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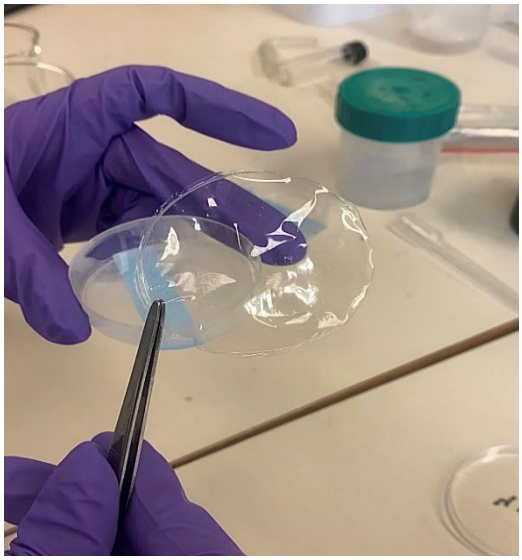

Creating a Hydrophobic Barrier Film by Modifying Carrageenan with a hydrophobic compound

An approach to generate a fit-for-purpose barrier in a medical device packaging

Bachelor's thesis in Chemical engineering

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Abstract

The Lofric Sense™ is an intermittent urinary catheter that is used by female users with bladder dysfunction. The catheter has a hydrophilic coating which is dry before use and therefore needs to be activated with water. The activation serves to activate the hydrophilic coating on the catheter which will facilitate the catheterization and prevent trauma on the urethra. Currently, the catheter is surrounded by a plastic packaging, which is considered to be a part of the medical device since it serves to encapsulates the water during activation of the hydrophilic coating and thereby aid the catheterisation. From an environmental point of view, it would however be more desirable to find a more sustainable packaging material for an intermittent catheter while being able to preserve its full function.

Bio-based materials such as paper and seaweeds are both promising and potential candidates as more sustainable packaging materials. Both paper and seaweeds materials are built up by polysaccharides which makes them compatible with each other as packaging material. One of the more interesting polysaccharides derived from seaweed is carrageenan. This study aims to use carrageenan to create a hydrophobic film for the potential use on the inside of a paper packaging that will substitute the plastic packaging in the Lofric Sense™. Two types of carrageenan, kappa- and iota- carrageenan, were evaluated for this purpose. To investigate the possibility of increasing the hydrophobicity of the films, modification with hydrophobic compound was performed. Furthermore, to improve the films mechanical properties addition of plasticisers was made.

The results, measured by water contact angle measurements and FTIR spectroscopy, showed that modification with a hydrophobic compound improved the hydrophobicity of iota-carrageenan films, which indicates that an interaction has occurred. There was no indication of interaction between kappa-carrageenan and the hydrophobic compound as no increase in hydrophobicity could be observed. The addition of plasticisers fulfilled its intended purpose on the pure kappa- and iota-carrageenan films and at the same time increased the hydrophobicity of the films. However, the addition of plasticisers to the iota-carrageenan films modified with a hydrophobic compound was shown to infer with the hydrophobic effect observed for the modified film without plasticiser. Moreover, only a slight improvement of the mechanical

properties was observed for the modified film with added plasticiser, which needs to be further investigated.
Keywords: Carrageenan, hydrophobic film, plasticiser, bioplastic packaging, FTIR, packaging barrier

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1. Introduction

Wellspect is a global company operating in the medical device field. The company works closely with their users and healthcare professionals to gain feedback and improve their products. The researched areas are bladder and bowel dysfunction, and the company focuses on providing better and sustainable continence care for their users. The development of Wellspect's products is focusing on the simplicity and the design as well as the environmental footprint (1). Wellspect is continuously looking to improve their current products regarding reducing their environmental footprint.

The Lofric Sense™ catheter is one of the products manufactured by Wellspect for the treatment of female bladder dysfunction and is designed to be discrete and carriable, see Figure 1. The Lofric Sense™ is intended for intermittent use with instant activation by pressing at the bottom of the catheter packaging. The activation aims to wet the catheter with sterile water on the inside of the packaging to swell the hydrophilic coating on the catheter to make it slippery and by that simplify the insertion of the catheter and minimise trauma on the urethra. The plastic packaging that encloses the catheter is also a part of the medical device as it encapsulates the liquid during activation. Another way to release the sterile water and activate the catheter coating is to fold the packaging, thus the packaging also needs to have sufficient mechanical durability (2). The catheter is used within six minutes and is then disposed with its packaging after single use, which is why a more sustainable alternative to the plastic packaging is of interest.

