersion with a biowax. It was observed that it was feasible to polymerise the polyacrylate dispersion in the presence of a biowax raw material; however, better barrier performance was observed for the coatings of the mixtures. It was also observed that the orthorhombic crystalline phase was more dominant among the samples where biowax raw material was mixed with the polyacrylate dispersion. These results confirmed the results obtained in Paper **I**, i.e. that the orthorhombic crystalline phase is a favourable structural property for obtaining the desired barrier properties for the coatings.

Characterising and understanding the nanostructures of biowaxes might thus be helpful in selecting the optimal biowax raw material for different applications. Deepening the understanding of the structural phases of all barrier coating formulation components such as polyacrylate, polystyrene acrylate, and pigments, may be critical in formulating the barrier coating material.

Related to this, in Paper **II**, it was concluded that the talc pigment was a more compatible filler when used with biowaxes. The interactions between talc pigment and biowaxes would be interesting to study at the molecular level. Also, the interactions with the other pigments such as kaolin or organic pigments could be studied further in the future studies.

Biowax incorporation strategies were studied in Paper **III**. One of the main observations was that mixing biowax into the polymer dispersion is more favourable. In addition, the Cobb water 1800 s test results demonstrated improved water resistance when the barrier layer was exposed to water for a longer time. It is interesting to study what happens dynamically at the coating layer surface during water exposure.

These kinds of *in situ* studies on the interactions between various components, particles, and solutions could be conducted, for example, by using synchrotron light sources, where scattering measurements can achieve millisecond time and nanosized spatial resolution. Thus, the drying and crystallinity kinetics of coatings can be followed *in situ* using synchrotron X-ray beams.

Biowaxes, especially rice bran wax and beeswax, are considered to have high oil-binding capacity due to an ordered crystal network with needle-like morphology. Thus, these types of waxes are suitable for trapping substantial amounts of liquid oil. (Blake & Marangoni, 2015; Shi et al., 2021) This study focuses on studying water and water vapour resistance. It is of interest to further understand the role of waxy structures and to optimise the selection of certain types of waxes to create a grease-resistant layer. For food packaging, both water and grease resistance are important. Typically, the industry prefers to have these properties simultaneously. However, the mechanisms of creating a water barrier differ from creating the grease-resistant barrier layer. Therefore, it would be interesting to strategically select two

complementary types of waxes based on their crystal structures and study their compatibility. Further, it is crucial to understand if the selected structures experience changes when they are combined.

This study highlights the importance of understanding the nanoscale structures of barrier coating formulation components. Biowax raw materials were studied, and biowax materials with orthorhombic crystalline phases proved structurally most favourable. Talc pigment was also found to be more compatible with the biowax containing polymer dispersions than calcium carbonate. It was also observed that polyacrylate-based dispersions generally showed better barrier properties than polystyrene acrylate dispersions when used as barrier coating material. The ultimate challenge remains optimising barrier performance in fibre-based food packaging materials. Consumer awareness and regulatory pressure drive the development of bio-based materials. Based on the results of this thesis, bio-based wax components can feasibly replace parts of barrier coating formulations while improving barrier performance.

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