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Master’s Programme in Chemical, Biochemical and Materials Engineering

Potential of red seaweed-based dispersion barrier for paperboard

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Abstract

Growing environmental concerns along with the EU's Single-Use Plastics directive (SUP), have driven innovations towards biobased alternatives to fossil-based barrier coatings. According to the directive, bio-based solutions should be chemically unmodified natural polymers to avoid classification as plastic.

Currently, food products are packed in paperboard packaging, which are traditionally coated with plastic-based barrier layers. Paperboard provides mechanical strength, while the barrier coating ensures protection against grease, water, water vapor, oxygen, and microorganisms.

This thesis focuses on the barrier properties of carrageenan-based barrier coatings applied to paperboard considering the requirements set by SUP-directive. The carrageenan-based barrier coating was applied to paperboard as a water-based dispersion. The barrier properties of carrageenan were evaluated in its pure form, mixed with bio wax and crosslinker and as a multilayer structure. The coatings performance was evaluated by surface characteristics and barrier properties. Results showed that carrageenan alone provide moderate grease resistance but poor water resistance due to its hydrophilic nature. The addition of crosslinkers improved grease resistance, while wax additives enhanced water resistance. A multilayer structure combining crosslinked carrageenan base layer and a hot melt coated bio wax as top layer, offered balanced barrier properties. However, challenges were observed in coating uniformity, layer thickness and gluability.

The study demonstrates that carrageenan, especially when combined with suitable additives, show promising properties for bio-based solution for paperboard food packaging. Further research is needed for example to find solutions to moisture resistance properties and to evaluate long-term performance under varying environmental conditions.

Keywords Barrier, carrageenan, red seaweed, paperboard, dispersion coating, bio-based

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Tiivistelmä

Kasvava huoli ympäristöstä sekä EU:n kertakäyttöisiä muovituotteita, koskeva SUP-direktiivi ohjaavat innovaatioita kohti biopohjaisia vaihtoehtoja fossiilipohjaisten materiaalien korvaajaksi. Direktiivin mukaan biopohjaisten ratkaisuiden tulee perustua kemiallisesti muokkaamattomiin luonnonpolymeereihin, jotta niitä ei luokiteltaisi muoviksi.

Nykyisin elintarvikkeet pakataan kartonkipakkauksiin, jotka on perinteisesti päällystetty muovipohjaisilla barrierpäällysteillä. Kartonkipakkaus tarjoaa mekaanisen kestävyyden, kun taas barrierpäällyste suojaa rasvalta, vedeltä, vesihöyryltä, hapelta ja mikrobeilta.

Tämä diplomityötyö keskittyy karrageenipohjaisen barrierpäällysteen mahdollisuuksien tutkimiseen, ottaen huomioon SUP-direktiivin asettamat vaatimukset. Karrageenipohjainen barrierpäällyste päällystetiin kartongille vesipohjaisena dispersiona. Karrageenin barrier ominaisuuksia arvioitiin sellaisenaan, sekoitettuna biovahaan ja ristisilloittajaan, sekä monikerrosrakenteena.

Tulokset osoittivat, että karrageeni tarjoaa kohtalaisen rasvankestävyyden, mutta sen hydrofiilisen luonteensa vuoksi se on herkkä vedelle. Ristisilloittajan lisääminen paransi rasvankestävyyttä, kun taas biovahan lisääminen paransi vedenkestävyyttä. Monikerrosrakenne, jossa ensimmäisenä kerroksena oli ristisilloitettu karrageeni ja pintakerroksena sulapäällystetty biovaha, tarjosi tasapainoiset barrier ominaisuudet. Haasteita havaittiin kuitenkin päällysteen tasaisuudessa, kerrospaksuuksissa ja liimattavuudessa.

Tutkimus osoittaa, että karrageenilla on lupaavia ominaisuuksia biopohjaisena barrier-päällysteenä kartonkisissa elintarvikepakkauksissa. Erityisesti monikerrosrakenteena ja sopivien lisäaineiden kanssa sen suorituskykyä voidaan parantaa. Jatkotutkimuksia tarvitaan kuitenkin muun muassa vedenkestävyyden parantamisessa ja barrier-päällysteen toimivuuden arvioimiseksi vaihtelevissa ympäristöolosuhteissa.

Avainsanat Barrier, karrageeni, punainen merilevä, kartonki, dispersiopäällystys, biopohjainen

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Preface and acknowledgements

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Äänekoski, 13 November 2025
Tiia-Maria Vahanto

Symbols and abbreviations

Symbols

A	Area
F	Force
v	Velocity
$\dot{\gamma}$	Shear rate
η	Dynamic viscosity
τ	Shear stress

Abbreviations

CMC	Carboxymethyl cellulose
CNC	Cellulose nanocrystals
EU	European union
FBB	Folding box board
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
PE	Polyethylene
PCL	Polycaprolactone
PP	Polypropylene
SFE	Surface free energy
SEM	Scanning electron microscopy
SFE	Surface free energy
SUP	Single-use plastic
TSC	Total solids content
WVP	Water vapor permeability
WVTR	Water vapor transmission rate

1 Introduction

The increasing demand for environmentally friendly packaging solutions has driven research into bio-based barrier coating for paperboard applications. Paperboard is widely used in food packaging due to its lightweight structure, recyclability, and printability. However, its inherent porosity and hydrophilic nature limit its barrier performance against moisture, grease, and gases, which are critical for preserving food quality and safety.

To overcome these limitations paperboard packaging often relies on fossil-based polymer coatings such as polyethylene (PE). While this is highly effective, these materials pose environmental concerns and regulatory pressure such as European Union's Single-Use Plastics (SUP) directive, which is guiding innovations towards unmodified biobased polymers.

Carrageenan, a natural polysaccharide extracted from red seaweed, offers a possible alternative due to its film-forming abilities, renewability, biodegradability, and potential barrier properties. Despite its possible advantages, its hydrophilic nature presents challenges. Carrageenan is already widely used in the food and pharmaceutical industries, but its application in food packaging materials, particularly as a barrier coating for paperboard, are not that studied.

This thesis studies the barrier properties of carrageenan-based dispersion coatings applied to paperboard. The thesis focuses on evaluating grease resistance, water absorption, water vapor transmission rate (WVTR), and surface characteristics. effectiveness in resisting moisture and grease penetration. By evaluating the performance of these, the research aims to contribute to the development of sustainable food packaging solutions that align with environmental, regulatory, and functional requirements.

2 Paperboard and its use in packaging

Paperboard is a fibrous, cellulose-based material made from wood pulp. It is widely used for packaging due to its renewability, recyclability, and mechanical strength. As a sustainable alternative to plastic, paperboard is especially valuable in applications such as food packaging and consumer product containers. (Auvinen & Lahtinen, 2008, pp. 286–288; Kiviranta, 2000, pp. 55–56)

Paperboard typically consists of multiple layers, example of layers in folding boxboard (FBB) is presented in Figure 1. Different layers have different purposes example provide rigidity, printability, and formability. Depending on the intended application, it can be made from virgin fibres, recycled fibre, or combination of both. The fibres can be either long (from coniferous species) or short (from deciduous species). Long fibres provide strength properties and short fibres create a denser structure, resulting in a smoother structure. (Kirwan, 2013, p. 20)

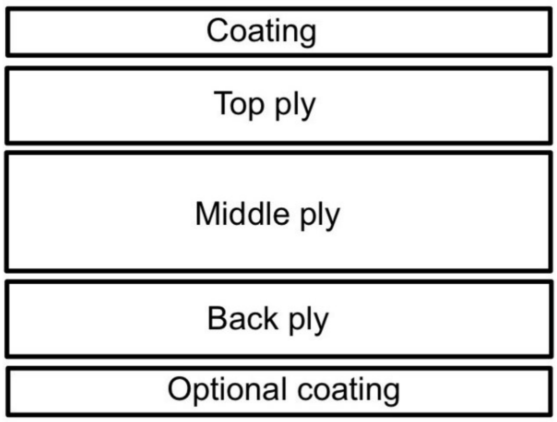

Figure 1. Typical structure of Folding box board. Redrawn from Kiviranta (2000).

Fibers are separated from wood either by mechanical or chemical pulping. Mechanical pulping involves physical breakdown of wood through crushing or grinding. This process generates heat, softens lignin, and separates individual fibres. Since lignin remains within fibres, the resulting pulp is stiff and less flexible. In contrast, chemical pulping uses chemicals to dissolve non-cellulosic and non-fibrous components to effectively separate fibres from wood. The most widely used chemical pulping method is sulphate or kraft process. Kraft process allows the recovery and reuse of both the wood components and pulping chemicals. The yield of chemical pulping is lower than that of mechanical pulping as it removes the non-cellulose content. Chemically separated pulp can be bleached to remove residual lignin and other wood-based material. (Gustafsson, 2011, p. 195; Kirwan, 2013, pp. 20–22; Sundholm, 2009, p. 21)

Recycled fibres are obtained from recovered paper and paperboard, which are repulped. Each repulping cycle causes fibres to lose their mechanical properties, such as fibre length and reduced bonding. Properties of fibres have impact on manufacturing of different paperboard grades and their end uses. (Ackermann et al., 2010, pp. 436–437; Kirwan, 2013, pp. 22–23)

Paperboard can be classified into several grades, such as cartonboards, containerboards and specialty boards. Typically, the basis weight of paperboard exceeds 150 g/m^2. A common grade of paperboard is FBB, which is widely used in applications for example food packaging products. (Kiviranta, 2000, p. 55) This grade is also utilized in the experimental part of the thesis.

Packaging plays an important role in the product distribution system. It not only protects the product but also facilitates production, handling, and transport. Packaging communicates important information about the contents and serves as a marketing function. Its primary purpose is to protect the product by acting as a barrier between product and environment. Additionally, packaging must meet legal and environmental requirements, preserve product and provide a means of communication between producer and consumer. (Auvinen & Lahtinen, 2008, pp. 286–288; Lahti et al., 2008, p. 244)

Although paperboard offers several advantages, such as stiffness formability and recyclability, its application in food packaging is limited by its poor barrier properties without additional coating. Untreated paperboard does not provide sufficient protection against moisture, water vapor, grease, and gases. To overcome this limitation, paperboard is often coated with fossil-based polymers, such as polyethylene (PE), which provide effective moisture and grease resistance. However, such coatings compromise the recyclability when coating layer goes to waste. Biodegradable coatings offer solutions that minimize environmental impact compared to traditional fossil-based coatings. Biodegradable alternatives to fossil-based polymers are currently under active research. (Jahangiri et al., 2024; Kimpimäki et al., 2008, p. 103; Mujtaba et al., 2022)

Increasing environmental concerns and tightening legislation, such as the European Union's Single-Use Plastics Directive (2019/904), are driving the development of recyclable and biodegradable biobased barrier solutions. The main goal is to improve the barrier properties of paperboard packaging while maintaining its recyclability and biodegradability and reducing dependence on fossil-based materials. Addressing these challenges is crucial for advancing sustainable packaging development. The following chapter discusses this directive and the driving forces behind the topic of this thesis.

3 Single-use plastics – Directive (EU) 2019/904

The growing global concern over plastic pollution, particularly in marine environments, has led to regulatory actions such as the European Union's SUP directive (EU) 2019/904. This directive aims to reduce the environmental impact of single-use plastic products, especially those most commonly found as marine waste, such as single-use plastic (SUP) items and fishing gear, which together comprises approximately 77% of waste found on beaches. (European European Comission, 2019)

Approximately eight million tons of plastic waste ends in ocean every year, and this is predicted to double by 2030 and double again by 2050 (Sedayu et al., 2018). 53% of single-use plastics accounts packaging (Teixeira et al., 2025). Additionally, 95% of food packaging is thrown away after a single use, with one-third of it not entering the recycling stream.(Elfawal et al., 2025).

The directive defines SUPs as products which are made fully or partly of plastic and is intended for single use before disposal. It includes plastics derived from fossil, synthetic or modified natural polymers. However unmodified natural polymers, which chemical structure remains unchanged, are excluded from the directive's scope. (European European Comission, 2021b)

The European Commission guidelines (2021/C 216/01) clarify that even if a material is biobased, it is considered plastic under the directive if it has been chemically modified or includes plastic layers. (European European Comission, 2021b) Consequently, paperboard packaging with plastic barrier coatings is included in the directive's scope when intended for single-use applications.

The directive has already led to reductions in SUP consumption, for example, polyethylene bag usage has decreased by up to 68% in some regions (Barone et al., 2025). These developments are driving innovation in recyclable and biobased barrier materials, such as bio-based dispersions, which are central to this thesis. The focus is shifting toward biobased and unmodified barrier materials that are considered as plastic-free.

4 Barrier coating techniques

Many packaging applications require materials with effective barrier properties. Two major coating techniques that are used to apply barrier layers onto paperboard substrates are extrusion coating and dispersion coating. (Tuominen & Lahtinen, 2008, p. 168) In this thesis, dispersion coating is the technique selected for the experimental part.

4.1 Extrusion coating

Extrusion coating involves melting a thermoplastic polymer and pressing it onto a rapidly moving substrate through a die. Upon cooling, this forms a thin, uniform film on a substrate surface (Figure 2). (Kuusipalo et al., 2008, pp. 108,119) This method is widely used in packaging applications requiring moisture, grease and gas barrier. (Perumal et al., 2025).

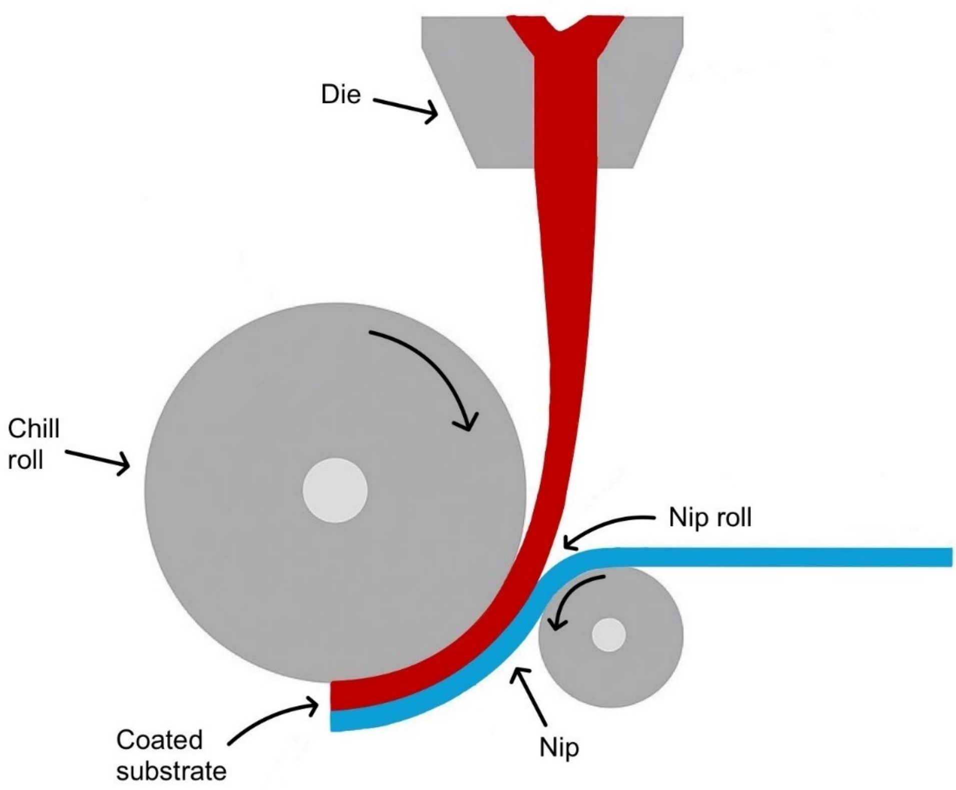

Figure 2. Extrusion coating process. Redrawn from Meyer (2017) with permission from Knovel.