Figure 1 Image by Wellspect of the Lofric Sense Catheter

Today a lot of single use packaging is made in plastic materials from non-renewable resources and are a big contributor to climate change (3). Since plastic is made from oil, it cannot decompose in nature. In Sweden a big part of the plastic used is collected and at the end of its

cycle it is incinerated to extract the energy. Recycling of plastic is preferred to increase the amount of loops the raw material can be part of before going to incineration. However, recycling of plastic is not performed to any large extent yet and in the end the incineration results in emissions of CO_2 (4). Moreover, not all plastic waste is collected and recycled or incinerated but instead ends up in nature which results in microplastics being released and harming the environment. Additionally, these microplastics have a potential toxic effect (5). Due to these disadvantages, a bio-based material such as paper is plausibly a better alternative than plastic due to its existing infrastructure for collection, recycling and reusing as well as its degradability in nature. Since plastic can be used in a wide variety of areas due to its properties, paper might need to be combined with bioplastics to obtain similar properties. The benefits of bioplastics are that they are non-toxic, have a shorter degradation time, reduce fossil fuel consumption, and reduce emission of greenhouse gases. Additionally, bioplastics are biodegradable thus when it is combined with paper it does not disrupt its recycling process. Due to this, bioplastics are a promising approach to substitute petroleum based plastic (3).

Biobased plastic can be made from various types of materials. Generally, proteins, polysaccharides and lipids are used to make bioplastic. Today many bioplastics are derived from biomaterials such as corn, food waste or cereal crops. A crucial aspect of bioplastics is that the material they are produced from is renewable. Advances in research have showed potential for the use of seaweeds as a biomaterial for bioplastic production as they have the ability to form films. There are many advantages of using seaweed as a feedstock due to its high availability and being planted in sea water instead of on land. Additionally, they reduce global warming and ocean acidity due to seaweeds ability to bind CO_2 during photosynthesis (3).

Seaweeds such as algae constitute of polysaccharides similar to wood and is therefore a potential source as a bio-based material. Carrageenan is a type of polysaccharide that is found in algae and can be used for bioplastics (3). Carrageenan is used in many applications for instance it is a common stabilizing agent in food and can used as a film for food packaging (3). However, pure carrageenan films are hydrophilic and can have weak mechanical properties (3),(6).

The aspiration of this thesis is to create a hydrophobic carrageenan barrier film on the inside of a paper packaging that will serve as a substitute for the current plastic packaging of the Lofric Sense™ catheter. To obtain a film with a more hydrophobic character and improved mechanical properties modification with hydrophobising agents and addition of plasticisers will be explored. These properties are important to retain the catheter functions. Considering that the Lofric Sense™ will be used within a short time span after activation, only a short-lived hydrophobic water barrier of six minutes is required (2).

1.2 Aim

The purpose of this thesis is to form a hydrophobic film by modifying carrageenan with a hydrophobic compound, which can be used as a barrier in the paper packaging for a female intermittent urinary catheter. To obtain the required mechanical properties needed for the film, addition of plasticiser will be studied.

1.3 Specification of question formulations

1. Is it possible to modify carrageenan with a hydrophobic compound?
2. If a film is formed, does it have hydrophobic properties?
3. What material properties of the film is obtained when modifying carrageenan with a hydrophobic compound?
4. What is the availability of raw materials? What are the current possibilities for upscaling?

1.4 Limitations

This project will investigate two types of carrageenan namely iota-, and kappa-carrageenan. Lambda-carrageenan is excluded since it does not form a film (6). Relevant issues such as biocompatibility and skin irritation will be considered in terms of previous use of carrageenan-based films, however, not be evaluated in this work. The shelf-life and mechanical properties will not be measured for the films obtained. Only one type of catheter packaging, Lofric Sense™, will be studied, which is the catheter type that remains dry in the packaging until activation. The film will therefore only be used on the inside of the catheter package, to hinder water to wet down the paper package. Regarding the experimental part of the study some

restrictions were made to have a realistic number of samples to evaluate under the limited time interval. Factors such as temperature, time for heating and concentration of carrageenan were not varied to minimize the number of samples. Different thickness of the films was not tested in this project. To improve the mechanical properties, plasticiser was added, namely glycerol and sorbitol. Due to time constraints, the investigation of the film and paper packaging combination was not evaluated in the scope of this study.

2. Theory

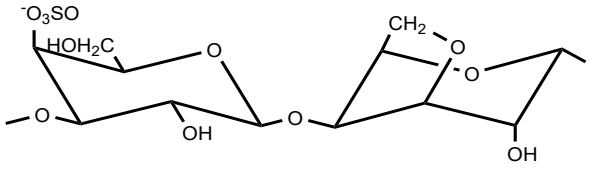
This section aims to provide a theoretical background for this thesis. Firstly, carrageenan's chemical structure and properties will be described to establish a foundation for the laboratory work. Moreover, the process of film formation of carrageenan will be explained, along with the function of plasticisers in this context.

2.1 Properties and Characteristics of Carrageenan Polysaccharide derived from seaweeds

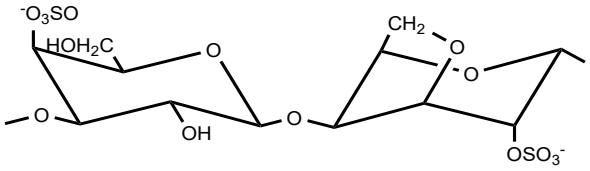
Seaweeds are a non-flowering organism called macroalgae and are found in both seas and oceans all over the globe occupying 71% of its total area. The availability of this feedstock is thus abundant (7). Seaweeds are known for their high content of minerals, vitamins, polysaccharides and bioactive substances like lipids and proteins. The large content of polysaccharides is produced in the growing process of the seaweed and can be extracted to form valuable products (6).

The structure of polysaccharides is defined by long chains with simple sugars called monomers, which are linked together with glycosidic bonds (8). Polysaccharides can vary in many ways in terms of altering monomers and chain length (8). The molecular structure of polysaccharides can be linear or highly branched. Additionally, polysaccharides can be composed of either heteropolysaccharides or homopolysaccharides, further adding to the diversity of their molecular composition (8). The use of polysaccharides has increased due to its eco-friendly nature and their versatility. However, this also makes it challenging to comprehend the general surface properties of polysaccharides (9).

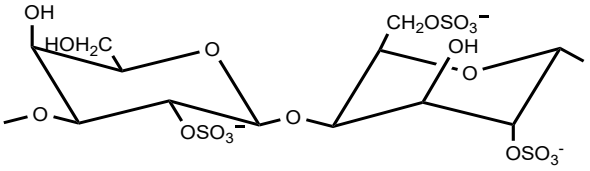
Carrageenan is a collective name for a polysaccharide which is extracted from various types of red algae. This polysaccharide is composed of linear chains, featuring alternating units of 3,6-anhydro-D-galactose and D-galactose, which are sulfonated, rendering it highly hydrophilic (10). The polysaccharides can consist of different monomer units with different sulphate content and positions. Carrageenan has therefore been classified into three different main groups: Kappa, iota and lambda (see Figure 2); The range from one to three sulphate ester units in the dimer of carrageenan provides different properties (6).



Kappa-carrageenan



Iota-carrageenan



Lambda-carrageenan

Figure 2 The chemical structures of the dimers for kappa-, iota-, and lambda-carrageenan.

The application of carrageenan's largely depends on their rheological properties such as their viscoelasticity and viscosity. Additionally, the reactivity of carrageenan is primarily determined by the sulphate groups of half-ester type present within its structure (6).

The chemical structure for all types of carrageenan provides properties such as water solubility, pH stability, and the ability of the polymer to form high-viscosity solutions. The viscosity increase can be caused by two mechanisms: 1) a decrease in free volume by interaction by linear chains or 2) crosslinking between chains resulting in the formation of a physical gel. Solutions of carrageenan can gelify, with apparent increase in viscosity (6). The viscosity of carrageenan depends on the temperature, concentration, and the solvent used. The viscosity increases almost

exponentially with increasing concentration, while it decreases with increasing temperature. Since, carrageenan is a polysaccharide, its viscosity will also depend on its molecular weight, as this can contribute to an increased entanglement of chains.

The gel formation of carrageenan is an important property since it can evaporate to a film and be used for different applications (11). A gel is defined as a crosslinked network structure with weak or strong bonds. The gel formation can be achieved through a heating cooling process that allows carrageenan to change structure. The solution forms gel due to a helix formation due to hydrogen bonds between the galactosyl units of the carrageenan structure, which further creates junction zones. The junction zones play a crucial role as crosslinkers within the network and significantly contribute to the overall structure of the gel (12). Hot carrageenan solution is in a conformation of random coils, and when the solution cools, it transforms to helical rods in a rigid structure. This process is illustrated in Figure 3 (12). However, it is only kappa- and iota-carrageenan that go through this process while lambda-carrageenan does not undergo gelation. This is because lambda-carrageenan do not have the 3,6-anhydrogalactose unit in the structure, contrary to kappa- and iota-carrageenan. The 3,6-anhydrogalactose unit allows the rotation in the structure while galactose unit form hydrogen bonds between the chains, resulting in the formation of helices which is crucial for the gel formation (6).