By extrusion coating can be achieved excellent barrier properties against moisture, grease, and gases, depending on type of polymer used. The method supports high-speed and large-scale production, making it widely used in packaging industry. It also offers smooth and seamless coating and is suitable for multilayer structures and label applications. (Perumal et al., 2025)

However, extrusion coatings are typically based on fossil-based polymer such as PE. There are also available biobased alternatives like polylactic acid (PLA). Both are classified as plastic and have same recyclability issues. (Mujtaba et al., 2022)

4.2 Dispersion coating

Dispersion barrier coating involves applying an aqueous or solvent based formulation with fine polymer particles onto the paperboard surface. Unlike extrusion polymers, these particles do not melt but coalesce during drying to form a continuous film. (Kimpimäki et al., 2008, p. 62)

Advantages of dispersion coating are compatibility with in-line and off-line processes, flexibility in machine width and speed. It also gives excellent adhesion due to partial absorption into the substrate. However dispersion coatings are generally more expensive and may not match extrusion coatings quality in high-barrier or heat sealing applications. (Kimpimäki et al., 2008, pp. 62–63,67)

Uniform thickness is more critical than surface smoothness, as it directly affects barrier performance. A balance is often needed between printability and barrier quality. Typical dispersion barrier coating weight range from 4-15 g/m^2. (Kimpimäki et al., 2008, pp. 63–64)

4.2.1 Film formation

Film formation is critical step in dispersion coating. In Figure 3 is illustrated the film formation process. As water evaporates, polymer particles move closer, deform, and coalesce into a dense, homogeneous film. This process involves particle packing, deformation and interdiffusion and consolidation into a continuous layer. As it determines the functionality and barrier performance of the final coating layer. (Kimpimäki et al., 2008, pp. 72–74, 83)

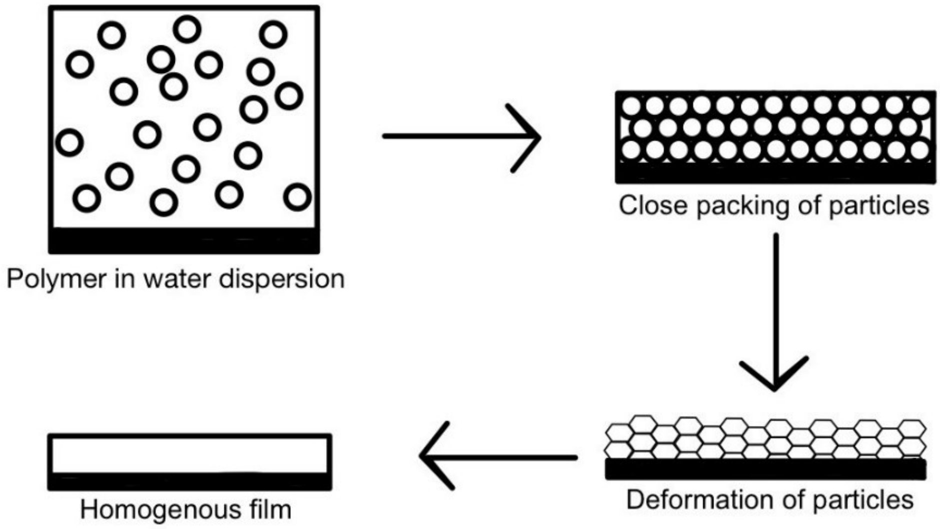

Figure 3. Film formation process. Redrawn from Keddie and Routh (2010) with permission from Springer Nature.

Incomplete coalescence can lead to defects such as pinholes, poor adhesion, and increased permeability. The factors affecting film formation are polymer particle size and deformability, drying temperature and additives such as surfactants and crosslinkers. (Kimpimäki et al., 2008, pp. 72–74, 83, 98–102)

Drying conditions, especially temperature, influence film quality. Higher temperature promotes tighter packing and better barrier properties. A well-formed film is nonporous, pinhole free, has uniform thickness and is strongly adhered to substrate. Proper control of film formation is essential for achieving wanted barrier properties and ensuring good runnability and surface quality. (Kimpimäki et al., 2008, pp. 63–64, 72–74, 83, 98–102)

4.2.2 Coating methods

Common metering methods in dispersion coating includes curtain coating, rod coating, and blade coating. In curtain coating a continuous sheet of liquid falls onto the moving substrate. Rod coaters apply the coating with a rotating rod that removes excess coating material, while blade coating uses a blade to control the coating thickness. These methods closely follow the surface profile of paperboard and are especially good options for rough and uneven substrates. (Kimpimäki et al., 2008, pp. 67, 69, 72)

Rod coating applies a uniform layer of coating dispersion onto a moving paper web using an applicator or metering rod. This method is fast and gives precise control over coating thickness. The thickness is controlled by rods of different diameters, each identified by a specific number. Rod coating is considered the simplest and most economical process for paper coating. This method works especially in applications where coating thickness is critical property. (Perumal et al., 2025)

Blade coating is also widely used in paper industry because it gives paper substrate enhanced printability, moisture resistance, and barrier properties. During the application process the paper web or sheet passes beneath the doctor blade. The coating thickness is controlled by adjusting the gap between blade and the paper surface. As the paperboard moves under the blade, the coating spreads evenly, resulting in a precise layer thickness and smooth surface finish. (Perumal et al., 2025)

Curtain coating is old invention but has not been used in paper and board industry for a long period of time. Curtain coating produces contour like coatings with low coating weights. There are two types of applicators, a slot dies and a slide die. Slot die is used for single-layer coating and slide die has a possibility to produce multilayer coatings. Advantages of curtain coating are good runnability due to low impact on substrate surface. (Kimpimäki et al., 2008, p. 72)

4.2.3 Polymer dispersion rheology

Rheology describes how material flow and deforms in response to applied stress. The magnitude and type of stress affect how material responds. Materials can undergo reversible (elastic) deformation, irreversible (flow) deformation, or exhibit both behaviors, in which case the material is said to be viscoelastic. In elastic deformation, the internal structure remains intact, whereas in flow deformation, it is permanently altered. (Roper, 2009, p. 318)

In paperboard coating, shear stress is the most applied force. Shear stress is defined as force per unit area as shown in Equation 1:

$$\tau = \frac{F}{A}, \tag{1}$$

where τ is shear stress [N/m^2], F force and A area. (Kimpimäki et al., 2008, p. 92)

Velocity gradient, shear rate is expressed as shown in Equation 2:

$$\dot{\gamma} = \frac{dv}{dx} = \frac{v}{x}, \tag{2}$$

Where $\dot{\gamma}$ is shear rate [s^{-1}], v velocity and x thickness. dv/dx equals v/x if the liquid is ideal.

Dynamic viscosity is calculated from stress divided by the shear rate, as expressed in Equation 3:

$$\eta = \frac{\tau}{\dot{\gamma}}, \tag{3}$$

where η is dynamic viscosity [Ns/m^2] (Kimpimäki et al., 2008, p. 93).

Most of coating materials exhibit non-Newtonian behaviour, meaning their viscosity depends on shear stress or shear rate. Non-Newtonian fluids can be divided into dilatant (shear thickening) and pseudoplastic (shear thinning). Pseudoplastic behavior, where viscosity decreases with increasing shear rate, is more common. (Roper, 2009, p. 320)

Viscosity is a key parameter in coating processes, as it affects how the material flows under different conditions. Polymer dispersions typically show a rapid decrease in viscosity with increasing shear rates, which is advantageous in coating applications. Commercial barrier dispersion usually has viscosities ranging from 500 to 1000 mPas. Adjusting viscosity by adding water is not ideal, as the evaporation process requires significantly more energy. Therefore, minimizing the amount of added water is preferred. The desired solids content is typically between 20–70%. Viscosity is influenced by the molecular weight of the polymers and generally decreases with increasing temperature. (Kimpimäki et al., 2008, pp. 94–96)

Understanding rheology in paperboard coating is essential, as it directly influences both the coating process, and the product quality. All components of a dispersion affect its rheological behavior, making it a complex system to analyze. However, a deep understanding of these properties enables the development of innovative dispersion formulations designed for specific performance requirements. (Roper, 2009, pp. 318–319)

5 Barrier materials in food packaging

Paperboard is a renewable and recyclable packaging material, however, its inherent porosity and hydrophilicity lead to poor resistance to moisture, grease, and gases. To be suitable for food packaging it requires functional coating that prevents the transfer of liquids and gases, thereby also extending products shelf life. (Perumal et al., 2025)

Barrier properties in packaging include resistance against grease, light, moisture, and gases. For food packaging water vapour transmission rate (WVTR) and grease resistance are important barrier qualities. In these applications barrier characteristics are critical in protecting freshness and increasing the shelf life of product. (Basak et al., 2024) Figure 4 illustrates multilayer barrier protection for food packaging materials. Materials are selected based on the specific need of the end product, including permeation of water, oxygen, grease, microorganisms, aromatic compounds, carbon dioxide, and grease. (Mujtaba et al., 2022)

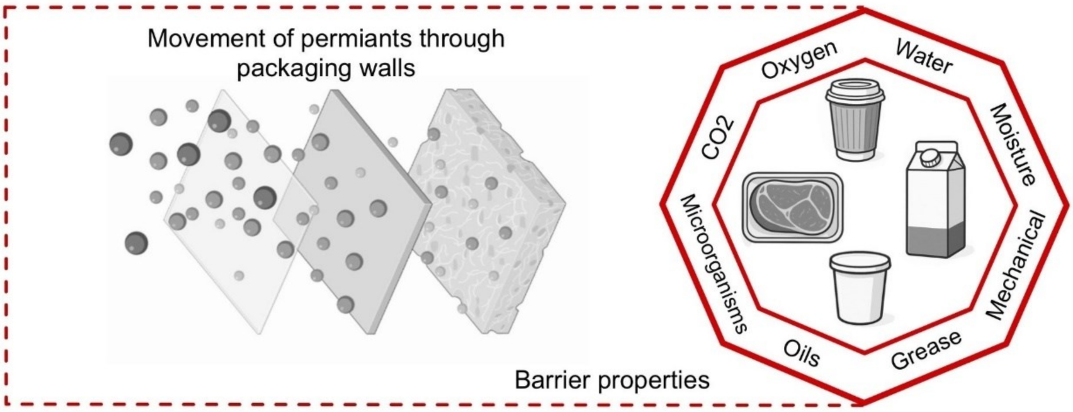

Figure 4. Different barrier properties for food packaging. Redrawn from Mujtaba et al. (2022) with permission from Elsevier.

The environmental and economic drawbacks of non-biodegradable packaging solutions have increased the need for sustainable alternatives. Fossil-based packaging can offer several advantages such as extending shelf life due to high barrier properties, safety and protection during transportation and storage. Challenges on biobased packaging materials align for example with water vapour barrier properties which are not achieved same level as their fossil-based alternatives. (Mujtaba et al., 2022; Wu et al., 2021)

Growing environmental concerns and regulatory actions, such as the SUP-directive underscore the need for sustainable unmodified barrier coatings. (Teixeira et al., 2025) Focus of the thesis is on unmodified bio-based polymers which have potential to be used as alternatives for fossil-based polymers.

5.1 Definitions

In the context of sustainable packaging development, it is important to understand the terminology related to material origin and environmental impact. This chapter defines the key concepts of bio-based, fossil-based and biodegradable.

Bio-based polymers are derived from natural or organic materials, when fossil-based polymers are derived from petroleum sources (Mujtaba et al., 2022). Figure 5 illustrates the relationship between fossil-based, bio-based, and biodegradable polymers. As shown in Figure 5 both fossil-based and bio-based polymers can be either biodegradable or non-biodegradable.

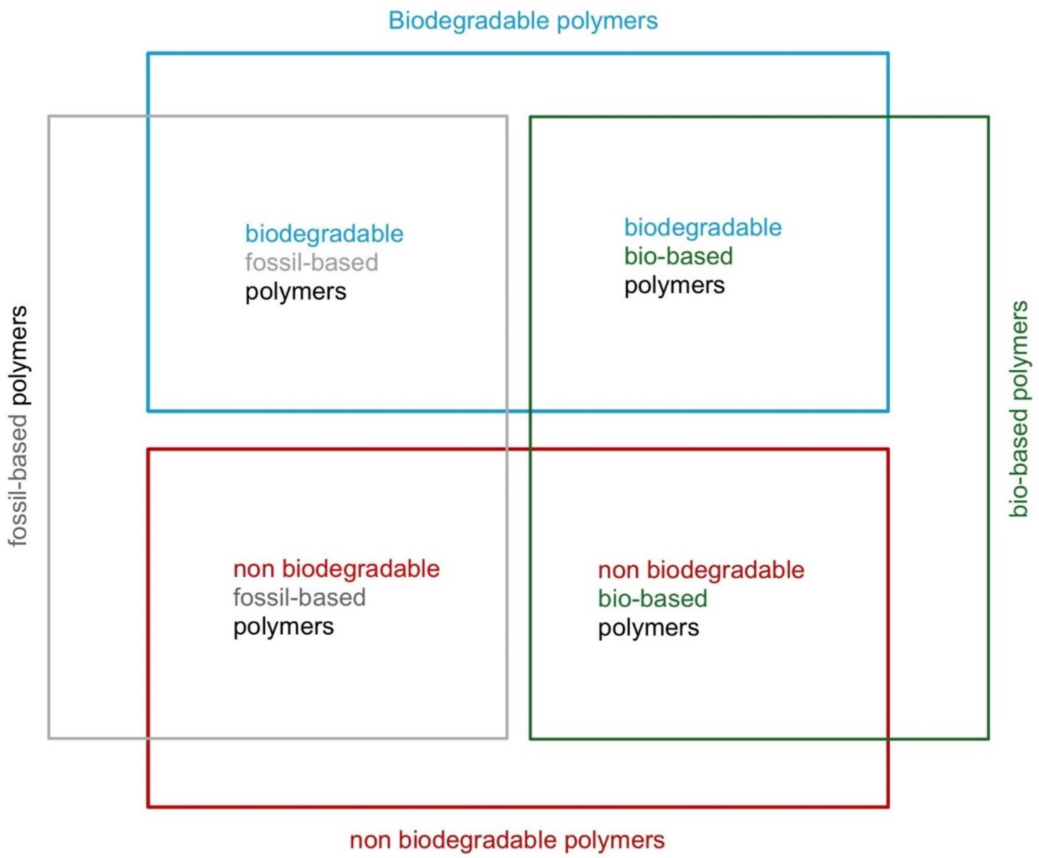

Figure 5. Relationships between fossil-based, bio-based, and biodegradable polymers. Redrawn from European commission (2021).

Biodegradability is defined that material degrade in a specific time and in a specific environment. Biodegradability has standards such as ISO 14855-1 for industrial composting and ASTM D6691 for aerobic biodegradability in seawater. (European Comission, 2005, 2021a, 2022; Narancic et al., 2018) If material is compostable, it is also biodegradable but if it is biodegradable, it does not mean it is compostable. The compostability of a packaging material is defined in the European standard SFS-EN 13432, which specifies the requirements for packaging recovery through composting and biodegradation. (Kimpimäki et al., 2008, p. 103). The classification of biodegradable polymers is shown in Figure 6. This includes polymers from non-renewable and renewable sources.

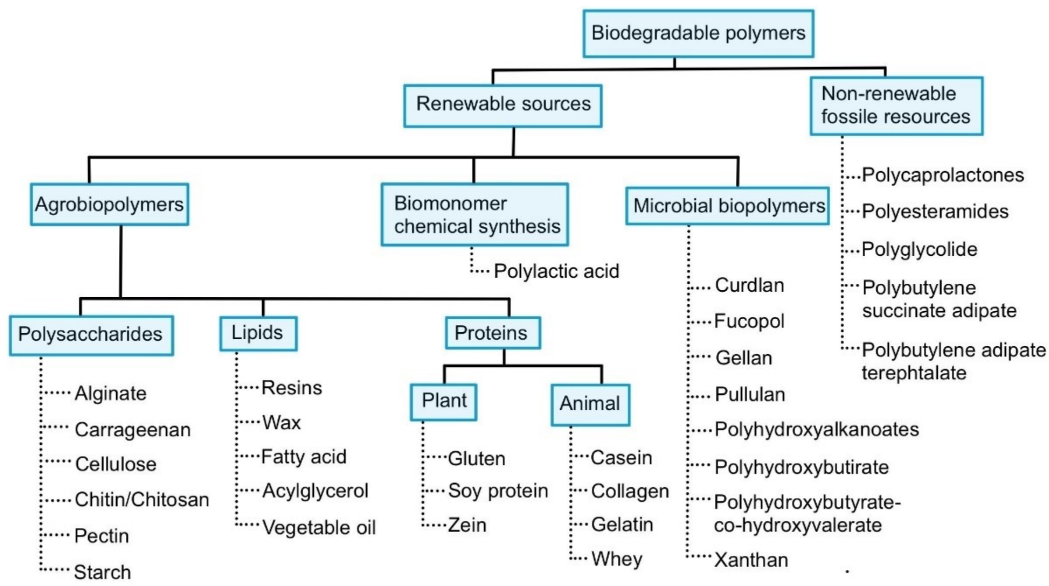

Figure 6. Classification of biodegradable polymers. Redrawn from Mujtaba et al. with permission from Elsevier.

It is important to notice that bio-based does not automatically mean biodegradable. For example, bio-based PE is chemically identical to fossil-based PE and is not biodegradable, despite it is derived from renewable sources. (Burelo et al., 2023)

5.2 Fossil-based polymers

Traditionally, fossil-based polymers have been used to provide barrier properties. These have been widely used in food packaging. They have excellent barrier properties, mechanical strength, and cost-effectiveness. Common fossil-based barrier material are example high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP). (Burelo et al., 2023; Mujtaba et al., 2022; Pang et al., 2022)

Among these LDPE is the most used, due to its flexibility and moisture, water and grease barrier properties. It provides excellent protection but its resistance to gases such as oxygen is relatively poor. (Burelo et al., 2023)

However, the use of non-renewable or non-biodegradable barrier materials pose environmental risks, like greenhouse gas emissions. Their use in coated paperboard packaging complicate recycling process, as these layers are not water-soluble and complicate repulping process. (Mujtaba et al., 2022)

5.3 Bio-based polymers

Bio-based polymer food packaging offer potential advantages such as, sustainability, carbon neutrality, and reduced dependence on fossil resources (Cheng et al., 2024). However, bio-based polymers often exhibit weaker barrier properties, especially against oxygen and water vapour. As well as lower heat resistance, reduced mechanical strength and higher costs. To address these limitations, research has focused on formulation improvements, including nanocomposites, multilayer systems, and active packaging technologies. Under optimal conditions, bio-based polymers have shown to provide excellent barrier properties. (Mujtaba et al., 2022; Teixeira et al., 2025)

Bio-based polymers are produced from renewable sources such as plants, algae, or microorganisms. Depending on their chemical structure and processing, they may be biodegradable or non-biodegradable. There are bio-based alternatives available for many fossil-based products, but the problem is that they still have the same recyclability problems. (Burelo et al., 2023; Mujtaba et al., 2022). This thesis focuses on chemically unmodified bio-based polymers which could have potential use as barrier material such as polysaccharides and lipids.