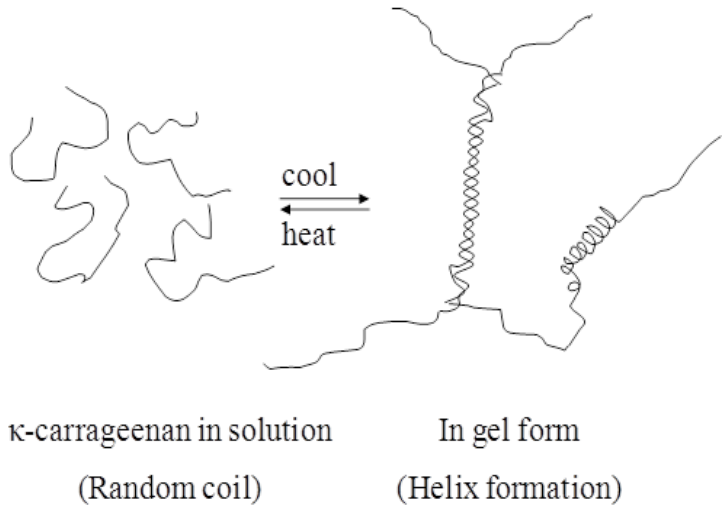


Figure 3 Helix formation of kappa-carrageenan forming a gel.

In the carrageenan structure, the strong anionic half-ester is primarily responsible for its reactivity. Since this free acid is present, carrageenan is often commercially sold with a positive

counterion such as sodium or potassium. The water solubility depends on the number of sulphate groups as well as the bound cations to these groups (6).

2.2 Carrageenan Extraction and availability

Carrageenan is extracted from the cell wall of red algae. The extraction can be made either by hot water to obtain a high yield or alkali treatment for a better gel-formation ability. The general extraction process of carrageenan is to treat a collection of dried red algae in powder-form by either of the two methods with the general purpose to let the cell walls of the algae swell and get raptured; and in this way the extract carrageenan. The advantage of the alkali compared to hot water extraction is that it increases the 3,6-anhydro-α-D-galactopyranose content and thereby gives a lower sulphate content since it modifies the carrageenan precursors into kappa- and iota-carrageenan. Thus, the gel formation is enhanced by the alkali treatment given that kappa- and iota-carrageenan is gel forming (10). Subsequently after the extraction process, the diluted carrageenan is filtered to concentrate and remove algal residues (10) .

Due to the increased use of carrageenan in various products the cultivation of carrageenan and the number of seaweed farms have risen. The demand for plastic remains high and despite algae's higher growth rates compared to land-based plants it may lead to challenges when it comes to scaling up algae production to meet this demand (3). Even if the carrageenan request is expected to increase in upcoming years the large-scale production of red algae has been hindered by a number of challenges, including environmental influences that affect carrageenan’s biochemical variability and hence its material properties (13). Abiotic factors such as salinity, light, temperature, and nutrients are factors that can affect the carrageenan’s biochemical content. Consequently, the quality of carrageenan can be adversely impacted due to these external factors (13).

2.3 Applications of Carrageenan in Food and Biomedical Applications

Seaweed polysaccharides, such as carrageenan, can be used as thickening, film forming and stabilizing agent in multiple areas including biochemical industries, food packaging and food additives. They are suitable as additives due to their biocompatibility, water retaining capacity, biodegradability as well as exceptional film forming characteristics (14).

Carrageenan has been utilized in food applications since 1970 due to its gelling and thickening properties, which provides structure to different food types such as jellies and processed meat. It can also be utilized in yoghurt production to prevent a phase separation during the processing or be implemented in meat production to increase the juicy texture that is a result of carrageenan's ability to retain moisture (13). Additionally, carrageenan is used to produce edible films for food packaging, since the films possesses protective properties which preserves fruits and vegetables. By incorporating oxygen and ethylene scavengers into the carrageenan films, it becomes possible to inhibit the growth of aerobic bacteria and effectively slow down the respiration rate of fruits (11).

Apart from the food industry, carrageenan is also commonly used in production of cosmetics such as shampoos, toothpastes, cleansing products and facial creams. In shampoos and facial creams, carrageenan interacts with carotene to smooths skin and hair (6). The use of carrageenan in pharmaceutical and medical industries has also been of great importance (13). In these areas the ability of carrageenan's antibacterial, antioxidant, antiviral and antitumour properties has been studied to be able to use is for treatment of diseases (13).

2.4 Film formation of Carrageenan

Carrageenan can form a film due to its gelling properties. The film is formed from the gel as the solution evaporates, thus the formation of the film is based on the same phenomena of physical entanglements (11). The film forming process involves different driving forces. One driving force is the electrostatic interaction. Carrageenan contains a negatively charged sulphate ion, and by introducing a positive ion the charge of sulphate is neutralized and the film formation is initiated. Another driving force are the hydrogen bonds present. Carrageenan contains several hydroxyl groups that can form intra- and intermolecular bonds with each other, which is critical for the film formation due to the double helices that are formed (11).

Carrageenan films can be shaped by several different methods. A common method is dip coating, which involves immersing a surface in a carrageenan coating solution, allowing it to air dry, and results in the formation of a film directly on the surface. This method is mainly used for improving the shelf-life of fruit and vegetables. Dip coating is rather simple to perform, however, it can be difficult to control the thickness of the film. Another commonly used coating method is solvent casting which involves spreading the carrageenan film solution on a mould

and letting it dry while the solvent evaporates. It is crucial to use a mould made of a material that interact as little as possible with the film forming chemicals and polymers. This method is also quite simple to perform and has a low cost, however since it requires a long drying time it might not be the best technique to use for large scale production (11).

2.5 Mechanical properties of carrageenan films and use of plasticisers

Film thickness can be affected by several different conditions. It has been noted that a higher carrageenan concentration will increase the thickness of the film (15) . A higher carrageenan concentration prevents mobility of the molecules in the film forming solution, resulting in the molecules being locked into these positions as the gel dries to form the film (15). The thickness is also affected by the drying environment. A higher temperature and a longer drying time will result in a thinner carrageenan film. This is because a higher temperature will create a more compact cross section in carrageenan as well as increasing the degree of crystallization (15).

The mechanical properties of the carrageenan film are usually determined by tensile strength and elongation at break. By using the tensile test, a stress-strain curve can be obtained and analysed to provide the average values of stress and strain. The tensile strength has been demonstrated to increase with thickness, while elongation at break and water vapour transport rate exhibit a decrease as the film thickness increases (16). Previous studies of kappa-carrageenan showed better mechanical properties in comparison to iota-carrageenan (11), (16). This is due to its low sulphate content and negative charge. However, the kappa-carrageenan film exhibited a more brittle behaviour (11). A higher concentration of carrageenan will result in a stronger intermolecular interaction which will lead to a loss of elasticity of the film (16).

To improve the mechanical properties of the carrageenan film, plasticisers can be added. A plasticiser is a low-volatile substance added to a material to improve the flexibility and elasticity. The addition of plasticisers has also been showed to increase film thickness**.** According to previous studies, addition of plasticisers in film formation results in fewer defects and thus improving the mechanical properties (15). Two common plasticisers for carrageenan are glycerol and sorbitol (11). The addition of glycerol and sorbitol to carrageenan speeds up the formation of double helices in the carrageenan structure due to carrageenan being less

soluble in glycerol and sorbitol. These helices are more randomly ordered compared to when carrageenan is dissolved in water (17).

Glycerol is commonly used as a plasticiser due to it being compatible and stable with biopolymers (18). Tarique and Sapuan showed that a higher concentration of glycerol increased the hydrophobicity in an arrowroot starch-based film due to glycerol's ability to form stronger hydrogen bonds with the arrowroot starch than water, which prevents the water molecules to combine with neither glycerol or arrowroot starch (19). As mentioned previously, a higher concentration of plasticiser has demonstrated an increase in film thickness. Despite glycerol having a low evaporation rate, it still evaporates at room temperature during film formation, resulting in a loss of glycerol as the film solidifies (15). Carrageenan does not evaporate at all, thus there is no loss of carrageenan as the films solidifies (17). In Figure 4, the structure of glycerol can be seen.

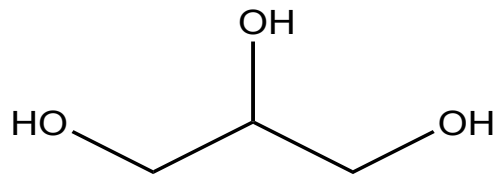


Figure 4 Chemical structure of glycerol

An alternative plasticiser is sorbitol, a polyol which is, a compound made up of many hydroxyl groups, see Figure 5. The addition of sorbitol as a plasticiser reduces internal hydrogen bonding in carrageenan, due to sorbitol being able to access between polymer chains, which results in an increased flexibility. The film thickness increases with an increasing sorbitol concentration because sorbitol can access in the carrageenan network which leads to pores in the matrix shrinking. This will in turn result in a difficulty for water to permeate the surface and therefore become more water resistant (20).