Lipids like beeswax and paraffin wax have shown excellent moisture barrier but lacks in mechanical strength. In other hand, polysaccharides such as cellulose and carrageenan show good gas and grease barrier, but poor water vapour resistance. (Adibi et al., 2023)

Polysaccharides have shown promising barrier performance against grease, oxygen, and carbon dioxide. They are stable, non-toxic, biodegradable and economically viable, and can be sourced from circular economy systems. Structurally, they are macromolecules composed of monosaccharides (e.g., glucose, galactose, xylose) linked by glycosidic bonds and typically contain hydroxyl groups. (Glberto Jiménez, 2015; Perumal et al., 2025) However, their hydrophilic nature and crystalline structure limit their resistance to water and vapour, which are desired properties. One promising solution could be the incorporation of nanomaterials to improve barrier properties. (Glberto Jiménez, 2015; Perumal et al., 2025)

Among biobased polymers, carrageenan, a polysaccharide derived from red seaweed, has been shown as a promising alternative due to its film-forming ability, grease resistance, and oxygen barrier properties. In this thesis, carrageenan is used as the primary coating material, highlighting its potential to be used in sustainable packaging applications. Lipids (bio wax) is addressed later in this thesis, since it is used as an additive.

6 Seaweed

Seaweed is considered one of the most rich and underutilized source of natural polysaccharides, including carrageenan, agar and alginate. (Alfatah et al., 2025) It plays important role in marine ecosystem by providing habitat, producing oxygen and supporting nutrient cycling. (FAO, 2021)

Natural polymers extracted from seaweed, such as carrageenan and alginate, have shown to be potential alternative for use in biodegradable barrier due to their film-forming properties and sustainability (Bashir et al., 2025). This thesis focuses on carrageenan, which is extracted from red seaweed. Carrageenan has been shown as promising candidate in meeting the sustainability requirements of the SUP-directive.

6.1 Species

Seaweed is classified into three groups based on their photosynthetic pigments: red (Rhodophyta), green (Phaeophyceae) and brown (Chlorophyta). The physical size of brown seaweed is typically the largest, ranging from 30–60 cm to over twenty meters in length. Red and green seaweeds are smaller, usually from a few centimetres to about one meter. (Cunha & Grenha, 2016)

Brown seaweed is source of alginate and red seaweed is rich in carrageenan and agar. Among red seaweeds Kappahycus and Eucheuma are the primary species used to extract carrageenan. These species are also consumed as food. (FAO, 2021)

Red seaweed is widely distributed in marine ecosystems but is scarcely found in freshwater systems. Their red colour comes from phycoerythrins, which allow them to absorb blue-green wavelengths of light that penetrates deeper into the ocean. As a result, red seaweed can be found also in extremely dark and deep regions. Red seaweed has significant role in the production of oxygen in seawater. (Bukhari et al., 2023)

6.2 Global production and cultivation

Seaweed cultivation has expanded rapidly in recent decades, while wild farming has remained relatively stable (Langford, 2024b). Production is concentrated in Eastern and Southeastern Asia, with Indonesia, China, and the Philippines as the leading producers. In 2019 seaweed accounted for 30% of worlds aquaculture production, with 97.4% of seaweed produced in Asia and 99.1% of that from cultivation. Of global production, China leads with 56.75% share , followed by Indonesia with 27.86% share. (FAO, 2021) Carrageenan-producing species are primarily cultivated in Indonesia (81%) and Philippines (15%). (Langford, 2024b, pp. 1–2)

Red seaweed cultivation has increased from 21 000 tonnes in 1950 to 18.3 million tonnes in 2019, representing over half of global seaweed production by weight and value. (FAO, 2021) Carrageenan extracted from red seaweed is classified as higher price and lower volume, which market share is only 2.8% but market share by value of 8%. It is widely used seaweed-based polysaccharide, with applications in the food, cosmetics, pharmaceutical and textile industries. Three main commercial types of carrageenan are kappa (κ), iota (ι), and lambda (λ) and they differ on which red seaweed specie is cultivated. (Alfatah et al., 2025; Rodríguez-Núñez et al., 2023; Zhang et al., 2024, pp. 24, 29–30).

Although same species of red seaweeds are genetically similar, their physical characteristics can differ depending on environmental conditions. Factors, such as temperature, salinity, light, water motion, nutrient levels, turbidity, epiphytes, grazing organisms, and pollution, can affect their color, shape, growth rate, and carrageenan content. (Langford et al., 2024, p. 154)

6.3 Sustainability

Seaweed farming is considered more sustainable than land-based agriculture, as it requires no freshwater, fertilizers, or arable land. It contributes to carbon sequestration, nutrient removal, and biodiversity enhancement in coastal ecosystems. Seaweed absorbs nitrogen and phosphorus from surrounding waters and captures carbon dioxide through photosynthesis. It can help mitigate eutrophication, treat waste waters, reduce ocean acidification and act as carbon sink. (FAO, 2021; Radulovich et al., 2015) Seaweeds also provide ecosystem services, such as habitat for marine organisms, shoreline protection by buffering wave action and food for various marine species including fish and worms. (Bukhari et al., 2023).

However, large-scale seaweed farming can also pose environmental risks. These include the genetic contamination of local species, disruption of water flow and sediment transport, competition of light and nutrients, and potential habitat degradation due to farming infrastructure. Although seaweed grows quickly and can capture carbon more rapidly than trees, short harvest cycles may limit long-term carbon sequestration. (FAO, 2021)

Seaweed contributes significantly to community cohesion and women's empowerment especially in coastal regions of developing countries. The labour intensive nature of seaweed farming, combined with low capital requirements and simple technology, makes it accessible to resource-poor households or vulnerable individuals. (FAO, 2021)

In Indonesia for example, coastal fishers and farmers have transitioned to seaweed farming, improving their livelihoods. This has abled them to build better homes, to get their children to school and buy vehicles. However, in some areas, rapid expansion has also led to environmental degradation. (Langford, 2024b, p. 5)

Plastic floats are widely used in seaweed farming due to their light weight, durability, and ability to submerge seaweed below the surface to reduce losses after rainfall. However, there are currently not available sustainable alternatives for plastic floats. Improper disposal of these often leads to pollution of river, oceans or on land. Educating farmers on end-of-life plastic management and developing biodegradable alternatives are essential steps toward improving the environmental footprint of seaweed farming. (Langford, 2024a, p. 234)

7 Carrageenan

Carrageenan is a high molecular weight linear sulphated galactan. Galactans are natural polysaccharides composed of galactose units and 3,6-anhydrogalactose, joined by alternating α-1,3 and β-1,4 glycosidic linkages. It is commonly used as a food additive due to its gelling, stabilizing and thickening properties. Carrageenan is hydrophilic and is found especially in cell walls of red seaweed. The degree and position of sulfate groups determine the type and functionality of carrageenan. (Cunha & Grenha, 2016; Ferreira et al., 2015; Sedayu et al., 2018)

The three main commercial types are kappa (κ), iota (ι), and lambda (λ). These types and their differences are illustrated in Figure 7. As shown in Figure 7, κ-carrageenan has one sulfate group per disaccharide unit, ι-carrageenan has two, and λ-carrageenan has three. Different seaweed species and extraction conditions produce different carrageenan types. (Alfatah et al., 2025; Cunha & Grenha, 2016; Udo et al., 2023) κ-carrageenan is the most widely used, while ι- and λ-carrageenan have more limited applications (Udo et al., 2023).

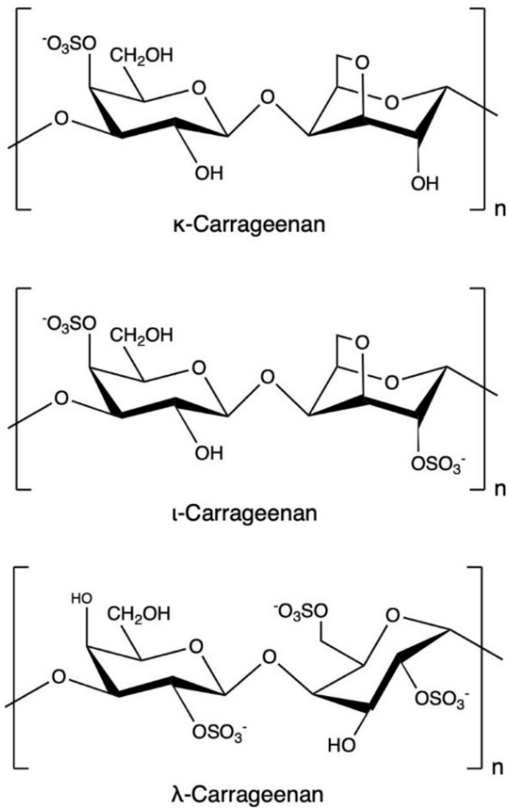

Figure 7. Main types of carrageenan. Adapted from Udo et al. (2023) with permission from Elsevier.

κ-carrageenan has the strongest gelling ability among the three types, due to its moderate sulfation (25–30%) and high 3,6-anhydrogalactose contents (28–35%). ι-carrageenan also forms gels and typically has 25–30% ester sulphate content and 20–30% 3,6-anhydrogalactose. In contrast λ-carrageenan contains the highest level of sulfation (32–39%) and lacks 3,6-abhydrogalactose entirely, making it unable to form gels and resulting in viscous solutions (Cunha & Grenha, 2016; Sedayu et al., 2019).

In packaging applications, κ-carrageenan has shown promising film-forming ability, mechanical strength, and gas barrier properties. Compared to ι-carrageenan, κ-carrageenan films are stronger but less flexible. Increasing concentration can improve flexibility but may reduce tensile strength. (Alfatah et al., 2025; Udo et al., 2023)

Film formation involves a coil-to-helix transition followed by helix aggregation (Figure 8). In aqueous solution carrageenan exhibits thermo-reversible solution gel transition. First carrageenan exists as random coils. Upon temperature decrease or by the presence of cations, hydrogen bonding induces helix formation, which then aggregate into junction zones. Higher the number of molecules in junction zone the more rigid the gel is. This explains why κ-carrageenan forms stronger, shear resistant gels compared to ι-carrageenan, which has fewer molecules per junction zone. (Cheng et al., 2022; Sedayu et al., 2019)

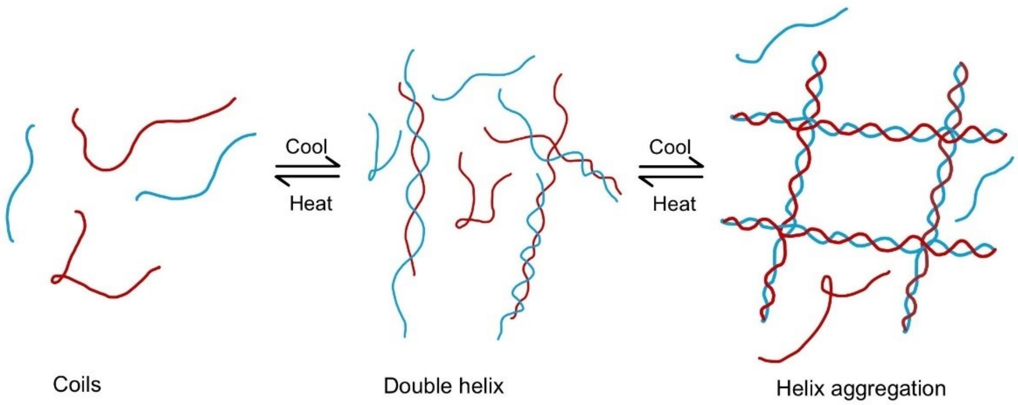

Figure 8. Carrageenan film formation process. Redrawn from Cheng et al. (2022) with permission from Frontiers.

The hydrophilicity of carrageenan arises from the presence of sulphate and hydroxyl groups in its structure. 3,6-anhydrogalactose residues are hydrophobic. As a result, κ-carrageenan, which contains more 3,6-anhydrogalactose, is less hydrophilic than ι- and λ-carrageenan. λ-carrageenan is the most water-soluble of the three due to the absence of hydrophobic residues.

(Cunha & Grenha, 2016) While the chemical structure is a major factor in solubility, temperature also plays a key role: all types are soluble in hot water, but only λ-carrageenan dissolves in cold water. (Udo et al., 2023) Hydrophilicity refers to the tendency of a material to attract and absorb water. In the context of packaging, this is an undesirable property because it allows water vapor to penetrate the material. When moisture enters the packaging, it can compromise food freshness, promote microbial growth, and promote chemical degradation processes such as oxidation and vitamin loss. Therefore, packaging materials should ideally be more hydrophobic than hydrophilic, which means that it is more resistant to water and would ensure better protection and longer shelf life of the contents. (Basak et al., 2024)

The manufacturing process of carrageenan typically involves extraction, purification, concentration, precipitation and drying. The exact procedure may differ depending on the red seaweed specie used. In traditional method, carrageenan is extracted from seaweed using aqueous solution. After filtration to remove insoluble residues, alcohol is added to the extract to precipitate carrageenan. The precipitate is then separated, dried, and milled to produce refined carrageenan. (Cunha & Grenha, 2016; Udo et al., 2023)

One alternative method involves washing the raw seaweed to remove soluble proteins, fats, and minerals, without dissolving the carrageenan. The remaining solid, which contains carrageenan along with other insoluble materials, and sold as semi-refined carrageenan. This process is shorter and more economical, but final product has lower purity. (Cunha & Grenha, 2016)

Carrageenan itself is chemically unstable and is commercially available as sodium, potassium, or calcium salts. Sodium salts are readily water soluble, while potassium salts are less soluble. (Cunha & Grenha, 2016) These cations also enhance the gel formation. κ-carrageenan forms strongest gel with potassium ion and ι-carrageenan with calcium ion. (Udo et al., 2023)

The viscosity of carrageenan solution is influenced by several factors, including type of carrageenan, its molecular weight, polymer concentration, temperature and the presence of salts or other solutes. In general, viscosity decreases with lower polymer concentrations, reduced sulphation, lower molecular weight and, increasing temperature. (Cunha & Grenha, 2016)

Due to its swelling behaviour, carrageenan can be challenging to disperse uniformly in water. Furthermore, exposure to acids or oxidizing agents may led to hydrolysis, resulting in degradation of its physical properties. (Cunha & Grenha, 2016)

Carrageenan solutions typically exhibit non-Newtonian, shear-thinning behaviour, meaning that their viscosity decreases as the shear rate increases.

This rheological property is particularly relevant for processing and application in biodegradable film formation. (Rajamani & Khora, 2025)

7.1 Comparison with alginate

Alginate is polysaccharide derived from brown seaweed, whereas carrageenan is extracted from red seaweed. Both are linear polysaccharides, but they differ significantly in monomer composition and structural feature.

Alginate is composed of two types β-D-mannonpyranuronate and α-L-gulopyranuronate monomers. These monomers are arranged irregularly along the polymer chain, and their ratio and distribution greatly influence the physical and gelling properties. (Draget & Taylor, 2011) This structural configuration is illustrated in Figure 9.

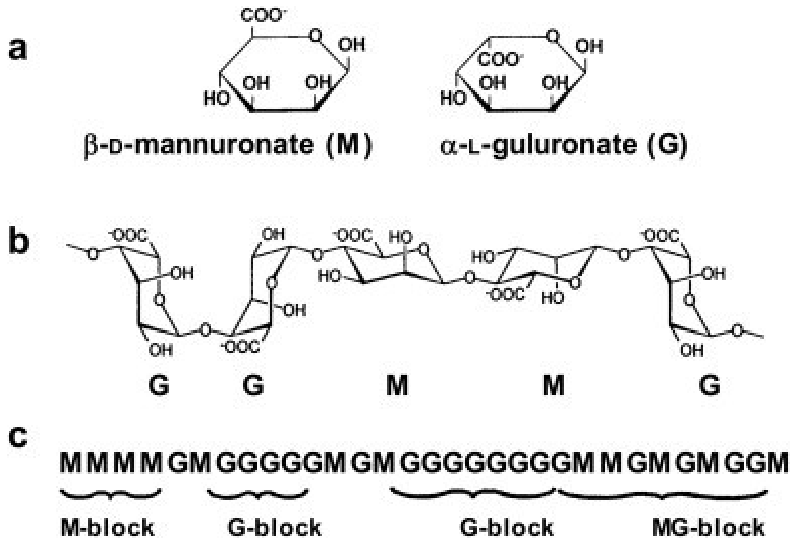

Figure 9. Alginate monomers (a), conformation of the polymer chain (b) and an example of a polymer sequence (c). Adapted from Draget and Taylor (2011) with permission from Elsevier.

In contrast, carrageenan is composed of repeating disaccharide units of D-galactose and 3,6-anhydrogalactose, with differing degrees of sulfation depending on the type (κ, ι, λ), as shown earlier in Figure 7. These differences in sulphate group content define the type and functional behaviour of carrageenan. While both alginate and carrageenan form gels, the mechanism and structural basis of gel formation differ. Carrageenan gel formation is driven by the presence and positioning of sulphate groups and can be influenced by specific cations, such as K^+ or Ca^{2+}, depending on the type. (Cheng et al., 2022) Alginate forms gels mainly through ionic crosslinking between Gblocks and divalent cations like calcium, creating an “egg-box” structure (Draget & Taylor, 2011).

In summary, although both alginate and carrageenan are marine-derived linear polysaccharides, their monomer composition, sequence regularity, and functional groups distinguish their behavior and applications.

7.2 Previous studies on use in barrier material

Carrageenan has been extensively studied for various applications, example in the development of biopolymer films. However, its use as a coating on substrates such as paper or paperboard has received relatively low attention. Most research has focused on free-standing films, rather than coated surfaces. (Cheng et al., 2022; Sedayu et al., 2019) While edible films and coatings have been widely investigated, studies using only carrageenan consistently report films that are naturally brittle and require blending or modification to enhance performance. (Sedayu et al., 2019; Udo et al., 2023)

According to Cheng et al. (2022), pure carrageenan films have limitations in water vapour performance due to their hydrophilic nature. To overcome this incorporation of nanoparticles, blending with polysaccharides and electrostatic interactions with proteins have been employed to reduce water vapour permeability. These modifications could improve film compactness, reduce hydrophilicity, and enhance cross-linking, leading to better moisture barrier properties suitable for packaging applications. (Cheng et al., 2022)

One notable research conducted by Shankar and Rhim (2018) studied a blend of alginate, carboxymethyl cellulose (CMC), and carrageenan as a coating solution for paper packaging. The biopolymer coating improved water and grease resistance, surface hydrophobicity, and tensile strength. All test papers were conditioned at 25 °C and 50% relative humidity (RH) for 48h. Water absorptiveness was measured using Cobb test according to ASTM D 3258-93 method. Water absorptiveness was reduced from 41.4 to 21.4 g/m^2 (thickest coating), the result was better than with PE-coated paper. Oil absorptiveness was conducted using Cobb test apparatus and it dropped from 22.7 to 2.1 g/m^2 (thickest coating), which was lower than with PE-coated (3.5 g/m^2). Water vapor permeability (WVP) was measured according to method ASTM E96-95 with some modifications, it dropped from 231.7×10^{-11} to 171.5×10^{-11} gm/m^{2}Pas (thickest coating). PE-coated paper WVP value was 0.91×10^{-11} gm/m^{2}Pas, which is much lower than biopolymer coating. Water contact angle increased from 69.1° to 100.1°, indicating better hydrophobicity (PE-coated 85.7°). As shown in Figure 10, scanning electron microscopy (SEM) images revealed a smooth surface like PE coatings and good adhesion between the coating and the paper substrate. The study concluded that such biopolymer-coated papers could be promising biodegradable alternatives for food packaging. (Shankar & Rhim, 2018)

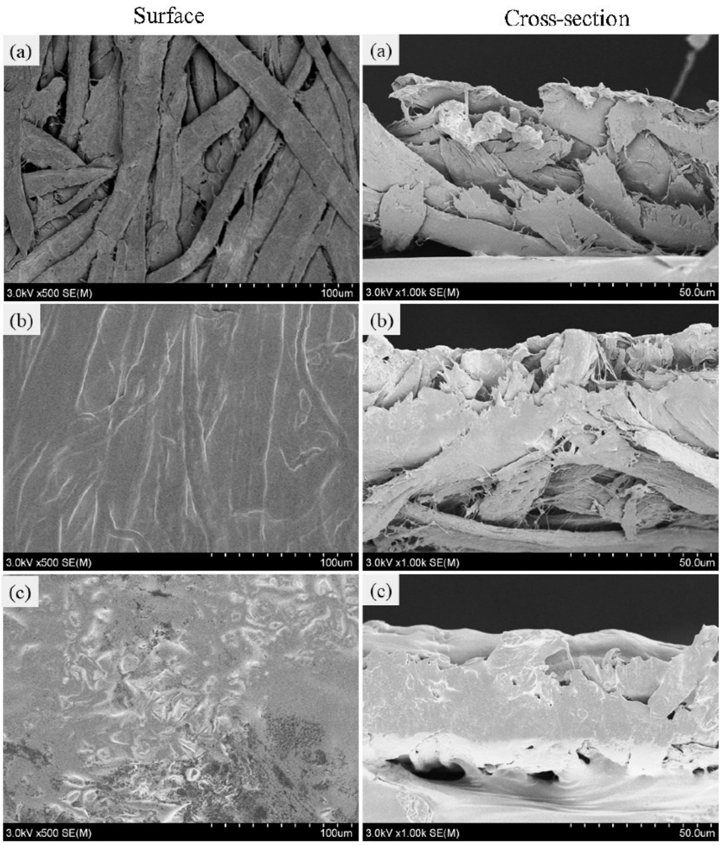

Figure 10. SEM micrographs of surface cross section of (a) uncoated, (b) biopolymer coated and (c) PE-coated papers. Adapted from Shankar and Rhim with permission from Elsevier.

Research aiming to improve the barrier properties of carrageenan composite films, especially against water vapor and gases is wide. For example, Alves et al. (2010) demonstrated that incorporating mica flakes into a κ-carrageenan/pectin blend (66.7% κ-carrageenan) significantly improved the water vapor and gas barrier properties. With mica content of 10% (w/w, dry polymer basis), water vapor permeability decreased by approximately 40%, while CO_2 and O_2 permeability dropped by 73% and 27%, respectively. (Alves et al., 2010) Also, Sanchez-García (2011) studied carrageenan blend with mica and zein.

Yadav and Chiu (2019) and Popescu et al. (2019)both investigated bio-nano-composite films composed of κ-carrageenan and cellulose nanocrystals (CNCs). In both studies, the use of CNCs enhanced the barrier properties of the films, particularly their resistance to moisture. Additionally, enhanced mechanical properties were observed, including increased tensile strength and flexibility. Yadav and Chiu used a 1 wt.% κ-carrageenan solution and achieved the best results with 7 wt.% CNC relative to the polymer. In contrast, Popescu et al. used a 3 wt.% κ-carrageenan solution and tested final film compositions containing 5–15 wt.% CNC, with the best performance observed at 15 wt.% CNC. (Popescu et al., 2019; Yadav & Chiu, 2019)

Similarly, Jaffar et al. (2025) developed κ-carrageenan based bionanocomposite film incorporating nanocellulose and silver nanocomposite. These films showed improvements in mechanical, antimicrobial activity, and moisture properties. WVTR of the films was measured gravimetrically at 25 °C under a 50% RH environment, using a desiccator setup with $CaCl_2$ (0% RH) and water (100% RH) to create a controlled humidity gradient. WVTR was reduced to 5.6 g/m²/24 h, though the film exhibited a relatively high-water solubility of 47.7%, which would limit certain applications. (Jaffar et al., 2025)

Study of κ-carrageenan and chitosan composite film was researched by Sun Y. Parka et al. (2000). κ-carrageenan and chitosan were blended. To this solution plasticizers glycerine and polyethylene glycol were added and different organic acids were used as solvent. Ascorbic acid was added at various concentrations (0–3%) as a cross-linker. Tensile strength increased with higher ascorbic acid content but decreased slightly WVP value. WVP increased when plasticizing effect dominated. (Sun Y. Parka et al., 2000)

Sedayu et al. (2021) studied the effects of surface photo-crosslinking on carrageenan films. Exposure to UV irradiation enhanced the film's barrier and mechanical properties. This process reduced the number of hydroxyl groups, increased crystallinity and improved tensile strength and elongation at break. While water vapor permeability (WVP) was reduced, the presence of photosensitizers increased overall water sensitivity. The optimum exposure time for achieving balanced properties was 20 minutes. (Sedayu et al., 2021)

Layering hydrophilic carrageenan films with hydrophobic substances would help to overcome limitations of carrageenan. Sedayu et al. (2020) studied the enhancement of semi-refined carrageenan films by incorporating nanoclay and applying a surface lamination with polycaprolactone (PCL). This bilayer structure significantly improved both the barrier and mechanical properties of the films. (Sedayu et al., 2020) In previous study, Sedayu et al. (2018) also studied semi-refined carrageenan-based film for food packaging applications. Adding glycerol to SRC enhanced the optical, mechanical, morphological, and thermal properties, but at the cost of moisture barrier properties. Compared to refined carrageenan, semi-refined carrageenan was found to be more cost-effective and suitable for rigid, non-transparent packaging applications, although it required further improvements in barrier properties. (Sedayu et al., 2018)

To address this, the Sedayu et al. (2020) study demonstrated that laminating SRC/NC composite films with PCL reduced water WVP by 20%, moisture uptake by 24%, and water solubility by 11%, while increasing the water contact angle from 72° to 95°, which indicates enhanced hydrophobicity. Mechanical properties also improved, tensile strength increased by 17.9% and elongation at break by 2.8%. Before measurements, all samples were conditioned for 48 h in 22 °C and 53% RH, which was achieved using $Mg(NO_3)_2$ solution in desiccator. These results highlight the potential of combining semi-refined carrageenan with nanoclay and a hydrophobic PCL layer to produce biobased films with improved functionality for food packaging applications. (Sedayu et al., 2020)

In summary, carrageenan exhibits oxygen barrier properties, comparable to materials, such as polylactic acid, but its hydrophilic nature presents a significant challenge. High water vapour permeability and water solubility limit its use in moisture-sensitive applications. (Sedayu et al., 2019) Therefore, while carrageenan shows potential for sustainable packaging, its use in barrier coating will likely require layering with hydrophobic substances or composite approaches to overcome these limitations. Next chapter discusses possible alternatives to use as an additive to dispersion solution.

8 Additives

Polymer dispersions are primarily composed of water and polymer, but small amounts of chemically active components, such as stabilizers, plasticizers, crosslinkers and fillers are often added to enhance specific functionalities, including barrier performance. These additives contribute to the chemical complexity of the dispersion and can significantly influence the final properties of the coating. (Kimpimäki et al., 2008, p. 81)

One approach to enhance the barrier properties of hydrophilic natural polymers is to blend them with lipid-based materials, which can enhance moisture resistance. (Jahangiri et al., 2024; Rajamani & Khora, 2025) Another strategy involves use of crosslinkers, which would enhance material strength, reduce solubility and improve barrier properties (Priyadarshi & Rhim, 2020).

8.1 Bio wax

Natural waxes are renewable, hydrophobic materials with high crystallinity and chemical stability. They consist of long-chain esters, fatty acids, hydrocarbons, and resins. However, their poor durability, low melting points, and tendency to soften or become brittle limit their use in coatings (Jahangiri et al., 2024; Wang et al., 2025). Waxes have good barrier performance against water vapour but poor durability against grease and oxygen (Zhang et al., 2014).

Barrier properties of lipids depend on factors such as chain length, degree of saturation, physical state, and molecular structure. Most waxes exhibit low melting points, for example, beeswax melts at 45–70 °C. It washes away easily, which is drawback for thermal stability in coatings. Increasing the wax content in a coating formulation can reduce WVP of the packaging material. However, poor adhesion to paper substrate limits the feasible amount of wax that can be incorporated. Even a small change in temperature can cause wax to soften or become brittle when applied on substrate. Low melting point can also be advantageous since wax can be emulsified easily with water. To overcome washing problem waxes can be mixed with other hydrophobic polymers, which would also improve waxes migration to surface and result improves coating hydrophobicity. (Jahangiri et al., 2024)

Beeswax, a natural lipid is gaining attention for its superhydrophobic, biodegradable and edible properties. It is used to increase the moisture barrier, mechanical strength, and UV protection of biopolymer-based films. Beeswax is composed of long-chain hydrocarbons, ester fatty acids, and alcohols. It is Generally Recognized As Safe (GRAS) – certified and approved in the EU

(E901) for food applications. It is superhydrophobic due to its high alkane content and internal methylene chains. Beeswax has been used example as emulsion, blend, and multilayer films. In emulsion and blend films beeswax is emulsified with biopolymers like starch or gelatine to improve water vapour resistance and mechanical properties. In multilayer films beeswax is combined with hydrophilic layers (e.g. polysaccharides) to create films with both moisture and oxygen barrier properties. (Hosseini et al., 2023)

Zhang et al. (2014) studied the chitosan and beeswax multilayer coating for paper to enhance water vapour and grease resistance. Chitosan or another biopolymer was applied as a base layer, followed by a top layer of molten beeswax. The study demonstrated that the chitosan-beeswax combination improved barrier properties, with the best performance observed at higher chitosan concentrations. The bilayer structure minimized beeswax penetration into the paper and created a synergistic interface, resulting lower WVTR and enhanced grease resistance, making it a promising biodegradable alternative for food packaging. (Zhang et al., 2014)

Singh et al. (2023) explored the use of natural waxes such as rice bran, carnauba, and beeswax, in combination with rubber, to develop coatings compliant with the EU SUP directive. The study used both dispersion and hot melt coating to apply wax. Among these two methods, hot melt coatings achieved a slightly better WVTR results compared to dispersion coating, but problems were observed in achieving lower coat weight. Higher coat weight did not improve the barrier performance in hot melt coating, due that at high coat weight of wax has a tendency to crack. Rice bran wax coating achieved WVTR values of 4.3 $g/m^2/24h$ at 23 °C and 50% RH. (Singh et al., 2023)

8.2 Crosslinker

Crosslinkers are chemical agents that form covalent or ionic bonds between polymer chains, resulting in a more compact and stable network structure. In the context of biopolymer coatings, crosslinking can enhance barrier properties but also mechanical strength and reduce solubility. (Priyadarshi & Rhim, 2020; Sedayu et al., 2021; Sun Y. Parka et al., 2000) This is particularly important for hydrophilic materials like carrageenan, which exhibit poor water resistance.

Crosslinker have been studied in various bio-based packaging applications. For example earlier mentioned Sedayu et al. (2021) studied surface photocrosslinking application to semi-refined carrageenan film, which resulted to improve tensile strength and reduced WVTR. Sun Y. Parka et al. (2000) demonstrated that the addition of ascorbic acid as a crosslinker in carrageenan-chitosan composite films increased tensile strength and slightly reduced WVP.

However, under the SUP-directive, the use of crosslinkers may fall into a regulatory grey area. If the crosslinking chemically modifies the polymer, the material is classified as plastic. This issue needs further clarification but crosslinkers could be a viable possibility for improving functionality of bio-based coatings.

9 Experimental

The aim of the experimental work was to find a solution to improve moisture resistance of carrageenan-based barrier. At the beginning of the experimental work, carrageenan's with different viscosities were evaluated for their suitability in coating applications. The most suitable carrageenan was selected based on its coatability and barrier performance. In the next phase, the goal was to enhance the properties of selected carrageenan using additives. Additives such as a crosslinker and bio wax were applied either as a blend or in a multilayer structure.

The dispersions and coatings were characterized based on their viscosities and barrier properties. Barrier coated paperboards were imaged using scanning electron microscopy (SEM) to visualize film formation and evaluated for pinholes. The evaluated barrier properties included water absorptiveness, water vapour transmission rate (WVTR), and grease penetration rate. Additionally, surface free energy was measured, and one sample was evaluated for gluability.

9.1 Materials

A coating grade of red seaweed containing carrageenan (pH 10%: 10.21, Viscosity 10%, 27 °C, Brookfield DV II + Pro viscometer, rpm 20, Spindle 63: 1178 mPas) from Sea6 Energy was used. For clarity, this material will hereafter be referred to as carrageenan. It should be noted that this is product under development and is not a commercialized material. Bio wax from Oy Keskuslaboratorio-Centrallaboratorium Ab (KCL) was used as an additive in the wax blend. Additionally, pure bio wax from the same source was hot melt coated to form a multilayer structure. A crosslinker from Sea6 Energy was also used as an additive, blended with carrageenan.

Metsä Board's pigment-coated Prime FBB Bright paperboard grade (235 g/m^2, thickness: 346 µm), coated on both top and reverse sides, was used as the reference material.

9.2 Sample preparation

Five different coating dispersions were prepared using carrageenan. Carrageenan was first dissolved in deionised water or additive slurry while mixing. The dispersion was mixed for one hour to ensure complete dissolution of the carrageenan. The solution was then filtered through a 5 mm filter to remove any undissolved particles.

Paperboard substrates were coated with Erichsen laboratory rod coater Model 510 Basis G at speed 86 mm/s. Excess water was removed with drying in an oven at 105 °C for 1 min. Coating and drying was repeated twice for all samples. After that coated samples were conditioned to 25 °C and 50% RH for 24 h before further characterization.

The dispersions with their total solids contents (TSC) are seen in Table 1.

Table 1. Coating dispersions.