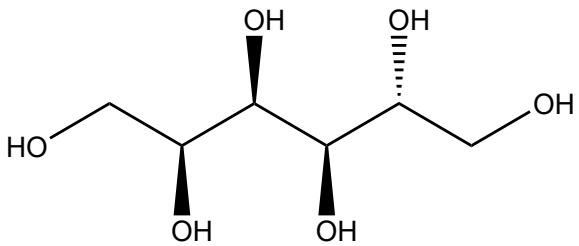


Figure 5 Chemical structure of sorbitol

It has been reported by several researchers over the years how plasticisers affect carrageenan based film (21). Previous studies have shown that a concentration of plasticiser with 20-45% (w/w) is efficient to form flexible and elastic films made out of bio-materials (19). As previous mentioned, the plasticiser can improve the film mechanical property, according to an article by Nouri and co-workers they saw that carrageenan films without glycerol had a moisture content of 3,6% in contrast to 31,8% with glycerol, where the moisture content is how much water the film contains. This is due to the hydrophilic nature of glycerol which contributes to an increase in moisture content (22). It has also been demonstrated that glycerol exhibits higher moisture content compared to sorbitol. Consequently, it can be implied that sorbitol may not exhibit the same extent of hydrophilic properties as glycerol (23).

2.6 Characterisation of biobased barrier films

2.6.1 FTIR-spectroscopy

Fourier Transform Infrared Spectroscopy, FTIR, is a characterization method mainly used to analyse and identify different organic substances (24). FTIR measures absorbance of infrared radiation applied to a sample. FTIR is a versatile technique that can analyse gaseous, liquid, and solid samples and provides real-time measurements (24). Another advantage with FTIR is that it is a non-destructive characterisation method meaning that the samples are not destroyed during analysis (24). This means that one sample can be analysed several times. From the FTIR measurements a FTIR spectra is obtained with absorbance peaks and wavenumbers (25).

The absorbance bands, the peaks of the spectrum, can be divided into two groups: group frequencies and molecular fingerprint frequencies. The group frequencies show the different bonds of typical functional groups in a molecule. These are typically above 1500 cm^{-1} in the spectra. The molecular fingerprint frequency group shows the frequency of the more specific bonds, and these are typically below 1500 cm^{-1} in the spectra. However, this region is less reliable since the functional groups can absorb light in this region as well. When interpreting the FTIR- spectrum one usually starts by identifying the functional groups present at the high frequencies. Then the functional groups are typically confirmed by analysing and confirming the structure of the compound in the sample. There are several IR spectra available to use as a comparison when trying to decide which compounds and functional groups are present in a sample (25).

There are several characteristic peaks present in a spectrum of carrageenan. These peaks are presented in Table 1.

Wavenumber (cm^{-1})	**Functional group**
3600-3000	O-H (stretching)
3000-2800	C-H (stretching)
1645-1640	Water
1126	Glycosidic bonds
850-840	C4-O-S in galactose (stretching)
805-800	C2-O-S in 3,6-anhydrogalactose

Table 1 Wavenumbers for different functional groups in carrageenan.

2.6.2 Water contact angle

Water contact angle measurements is a simple, rapid, and in-expensive method which gives an indication of a surface hydrophobicity. The measurement is however limited which can lead to discrepancies in the results due to wetness of the sample surface and surface morphology, e.g., roughness (9). Water contact angle is the measure of wettability. When a drop of water is placed on a surface, the liquid will interact differently depending on the intramolecular bonds in the material of the surface. There will be an angle formed between the liquid and the solid surface, and this angle is called the contact angle. The contact angle can be divided into static, dynamic, and roughness corrected contact angles (26).

The water contact angle is measured by an optical tensiometer. It consists of a camera, a dispenser, sample stage and a light source. The most common method of measurement of water contact angle is the sessile drop method. A drop of distilled water is placed on the sample surface. A direct measurement is taken by the camera and the angle surface is assessed. If the angle of the droplet is below 90°, then the surface is said to be wetted. This means that the water drop will be spread out on the surface. Conversely if the water contact angle is more than 90°, the surface is not wetted. The water drop will stay on the surface as a bead and is said to be showing hydrophobic properties (27). For the experiment a cut-off value 65° was chosen for the definition of hydrophobicity based on previous studies (28).