Dispersion solution code	Carrageenan/ additive (%)	Additive	TSC (%)
Carrageenan	100/0	-	14.2
Blend wax 5%	95/5	Wax	11.8
Blend wax 10%	90/10	Wax	12.3
Blend wax 30%	70/30	Wax	14.3
Crosslinker 16%	84/16	Crosslinker	16.3

Coated samples are presented in. One of the samples is coated with wax as a multilayer structure so that wax is the first layer and carrageenan-crosslinker dispersion the second layer.

Table 2. Coated samples.

Sample code	Multilayer structure
Carrageenan	-
Blend wax 5%	-
Blend wax 10%	-
Blend wax 30%	-
Crosslinker 16%	-
Multilayer	Crosslinker 16% as a first layer and pure wax hot melt coated as a second layer
Pure wax	-

Additive content is expressed as a percentage of the total solids in the coating dispersion.

9.3 Hot melt coating

Pure wax was melted in the oven in 90 °C in small batches. The coating rod and paperboard were preheated. Line of melted wax was poured onto the coater. Wax was let to solidify before moving the sample to the standard conditions.

9.4 Viscosity

The viscosities of dispersions were measured using Brookfield RVDV-III Ultra rheometer. Viscosities were measured twice as function of TSC at 25 °C at spindle speed 100 rpm. Results were reported as average of the two duplicate tests. The viscosity as a function of temperature was measured every 10 second for 30 minutes. The development of viscosity was observed for seven days measuring the viscosity every 24 h.

9.5 Surface characteristics

The morphology of the samples was characterized by observing pinholes and SEM images. SEM images were taken from both the surfaces and the cross-section of the barrier coating. For the multilayer sample SEM images of the surface and cross-section were taken from the both the beginning and the end of the coated area on the paperboard. These images were taken from both ends of the barrier coated area to evaluate the consistency and quality of the coating process. This helps to identify potential variations in coating morphology that may have occurred during coating process, such as uneven material distribution or changes in coating behaviour during application.

Pinholes were evaluated by applying approximately 1.5 ml dyed oleic acid on sample surface. Oleic acid was left on sample for 70 seconds and then removed with a towel. Pinholes were visually examined.

9.6 Barrier measurements

This chapter introduces barrier measurement methods used in this thesis.

9.6.1 Water absorption

Water absorption was measured with the Cobb test according to standard ISO 535:2023. The method determines the mass of water absorbed into the sample in a given time. Time is measured as seconds and displayed in the subindex of the word Cobb, e.g. $Cobb_{60}$ and the result reported in g/m^2.

The test apparatus consists of flat, rigid base and a metal cylinder, which holds the water on certain area, typically 100 cm^2. After the test period, water is removed, and the test piece is placed between absorbent papers and rolled with a 10 kg metal roller. Test equipment also include a timer and a balance with a sensitivity to 1 mg. (International Organization for Standardization, 2023)

The test method differed from the standard in that the test area of the cylinder was 10 cm^2. Test was conducted in 50% RH and 25 °C.

9.6.2 Water vapour transmission rate

Water vapour transmission rate (WVTR) was measured according to standard ISO 2528. Method determines the mass of transmitted water vapour in specific time per specific area. The results are reported in $g/m^2/24$ h.

A circle sample is sealed between a cup and a lid, with a supporting rim beneath the sample. The cup is filled with calcium chloride up to 0.5 cm below the sample. Water vapour penetrates through a circular opening in the lid, and the calcium chloride absorbs the incoming moisture. The water vapour transmission is determined based on the mass change of the cups over a minimum period of 48 h. A WVTR result is considered valid when three consecutive measurements show less than 5% deviation. The test was conducted in 23 °C and 50% RH for four parallel test points.

9.6.3 Grease penetration rate

Grease penetration rate was measured according to the standard ASTM F119-82(2015). Samples are placed on a glass plate the barrier-coated side facing upward, positioned within a sample grid. A round cotton patch is placed on the sample, and a 50 g weight (diameter 18 mm) is used to apply pressure. Before starting measurement, samples are conditioned for 2 h in a climatic chamber at 40 °C and 10% RH. The measurement is conducted under the same conditions.

After conditioning, weights are removed and 200 µl of dyed olive oil is pipetted onto cotton patch. The weights are then put back, and the chamber is closed. There is a camera inside the chamber which records the underside of the samples, and the computer program detects the moment when oil penetrates through the sample. The measurement runs for 120 h or until oil penetrates through sample.

Four parallel samples were measured, starting from the flat surface. If the measurement lasted more than 30 min, it was continued to the creased, 90° bent and 180° bent crease.

9.7 Gluability tests

Gluability test and surface free energy (SFE) measurement are introduced together, since SFE has influence on gluability.

9.7.1 Surface free energy

Surface free energy (SFE) of the sample surfaces was measured using a Krüss Mobile Surface Analyzer. The device determines the contact angles of deionised water and diiodomethane and calculates the SFE based on these values. Owens, Wendt, Rabel and Kaelble methods is used to calculate the SFE in polar and disperse parts. Contact angles are recorded 0.1 s after the droplets are applied to the sample surface. For each coating, two different samples were evaluated, with at least five droplet pairs per sample. The results are reported in mN/m.

9.7.2 Gluability test with hot melt and dispersion glue

Gluability of coated paperboard was measured. Barrier coated sample surface is glued on to reference sample top side. Glue is applied between two layers: the top layer being the barrier coated back side, and the bottom layer being the pigment-coated topside of the reference paperboard. After a conditioning period layers are manually separated, and a fibre tear at the glue seam is evaluated. The results are reported on a scale from 1 to 5, based on the degree of adhesion and fibre tear. Higher fibre tear indicates stronger adhesion and better gluability. The test was conducted in 23 °C and 50% RH for three parallel test points.

Results are evaluated based on the rating scale 1-5 presented on Table 3.

Table 3. Gluability rating scale.

1	No adhesion
2	Adhesion, no tear
3	Under 50% fibre tear
4	Over 50% fibre tear
5	100% fibre tear

Hot melt gluing test is performed using Smithers Pira PAPT3 machine and Nordson ProBlue 4 glue heater and pump. The top sample is the barrier coated sample, which is attached to the upper pedal using double sided tape. It is attached barrier coated side facing downwards. The bottom sample is the top side of reference paperboard and is attached to a moving bottom cart. The bottom cart moves under the glue dispenser to under the top pedal. The upper pedal presses the two samples together creating a seal. Hotmelt gluing was evaluated with a conditioning time of 2 min, 10 min, 24 h and 72 h before tearing test.

Dispersion gluing is conducted using the same equipment and procedure, but without the glue heater. The dispersion glue is water-dilutable and forms a bond as the water evaporates and glue hardens. Dispersion gluing was evaluated on curing time of 48 h before tearing test.

10 Results and discussion

This chapter presents and discusses the properties of carrageenan dispersion, the characteristics of the barrier coatings and the results of their barrier performance. Barrier properties were evaluated through water absorption, water vapour transmission, and grease penetration tests. Further convertability for packaging is presented and discussed through surface free energy and gluability test.

10.1 Barrier dispersion

Carrageenan formed a brown dispersion with deionised water, which had a sea kind of smell. It had ability to develop viscosity for seven days. Carrageenan was in granulate form and had to be mixed for one hour to dissolve properly. After that it was needed to filter for undissolved particles.

In wax blends wax was first mixed into deionised water and after that carrageenan was added to mixture. Crosslinker was added to dispersion after carrageenan was added to deionised water.

10.2 Hot melt coating

Pure wax was hot melt coated on top of carrageenan-crosslinker coating layer to form a multilayer structure. To evaluate the barrier property of the wax independently, pure wax was also applied directly onto the reference paperboard.

Wax was observed to penetrate through the paperboard, indicating that the substrate had poor coating holdout for wax. However, this phenomenon did not occur when wax was coated as a second layer on top of carrageenan-crosslinker layer in a multilayer structure.

Same findings were reported on earlier mentioned study by Zhang et al. (2014) where beeswax was observed to penetrate into paperboard. By applying a biopolymer as a bottom layer, it was noticed to prevent the penetration of beeswax. At the same time properties such as WVTR and grease penetration was enhanced.

10.3 Viscosity

In Figure 11 is presented viscosity behaviour of carrageenan dispersion as a function of TSC. The viscosity behaviour was measured from TSC 10% to

20%. Carrageenan could reach 15% total solid content with still manageable viscosity to be used with laboratory scale coater.

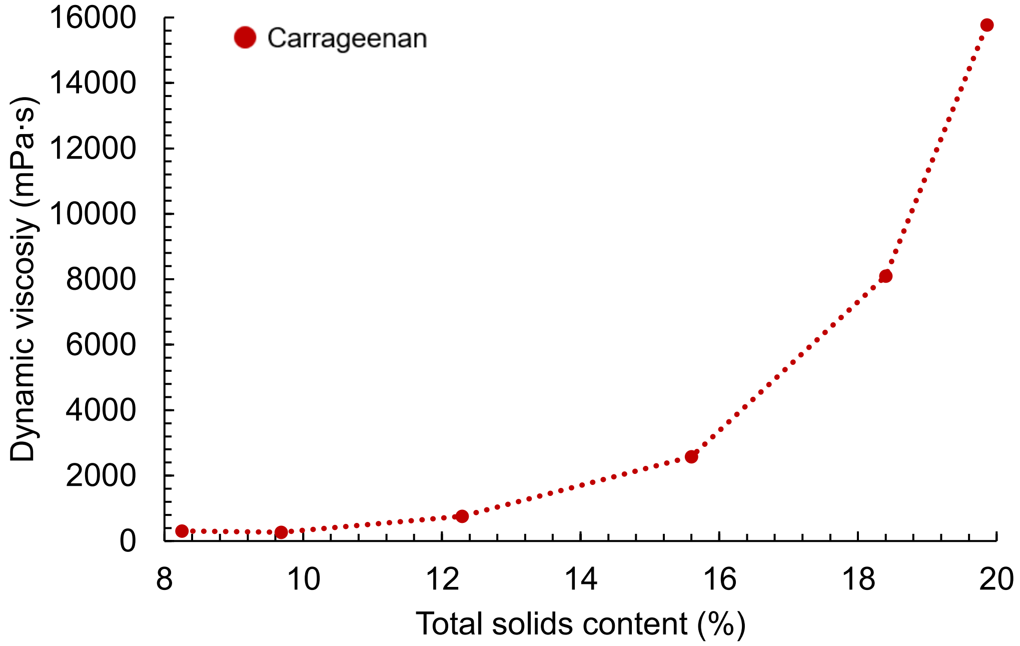

Figure 11. Dynamic viscosity as a function of TSC, Brookfield rpm 100. 8–10% spindle RV-2, 12,5% spindle RV-3, 15% spindle RV-5, 17,5% spindle RV-6, 20% spindle RV-7.

Figure 12 presents the ability of carrageenan to develop viscosity over a period of seven days. As shown in figure, viscosity increases most rapidly during the first 24 hours, nearly doubling within that time. Due to this significant change, the dispersion was needed to be used for coating applications on the same day it was prepared.

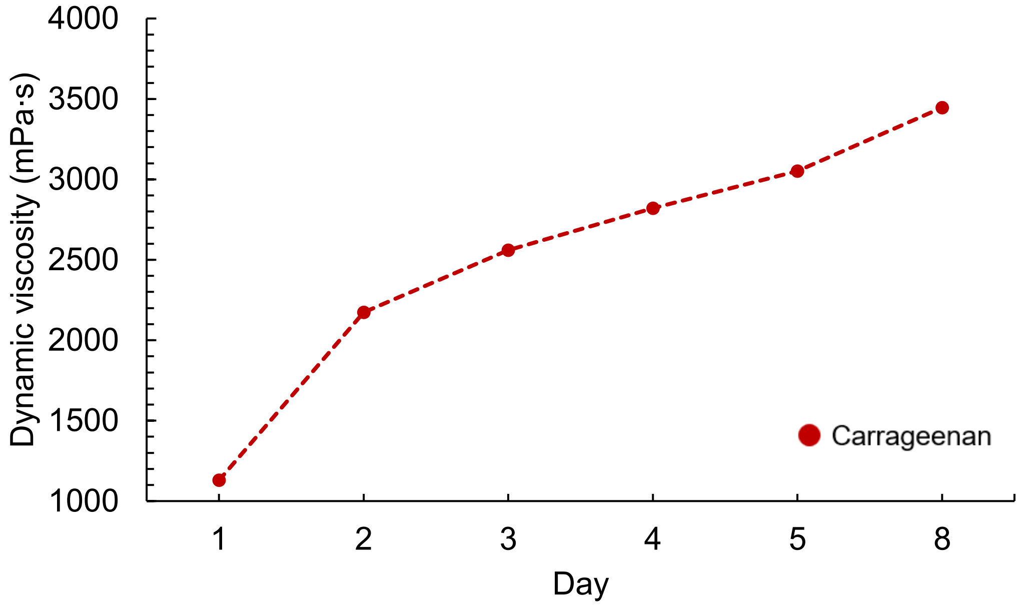

Figure 12. Dynamic viscosity development as a function of days, Brookfield rpm 100. Day 1 spindle RV-4, days 2–8 spindle RV-5.

Figure 13 illustrates the behaviour of carrageenan as a function of temperature. The targeted TSC in mill-scale applications is a significantly higher (50% TSC) than what this type of material can typically achieve. Therefore, understanding the temperature-dependent behaviour of carrageenan is of interest to determine whether increasing the TSC is feasible while maintaining viscosity manageable. As shown in Figure 13, the viscosity of 15% TSC dispersion decreases between 23–33 °C, after which the rate of decrease slows. The viscosity drops from approximately 2500 mPas to around 1750 mPas. This behaviour could offer more flexibility to the viscosity range for processing.

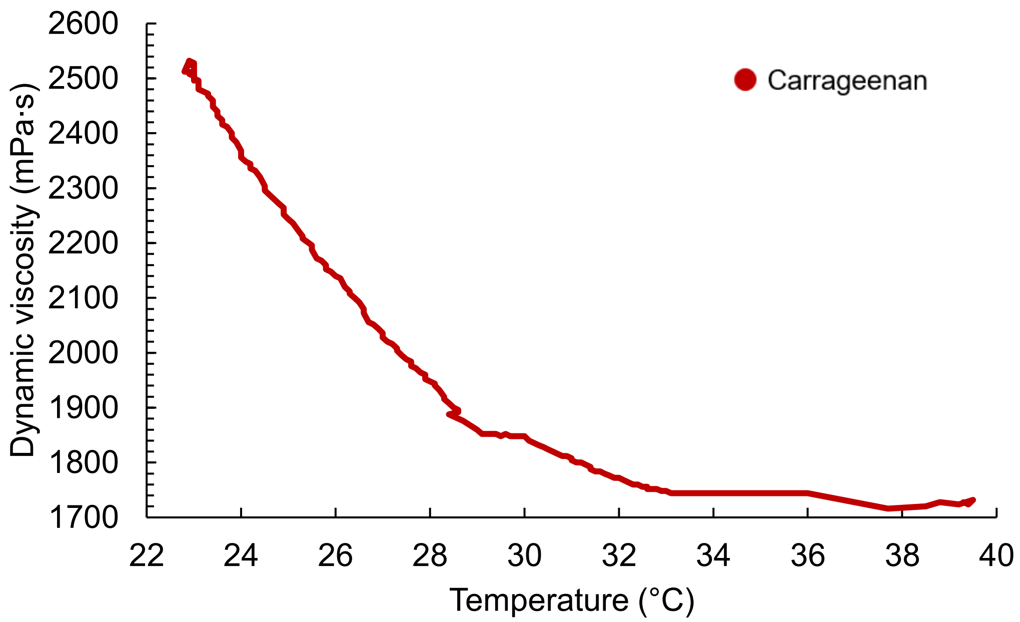

Figure 13. Dynamic viscosity as a function of temperature, Brookfield 100 rpm, Spindle RV-5.

Although the carrageenan dispersion was cooled down to room temperature (23 °C), it became significantly more viscous than at the beginning of the measurement. Therefore, it could no longer be used for barrier coatings. This could be a challenging property to manage at mill scale. The developing viscosity posed difficulties for the coating process, as it was an unpredictable variable.

Viscosities varied between different dispersion from 600–2500 mPas. Viscosity is an important process variable and must be considered, especially if the tests are further scaled up for production.

10.4 Coating amount

All barrier coating weights are presented in Figure 14, with their standard deviations. Barrier coating applications were conducted in a manner that the coating weight remained consistent, ranging between 8–10 g/m² across the samples. Excluding pure wax sample, which had a coating amount of only 4 g/m². This should be taken into account when evaluating the barrier results.