3. Experimental

The two types of carrageenan that was investigated in the present thesis are kappa- and iota-carrageenan. To achieve the desired hydrophobic surface, the interaction of three different hydrophobic compounds with carrageenan was evaluated. To enhance the mechanical properties of carrageenan films previous studies have used plasticisers. In this thesis the effect of glycerol and sorbitol was evaluated (23).

3.1 Chemicals

Iota- and kappa-carrageenan powders of commercial grade were purchased from Sigma-Aldrich and used without further purification The hydrophobic compounds, A, B and C were prepared by the group of Gunnar Westman. The plasticisers, sorbitol and glycerol were purchased from Sigma-Aldrich.

3.2 General preparation of carrageenan film solutions

Iota- and kappa-carrageenan (1wt%) were dissolved in deionized water in a vial. The vial was then sealed with a lid and transferred to a heating block at 70°C for two hours. In absence of magnetic stirrer's, the vials were instead stirred with a glass rod after one hour. After the total time of two hours the sample solutions were transferred to plastic petri dishes. The plastic petri dishes were then left in contact with surrounding air to let the water in the films evaporate for a minimum of 48 hours. The sample plan with all films prepared is shown in Table 2. Films were prepared both with and without a hydrophobic compound and plasticisers according to the methods described below.

Sample name	**Type of carrageenan**	**Hydrophobic compound (molar ratio)**	**Plasticiser (wt%)**
1	Kappa	-	-
2	Kappa	A (1:1)	-
3	Kappa	A (2:1)	-
4	Kappa	B (1:1)	-
5	Kappa	B (2:1)	-
6	Kappa	C (1:1)	-
7	Kappa	C (2:1)	-
8	Kappa	-	Glycerol (45)

9	Kappa	-	Glycerol (20)
10	Kappa	-	Sorbitol (45)
11	Kappa	-	Sorbitol (20)
12	Iota	-	-
13	Iota	A (1:1)	-
14	Iota	A (2:1)	-
15	Iota	B (1:1)	-
16	Iota	B (2:1)	-
17	Iota	C (1:1)	-
18	Iota	C (2:1)	-
19	Iota	-	Glycerol (45)
20	Iota	-	Glycerol (20)
21	Iota	-	Sorbitol (45)
22	Iota	-	Sorbitol (20)
23	Iota	A (1:1)	Glycerol (45)
24	Iota	A (1:1)	Glycerol (20)
25	Iota	A (1:1)	Sorbitol (45)
26	Iota	A (1:1)	Sorbitol (20)
27	Iota	B (1:1)	Glycerol (45)
28	Iota	B (1:1)	Glycerol (20)
29	Iota	B (1:1)	Sorbitol (45)
30	Iota	B (1:1)	Sorbitol (20)
31	Iota	C (1:1)	Glycerol (45)
32	Iota	C (1:1)	Glycerol (20)
33	Iota	C (1:1)	Sorbitol (45)
34	Iota	C (1:1)	Sorbitol (20)

Table 2 Overview of all samples.

3.2.1 Addition of hydrophobic compounds

Addition of hydrophobic compound was made to selected carrageenan solutions. All three compounds were weighed with two different ratios in respect to the molecular weight of the sulphated monomer in carrageenan. Two molar ratios 1:1 and 2:1 was used. The sample plan for the different compositions is shown in Table 2.

3.2.2 Addition of glycerol and sorbitol

Two different concentrations of glycerol and sorbitol was tested as plasticiser. 20wt% and 45wt% (based on the dry weight of the carrageenan powder). 20 or 45wt% of these plasticisers was added to the prepared kappa-, and iota-carrageenan solutions and film was prepared according as the method described above.

3.3 Characterisation

To analyse the samples two techniques were employed: Fourier Transform Infrared Spectroscopy (FTIR) and water contact angle measurements. FTIR was used to detect the possibility of chemical interaction and water contact angle was used to approximate the hydrophobicity of the formed films. FTIR was recorded on two different PerkinElmer spectroscometers, namely PerkinElmer Frontier Fourier Transform Infrared Spectrometer at Chalmers University and PerkinElmer Precisely Spectrum 100 FTIR Spectrometer at Wellspect. Experiments of FTIR were performed at room temperature and recorded at 4000-400cm^{-1} with 16 scans and a resolution of 4 cm^{-1}. All samples without plasticisers were analyzed with the FTIR at Chalmers, while the samples with plasticisers were characterized at Wellspect. All spectras were normalised to the peak of maximum absorbance (in the peak range 1024-1035cm^{-1}) (34).

To measure the water contact angle a Krüss DSA 100 was used at room temperature. The measurements of water contact angle were taken at 0, 30 respectively 60 seconds to see how the hydrophobicity of the films perform over time. The cut of value of 65° was used to evaluate if the films were sufficiently hydrophobic. Some values in the measurements show an angle-increase after time, which can be due to the machine's sensitivity unevenness on the film surface.