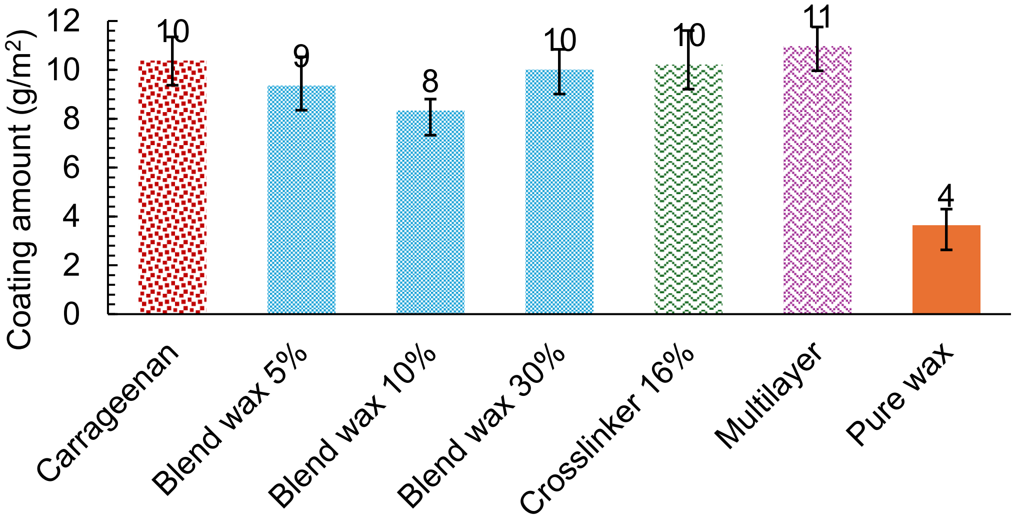

Figure 14. Coating weights of samples. Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax.

However, hot melt coating of wax was studied by Singh et al. (2023). It was observed that controlling the coat weight was challenging, and higher coating thickness often led to brittleness. Better WVTR results were achieved at lower coating weights, while increasing the amount of coating did not improve barrier performance. So, it is not straightforward to determine how increase of coat weight would affect to pure wax sample results.

10.5 Surface characteristics

In this chapter, the surface characteristics of the coatings are presented and discussed .

10.5.1 SEM images

Figure 15 presents SEM images of all the barrier coated samples and the reference. Reference (a) paperboard has a relatively smooth and uniform surface due to pigment coating, although small holes, which are most likely pinholes, can be observed. The carrageenan-coated surface (b) shows some irregularities, while the crosslinker-coated surface (c) shows even more irregularities — almost fibre like structures. Wax blends (e, d, f) exhibit rougher surfaces, with the 30% wax blend appearing the roughest. This may be due to drying process or compatibility between carrageenan and wax. Despite these, all barrier coatings formed continuous layer, but the surfaces are not smooth. However, no cracks or holes were observed in the barrier coating layers.

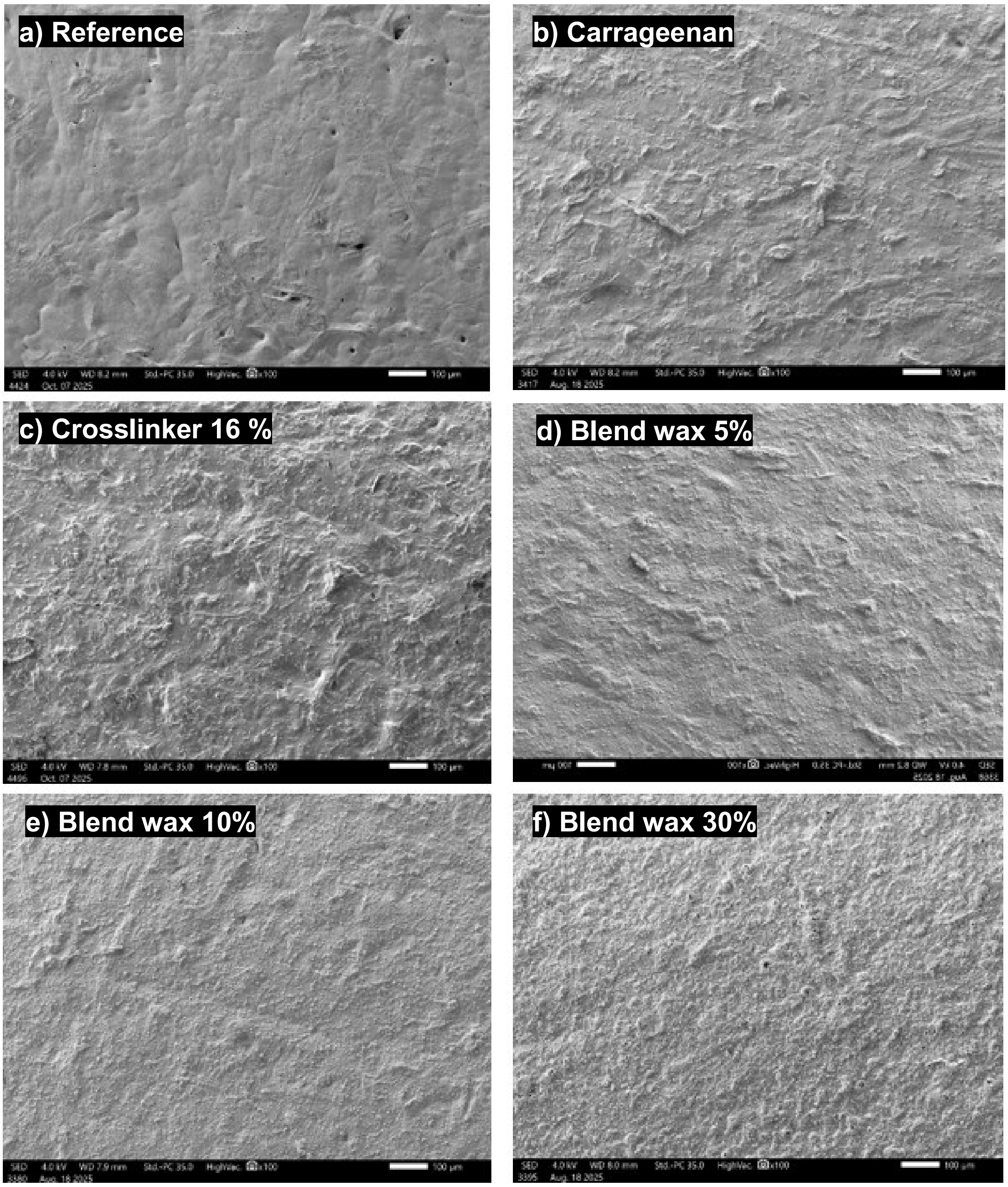

Figure 15. SEM images of sample surfaces x100. Additive content is expressed as a percentage of the total solids in the coating dispersion.

Cross-sections of the barrier coated samples are presented in Figure 16. In all images, a relatively wide pigment coating layer can be seen, and on top of that the barrier coated layer. Applying the barrier coating twice was successful for all samples, as no layering structure is visible within the barrier coating layer. The carrageenan coating layer (a) closely follows the surface and appears uniform. The crosslinker coating layer looks slightly rougher. Wax blend coatings (c, d, e) all show dark, circular spots on the barrier layer, which are most likely wax particles. The barrier coating layer also becomes rougher as more wax is added to the dispersion.

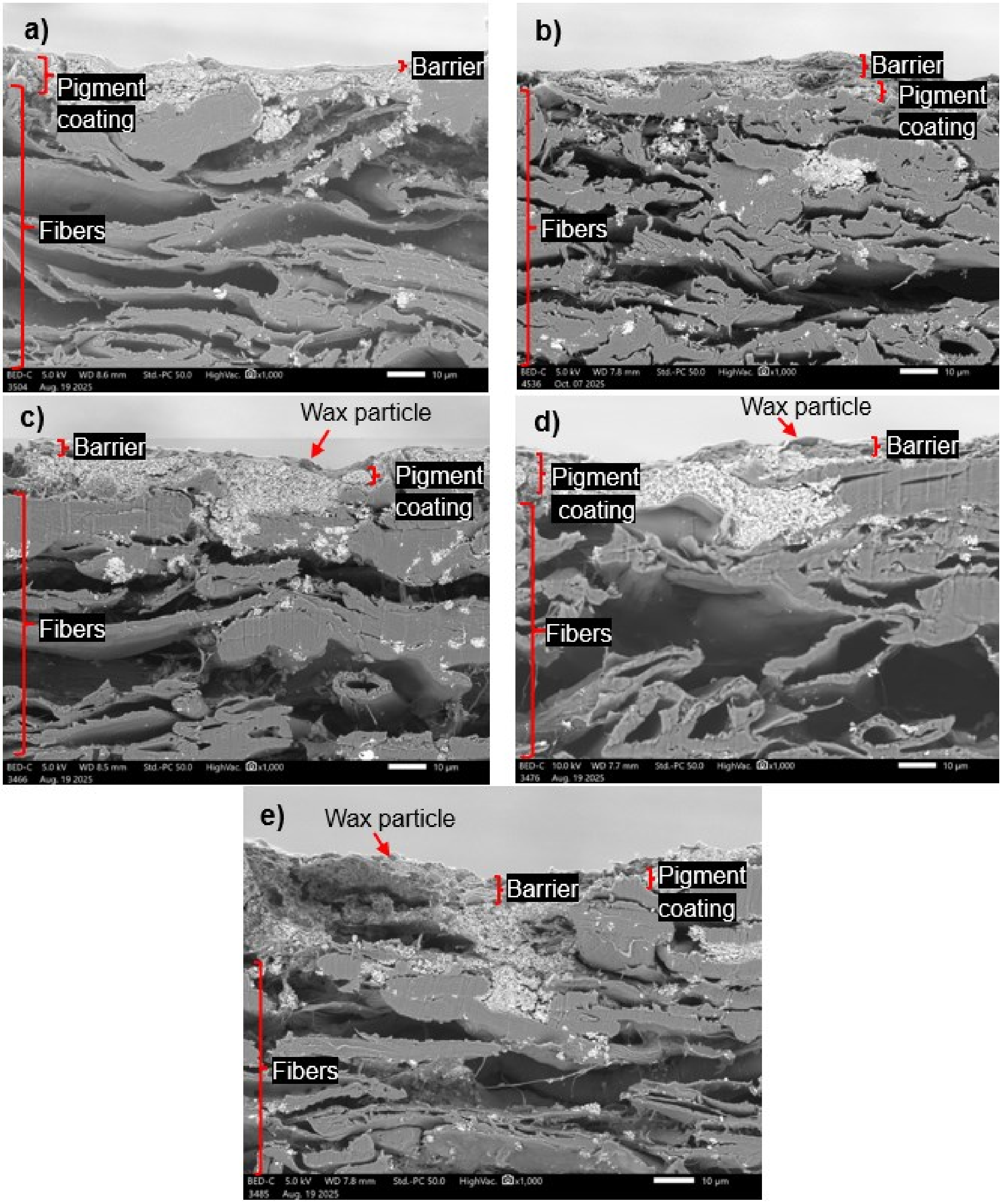

Figure 16. Cross-section SEM images of the barrier coated samples x1000. a) Carrageenan, **b)** Crosslinker 16%, **c)** Blend wax 5%, **d)** Blend wax 10%, **e)** Blend wax 30%. Additive content is expressed as a percentage of the total solids in the coating dispersion.

Figure 17 shows multilayer sample surface and cross-section SEM images from beginning and end of the barrier coated area of the paperboard. To assess consistency of the coating process, these two sections were analysed separately. This comparison helps to identify potential variations in coating quality across the surface and its further effect to barrier performance.

Surface images (Figure 17) taken from the beginning of the barrier coating layer (a) revealed irregularities and holes in the wax layer. In contrast, images from the end (b) of the barrier coating layer showed a smoother and more uniform surface. Holes in the barrier coating layer have a significant impact for example on grease resistance results, as they provide direct pathway for grease to penetrate deeper.

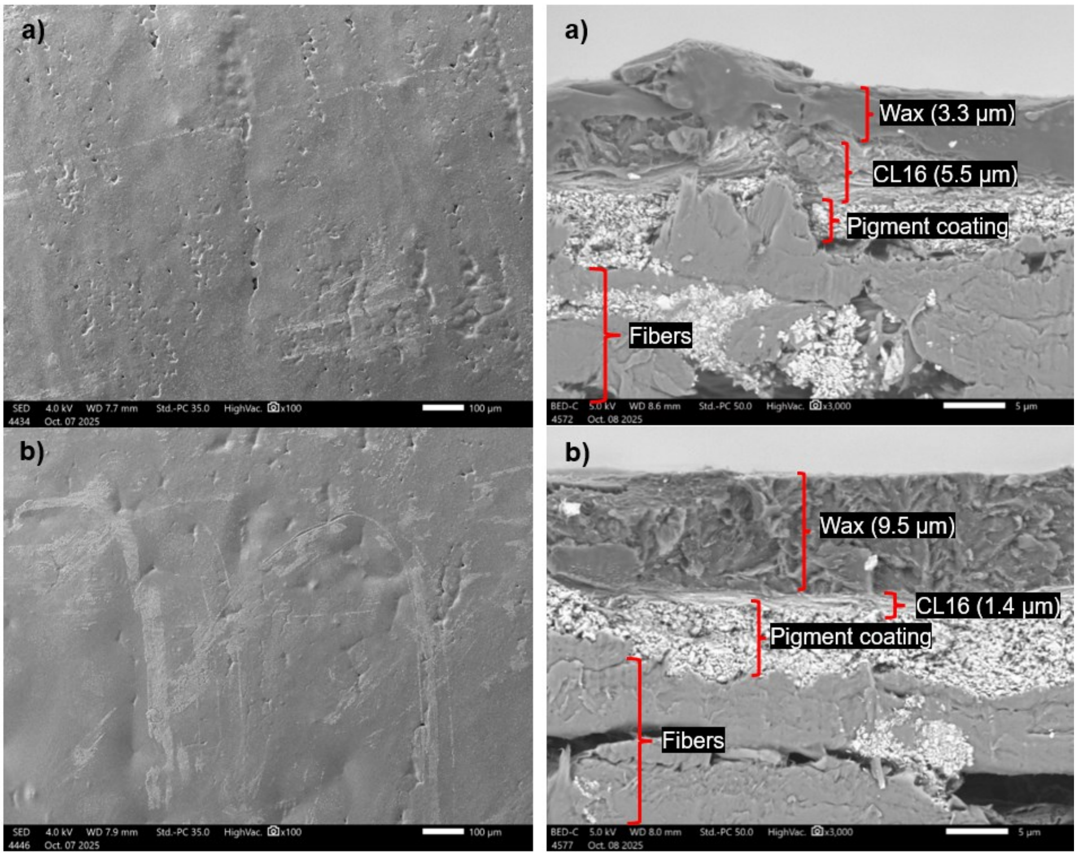

Figure 17. SEM images of the beginning and end of the multilayer coated paperboard surface (x100) and cross-section (x3000). a) beginning, **b)** end of the board. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax. Additive content is expressed as a percentage of the total solids in the coating dispersion.

Cross-section images (Figure 17) illustrate the thickness of barrier coating layers at both the beginning and end of the paperboard. At the beginning (a) the carrageenan and wax layers show good stability. Toward the end (b), the amount of carrageenan decreases while the wax layer becomes thicker. The paperboard surface is not even, which also would affect to the thickness of barrier coating layers

Although this represents only a small section of the barrier coated paperboard, it indicates that the coating amount may vary, which could affect barrier performance. Further investigation is needed to fully address this issue. Additionally, wax appears more melted at the beginning of the barrier coating layer but in the end, the structure looks rougher. This would be due to the wax starting to solidify too quickly before reaching the end of the paperboard, which may also be possible reason for the thickness variation of wax layer.

10.5.2 Pinholes

Figure 18 presents the pinholes observed in the barrier coatings. Visual evaluation revealed that pure carrageenan coatings had the highest number of pinholes, suggesting poor film formation and reduced uniformity. This indicates that carrageenan alone may lack sufficient film-forming capability under the applied conditions, which could lead to compromised barrier performance. Barrier coatings with wax blends and crosslinkers showed fewer or no pinholes, which suggests better film formation.

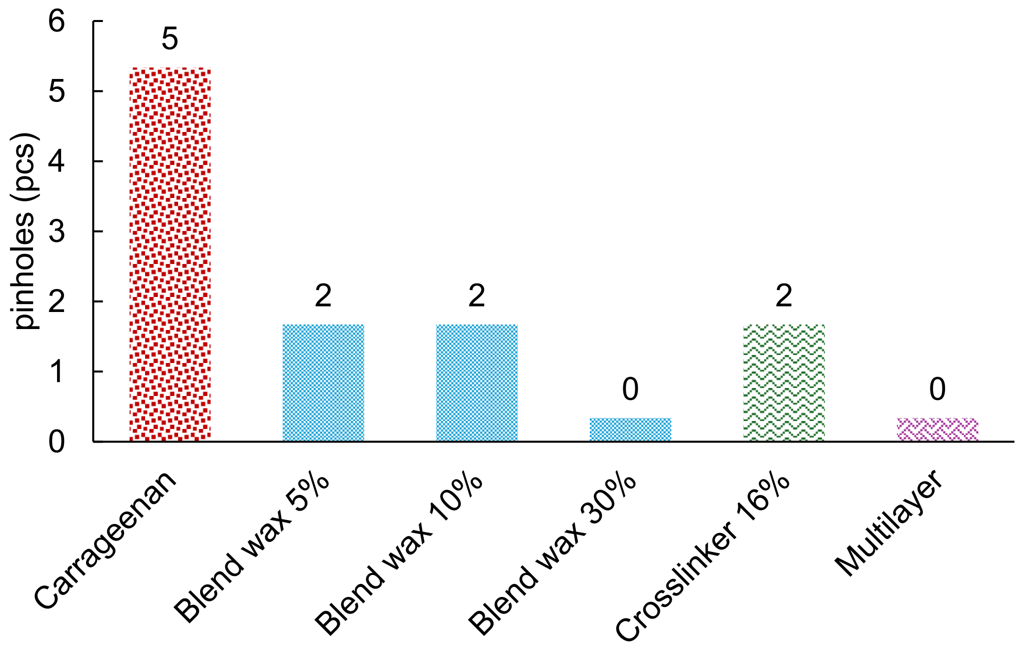

Figure 18. Pinholes of barrier coated samples. Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax.

It should be noted that the pinholes were visually approximated, and not all are visible to the naked eye. Pinholes must be taken into account when evaluating barrier performance, since they can function as pathways for moisture, gas, or grease penetration.

10.6 Barrier measurements

In this chapter, results from barrier measurements are presented and discussed. Melt coated pure wax sample is evaluated for its barrier properties as a reference for multilayer sample.

10.6.1 Water absorption

$Cobb_{60}$ results for barrier coated samples and reference are presented in Figure 19. Barrier coating weight is included in the figure. From the results, it can be seen that $Cobb_{60}$ result improved with all barrier coatings compared to the reference. $Cobb_{60}$ tests showed that only the multilayer and pure wax samples remained undissolved during testing, indicating the best water resistance of the samples. All other samples dissolved, limiting the reliability of their Cobb results.

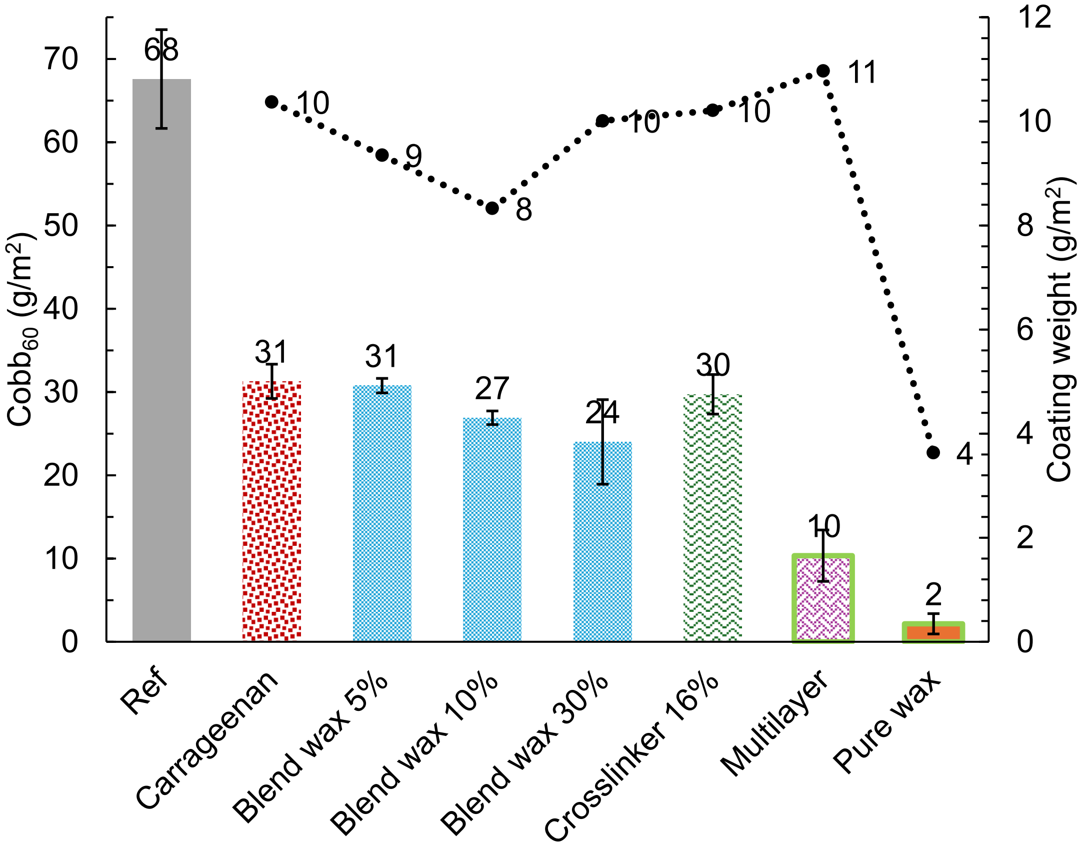

Figure 19. Water absorption test $Cobb_{60}$ on barrier coated samples. Multilayer and pure wax samples are highlighted with green for not dissolving in the test. Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax. Coating weight has been added to the figure to highlight its potential impact on the results.

Figure 20 is presented how clearly coating layers have been dissolved. In the figure, the brown area is the remaining barrier coating, and the white area is the pigment-coated surface of the reference paperboard.

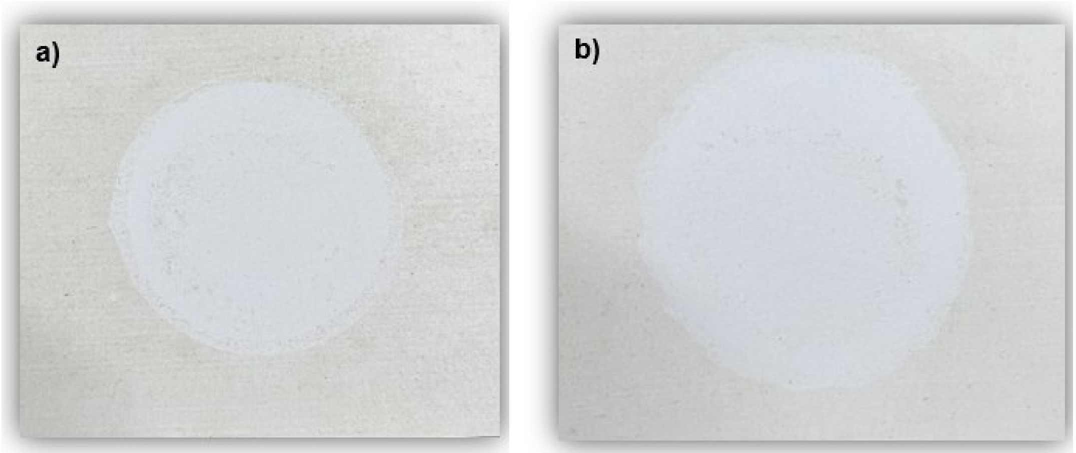

Figure 20. Images after $Cobb_{60}$ test for a) carrageenan and b) blend wax 30% samples. Additive content is expressed as a percentage of the total solids in the coating dispersion.

Figure 21 shows, the surface of multilayer structure after the $Cobb_{60}$ test. The barrier coating did not dissolve. When compared to Figure 22, which shows the result of the $Cobb_{300}$ test, a noticeable whiter area appears inside the ring where the Cobb cylinder was pressed. The multilayer sample evaluated with $Cobb_{300}$ resulted in a water absorption value 56 g/m^2. During the test, it was observed that the wax layer formed a bubble-like structure, suggesting that water may have penetrated beneath the wax. This could indicate that the hot melt coated wax layer may crack or deform when pressure is applied by the Cobb cylinder. Also, the holes observed in the SEM images could have an impact if they act as pathways for water under the wax layer.

Figure 21. Multilayer samples after $Cobb_{60}$ test. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax. Additive content is expressed as a percentage of the total solids in the coating dispersion.

Figure 22. Multilayer sample after $Cobb_{300}$ test. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax. Additive content is expressed as a percentage of the total solids in the coating dispersion.

As a summary, the pure wax sample showed the best results in $Cobb_{60}$ test, and the multilayer a slightly higher, but still fair value. This may be due to the pure wax been coated directly onto the paperboard, potentially forming a more uniform and durable layer.

10.6.2 Water vapour transmission rate

The results of WVTR are presented in Figure 23. The reference exhibited the highest WVTR value, and all the barrier coatings improved the WVTR compared to it. The carrageenan coating reduced the WVTR, while addition of a crosslinker further improved it. Wax blend samples showed similar WVTR values around 180 $g/m^2/24h$, suggesting that small wax additions did not significantly improved moisture barrier properties. However, increasing the wax content to 30% reduced WVTR to 93 $g/m^2/24h$, indicating a positive correlation between wax concentration and moisture resistance.The most significant reduction was with the multilayer structure, which achieved WVTR value 11 $g/m^2/24h$. The pure wax sample showed almost the same WVTR results as the multilayer sample. However, based on findings of Singh et al. (2023), increasing the coating weight does not necessarily improve moisture resistance, and may even lead to brittleness in the coating layer. So, could be assumed that the increase in coating weight of the pure wax sample would not improve its WVTR results.

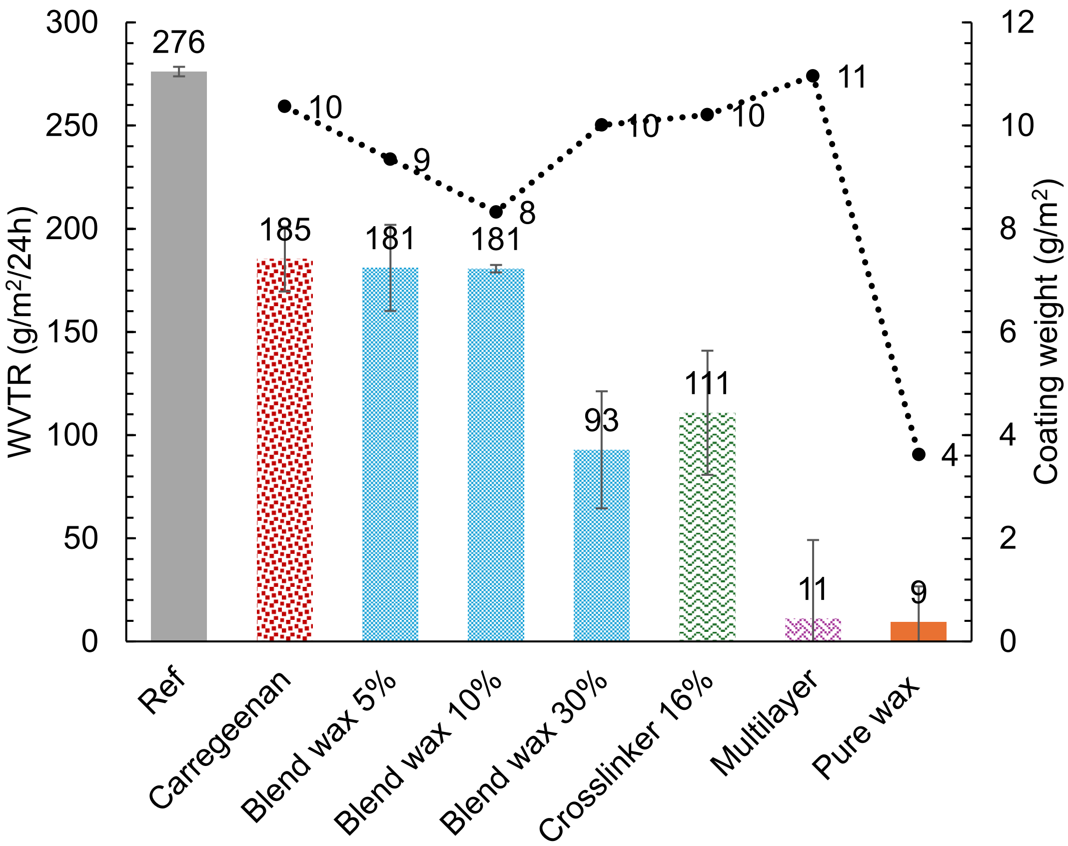

Figure 23. WVTR results of the barrier coated samples. Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax. Coating weight has been added to the figure to highlight its potential impact on the results.

Water vapor permeability (WVP) was calculated, and the results can be seen in Appendix A.

10.6.3 Grease penetration rate (ASTM F119-82)

Table 4 presents the best grease penetration rates of the barrier coatings. Deviation between parallel points was high. This is most likely due to several factors, such as the pinholes or surface defects in the barrier coating layer. Grease penetration is extremely sensitive to localized weaknesses in the coating, even small variations in barrier coating thickness or integrity can lead to noticeable differences in test results. For example, in the multilayer sample if the thickness of the barrier coated layers varies across the paperboard it would have influence on grease resistance results.

The highest grease resistance was observed with the carrageenan-crosslinker sample, which doubled the resistance time compared to the carrageenan coated. Blended wax samples showed reduced grease resistance, likely due to wax's limited grease resistance. The multilayer sample had lower grease resistance than the crosslinker sample, suggesting that the wax top layer may compromise grease barrier performance. The pure wax sample had the lowest resistance, but it must be considered that it also has lowest coating amount 4 g/m², which might affect the result.

Table 4. Grease penetration rate results on flat surface of barrier coated samples.

Sample code	Grease penetration rate (h, flat surface)	Coating weight (g/m²)
Carrageenan	8.4	10
Blend wax 5%	7.3	9
Blend wax 10%	6.8	8
Blend wax 30%	4.0	10
Crosslinker 16%	16.6	10
Multilayer	6.3	11
Pure wax	1	4

Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax. Highlighted the best achieved result. Coating weights of all samples are listed and highlighted the small coating weight of pure wax sample.

It is possible that pinholes in the barrier coating layer affect the grease penetration results. For example, the carrageenan-crosslinker sample might have performed better, but oil likely penetrated through pinhole, as only a tiny dot was visible in the camera image. This suggest that the sample could have achieved better results if the coating layer had been more uniform.

All grease penetration results can be seen in Appendix B.

10.6.4 Summary of barrier results

Summarized barrier results of coated samples are presented in Figure 24. From the results it can be seen that the carrageenan coating exhibited moderate grease resistance but poor water resistance. In addition, its WVTR values were high, indicating limited moisture barrier properties. The addition of crosslinker improved grease resistance and enhanced the WVTR, while water resistance remained poor. 30% wax blend improved water resistance and reduced WVTR values compared to 5% and 10% wax blends. However, it should be noted that it still dissolved in the $Cobb_{60}$ test. The best overall barrier properties were achieved with multilayer structure. This provided grease resistance and water resistance, and the second lowest WVTR values at 11 $g/m^2/24h$.

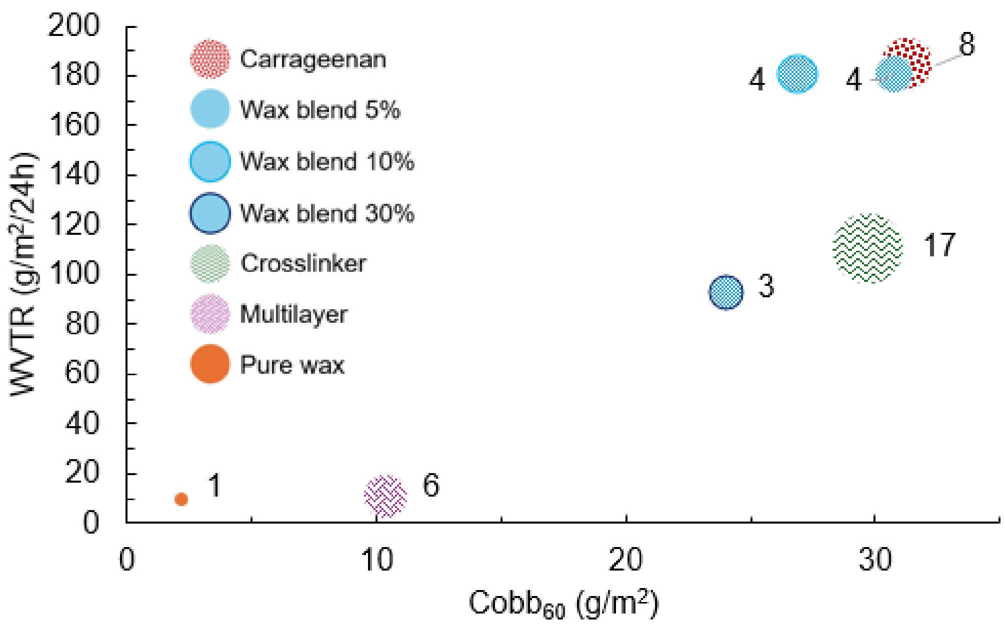

Figure 24. Summary of barrier results of coated samples. The bubble size and number indicate grease penetration (h): higher the value, the better the grease resistance. Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax.

The balanced barrier properties were achieved on multilayer sample. The first layer composed of crosslinked carrageenan, which itself had the best grease resistance results. The second layer composed of pure wax, which in other hand had the best moisture resistance values. Combined, these layers provided a balance between grease and moisture resistance. Although the grease resistance decreased but the moisture resistance improved significantly compared to other samples.

10.7 Surface free energy and gluability test

Surface free energy and gluability results are presented and discussed in this chapter.

10.7.1 Surface free energy (SFE)

Contact angles of the samples with deionised water are presented in Figure 25. The results show that the presence of wax increased the contact angle, especially with multilayer sample. It reached value above 100°, indicating a hydrophobic surface. This is due to the non-polar nature of wax, which repels water and reduces surface wettability. Crosslinker addition did not significantly affect water contact angles compared to carrageenan coated sample, suggesting that the surface polarity remained relatively unchanged.

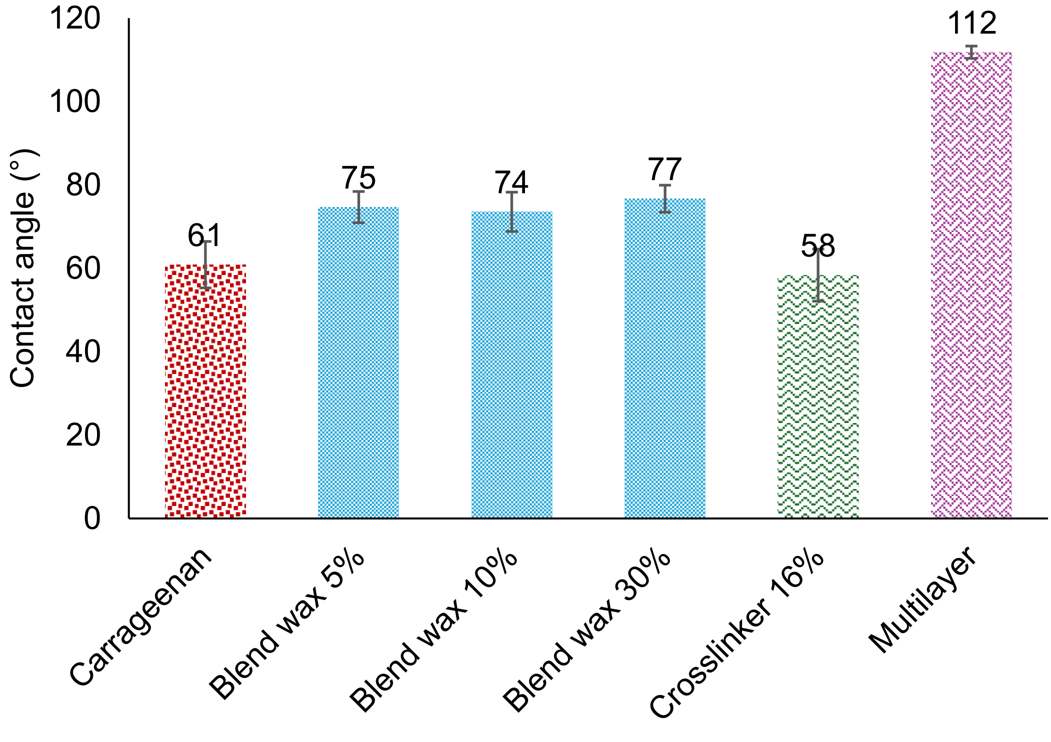

Figure 25. Contact angles of water. Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% crosslinker and a second layer of pure wax.

Figure 26 presents the SFE values of the samples. The blended wax samples show slightly lower polar components compared to those coated with carrageenan or carrageenan-crosslinker. This is likely due to the chemical nature of wax, which consists of long-chain hydrocarbons and is inherently non-polar. As a result, wax reduces the overall surface polarity. In the multilayer structure wax layer covers the entire surface, leading to an almost negligible polar component.

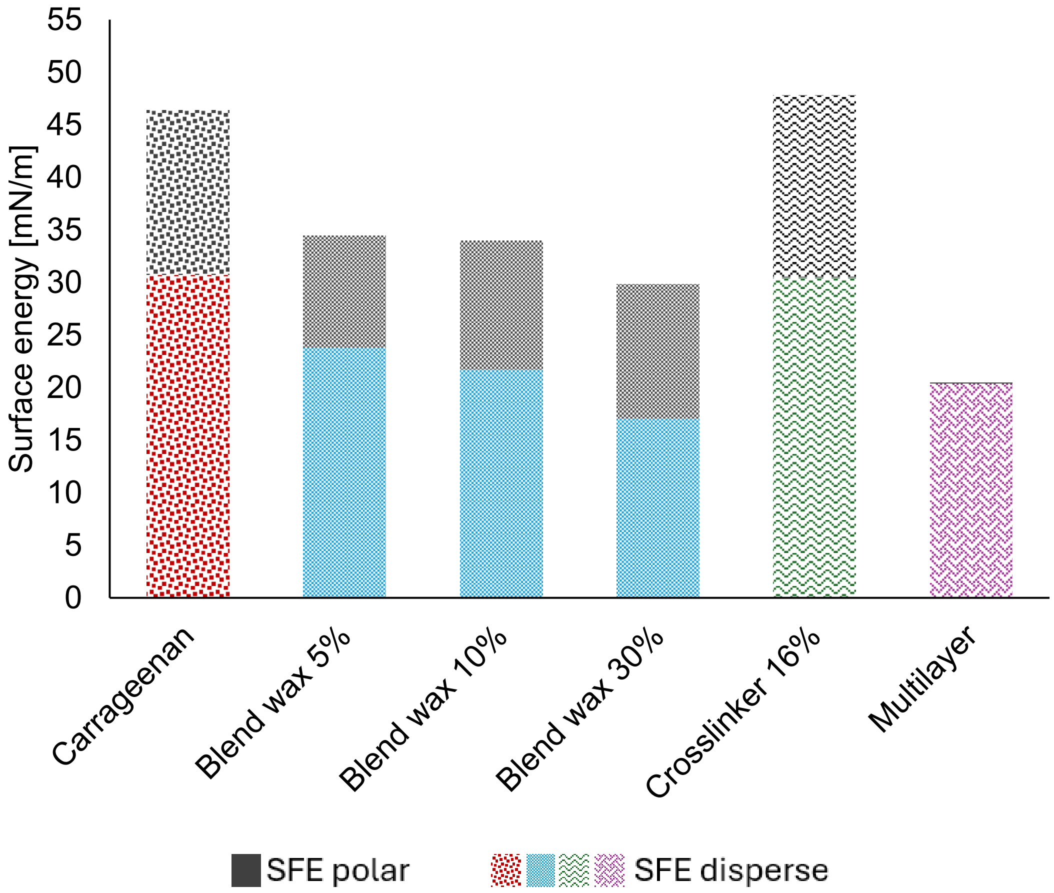

Figure 26. SFE of the coated samples. Percentage indicates the ratio of total solids content of additive in carrageenan dispersion. Multilayer has crosslinker 16% as a first layer and pure wax as a second layer.

Contact angles and SFE gives information about the coating surface and how it would work when it is further converted. Printability of the surface, the adhesion between multiple layers and gluability are affected by SFE.

SFE at least 36 dyn/cm (mN/m) is generally required to ensure sufficient wetting and strong adhesive bonds, indicating good gluability. Materials with high surface energy allow glues to spread evenly, forming strong bonds, while low energy surfaces may resist wetting and result poor gluability. (3M, n.d.)

10.7.2 Gluability test with hot melt and dispersion glue

Gluability was evaluated on multilayer sample. The purpose of the test was to evaluate influence of wax on gluability if it would be further converted into packaging. Hypothesis was that it will not have a good adhesion, since its SFE were low. In addition, it was assumed that dispersion glue might not stick since surface is hydrophobic and used dispersion glue is water based.

From results in Table 5 it can be seen that both hot melt and dispersion glue had weak adhesion, without fibre tear. All results despite the glue or curing time where the same.

Table 5. Gluability test results according to evaluation in Table 3.

Glue	Curing time	Average result
Hot melt	5 min	1.5
Hot melt	10 min	1.5
Hot melt	24 h	1.5
Hot melt	48 h	1.5
Hot melt	72 h	1.5
Dispersion	48 h	1.5

In Figure 27, it is shown that the hot melt glue (a) left a clear mark on the wax layer, whereas the dispersion glue (b) left only a slight mark on the wax surface.

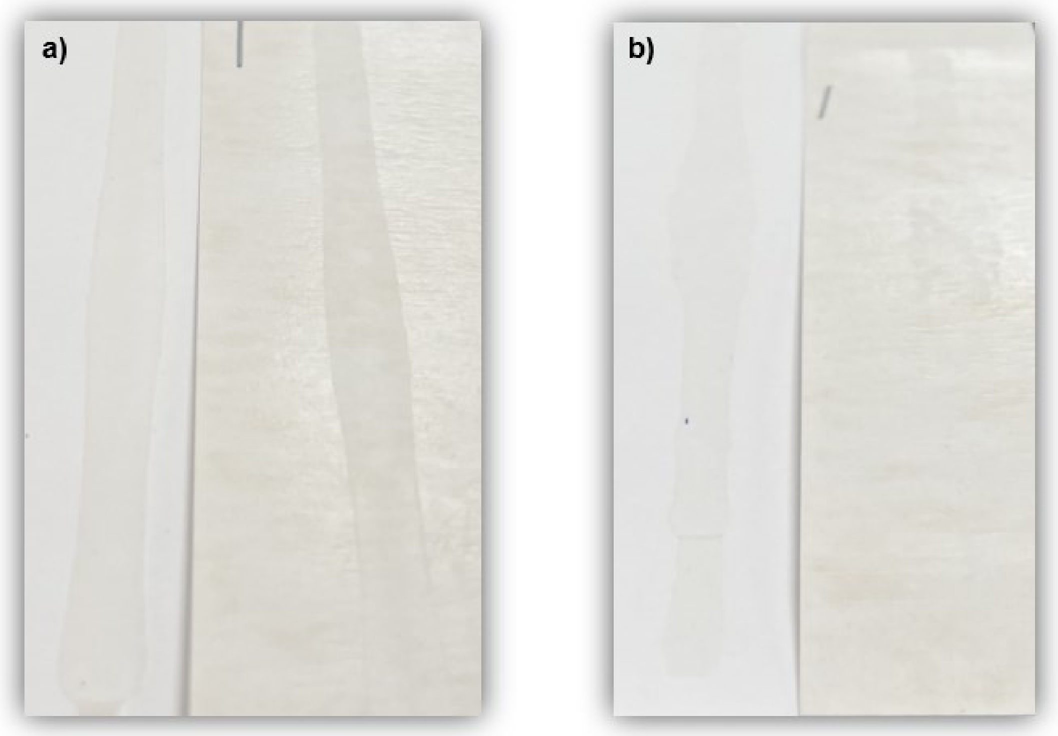

Figure 27. a) Hot melt, b) dispersion glue after 48 h condition time.

In addition to the SFE results, gluability of the multilayer sample was also tested. The idea behind the hot melt adhesive test was that if the wax layer melted under the influence of the heat of hot glue, the glue would be able to penetrate to the paperboard and form an adhesive bond. The dispersion glue was also evaluated for how it acts on this kind of surface, despite the unideal properties for gluing. Although, the results where poor in this case it should be noted that only one glue was evaluated on both tests.

11 Conclusions

This thesis investigated the barrier properties of carrageenan-based barrier coatings as a sustainable solution for paperboard packaging. The study focused on evaluating surface characteristics of different carrageenan barrier coatings including additives and multilayer structure and barrier performance through water absorption, water vapor transmission rate (WVTR), and grease resistance.

Carrageenan demonstrated promising grease barrier properties, especially when combined with a crosslinker. Adding a pure wax layer improved water vapor resistance but slightly decreased the grease resistance. Among the tested samples, the carrageenan-crosslinker coating provided the best grease resistance, while wax additive improved water resistance, especially in the multilayer sample.

However, carrageenan's hydrophilic nature remains a challenge, as most barrier coatings dissolved during water absorption tests. Additionally, viscosity behaviour of this carrageenan grade was sensitive to time and temperature, complicating the coating process and would pose challenges for process scalability.

Wax additive improved water resistance and surface hydrophobicity. The pure wax sample performed the best in water absorption tests and WVTR, though its grease resistance was lower. The multilayer structure, combining crosslinked carrageenan as the first layer and pure wax as the second layer, demonstrated balanced barrier properties among these samples. It showed moderate performance in both water and grease resistance.

Multilayer sample should be further evaluated under tropical conditions to evaluate WVTR performance in high humidity environments. Poor gluability of multilayer sample due to a wax topcoat indicate the need to assess other glue options or other ways to improve gluability.

Hot melt wax coating is old method so different possibilities for applying wax at mill-scale should be further explored. One possible approach would be to use curtain coating, which could provide uniform layering and consistent coat weight for molten wax. Uniform layering and consistent coating weight across layers would help to improve barrier performance. Additionally, optimal coating weight and thickness of wax layer should be further investigated to determine the level at which the best barrier performance is achieved.

Although multilayer structures with carrageenan appears promising, its hydrophilic nature limits compatibility with water-based dispersions. On potential solution for future investigations could be the use of solvent-based dispersion for multilayer formation.

Optimizing viscosity is critical for mill scalability. Exploring different carrageenan grades or blends that allow higher TSC with manageable viscosity would enable more efficient coating process and reduce water usage in dispersion and make the process more energy efficient.

Oxygen transmission rate was not measured in this thesis, but carrageenan is known to exhibit good oxygen barrier properties. Additionally, sensory analysis for odour and off-flavour testing should be conducted. These measurements could give valuable information about carrageenan compatibility for food packaging.

Overall, the results show that the carrageenan-based barrier coatings are a promising bio-based alternative to fossil-based barrier materials for paperboard food packaging. While carrageenan alone may not meet all the functional requirements, its performance can be improved with additives, for example with wax and crosslinkers. The multilayer structure demonstrated the most balanced results of the samples. However, further research is still needed on the multilayer structure to optimize coating uniformity, improve gluability, especially if wax is included, and long-term performance under varying environmental conditions.

Carrageenan has not been extensively studied for paperboard barrier coating applications, and this thesis highlights many areas where further research is needed. A key challenge is the carrageenan’s poor water resistance, which comes from its hydrophilic nature. Future studies could explore alternative crosslinkers or other additives, which could enhance carrageenan moisture barrier properties.

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Appendix A. Thickness and WVP values

Table 6. Thickness of barrier-coated and reference paperboard samples.

Sample code	Thickness (µm)
Ref	346
Carrageenan	372
Crosslinker 16%	365
Multilayer	360
Blend wax 5%	369
Blend wax 10%	367
Blend wax 30%	366
Pure wax	356

Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% cross-linker and a second layer of pure wax.

Water vapor permeability (WVP) values are presented in Figure 28.

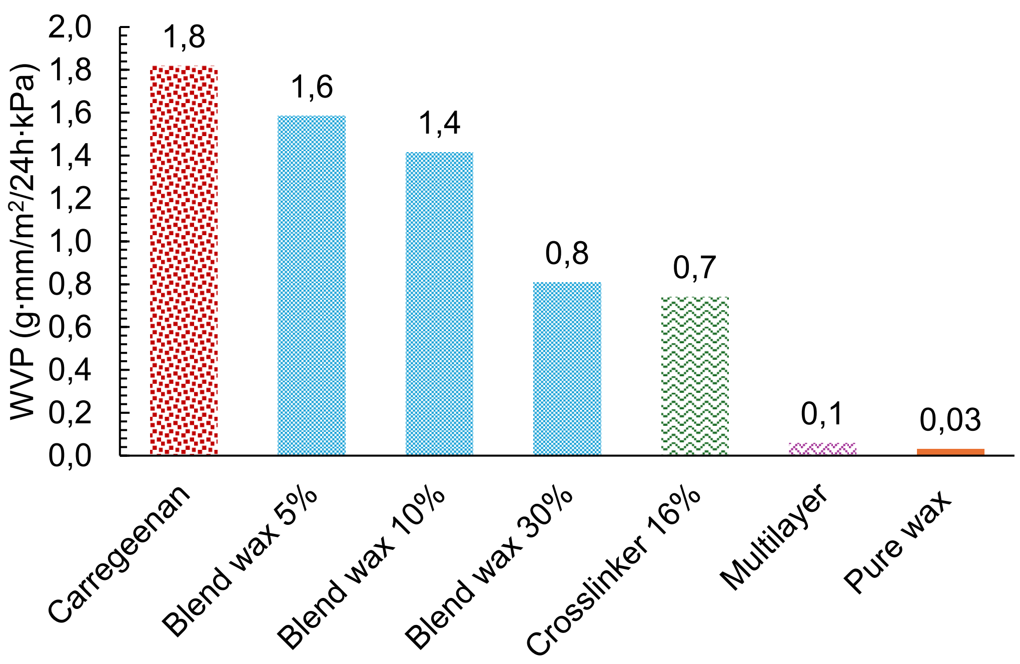

Figure 28. Water vapor permission. Percentage indicates the ratio of total solids content of additive in carrageenan dispersion. Multilayer has cross-linker 16% as first layer and pure wax as second layer.

Appendix B. Grease penetration results

Table 7. All results of grease penetration (ASTM F119) tests.

Sample	Flat (h)			
Carrageenan	8.4	6.9	5.84	4.34
Blend wax 5%	4.4	7.3	1.84	4.29
Blend wax 10%	3.8	1.0	5.8	6.8
Blend wax 30%	3.0	4.0	2.8	3.3
Crosslinker 16%	7.14	7.34	16.63	3.84
Multilayer	6.34	5.84	4.34	4.34
Pure wax	0.5	0.5	0.67	1

Additive content is expressed as a percentage of the total solids in the coating dispersion. The multilayer consists of a first layer with 16% cross-linker and a second layer of pure wax.

All creased samples failed under 0.5 h.