3.5 Six minutes functional water-resistant evaluation

To see if the films had obtained a sufficient water barrier for six minutes, a drop of deionized water was placed on a selection of films during. After six minutes the films were evaluated by whether the water drop remained on the film surface or if the drop passed through the film.

3.6 Sources of error

Depending on the temperature when the films are drying, the thickness of the film is affected and some films were left to dry for a longer time than other, which may affect the outcome of film thickness.

When measuring the water contact angle, the films were very thin and easily moved by wind, resulting in dust sticking to the exposed surface. This may affect the outcome of the water contact angle test. Another issue that arose when measuring the contact angle was the fact that the films became more gel-like upon touching for a longer time which could interrupt the water contact angle measurement result. However, this could also be interpreted as a result since this could be an indication that the films have not obtained a sufficient water barrier.

4. Results and discussion

4.1 FTIR

In Figure 6 and Figure 7 results from FTIR measurements on films from iota-carrageenan functionalised with different hydrophobic compounds at different molar ratios are presented. It appears that the sulphate group in carrageenan is where the hydrophobic compound binds. Due to this the FTIR spectras is focused on the frequencies for the sulphate groups in carrageenan. In both figures we can see a change in frequency around the peak for C2-O-S in anhydrogalactose unit for all films functionlised with hydrophobic compounds in comparison to the reference film. This could be an indication that the hydrophobic compound has interacted with iota-carrageenan. Subsequently, a change in frequency implies the formation of a new bond and further underlines that an interaction has occurred, which also has been reported by others (29). We can also deduce from Figure 6 and Figure 7 that the change in frequency is larger in Figure 6 showing the films functionalised at a 1:1 molar ratio. This can be interpreted as a higher molar ratio being more favorable than a lower molar ratio. Additionally, it is

interesting that no change in frequency corresponding to the C4-O-S, 850-840 cm^{-1}, in galactose region can be observed in neither Figure 6 nor Figure 7.

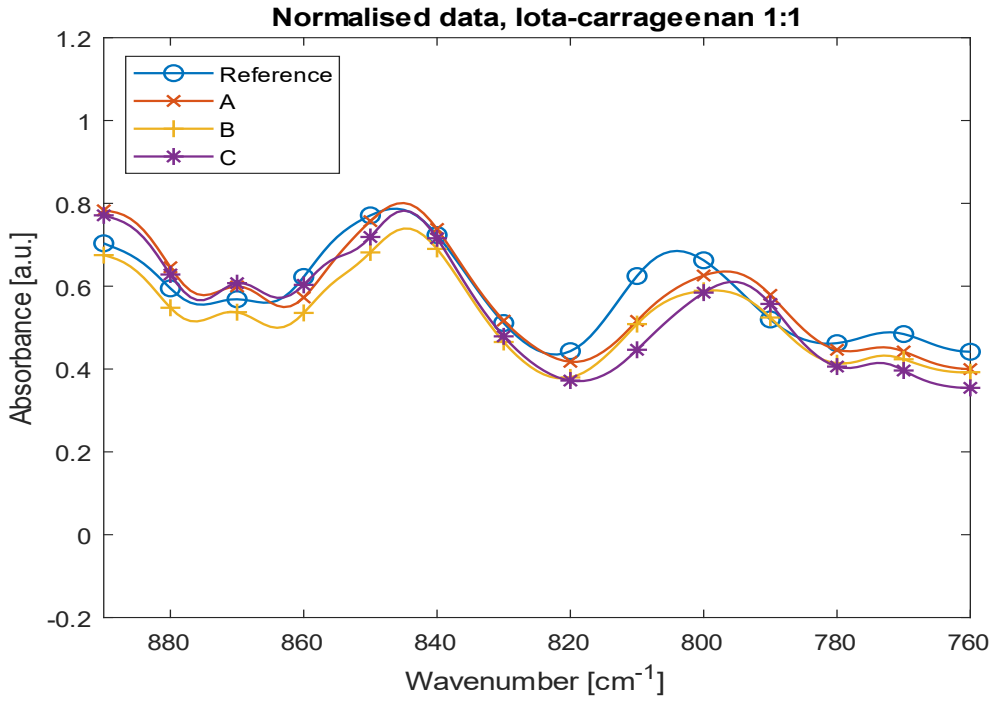


Figure 6 FTIR spectra of iota-carrageenan with added a hydrophobic compound in 1:1 ratio. The spectra are normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1).

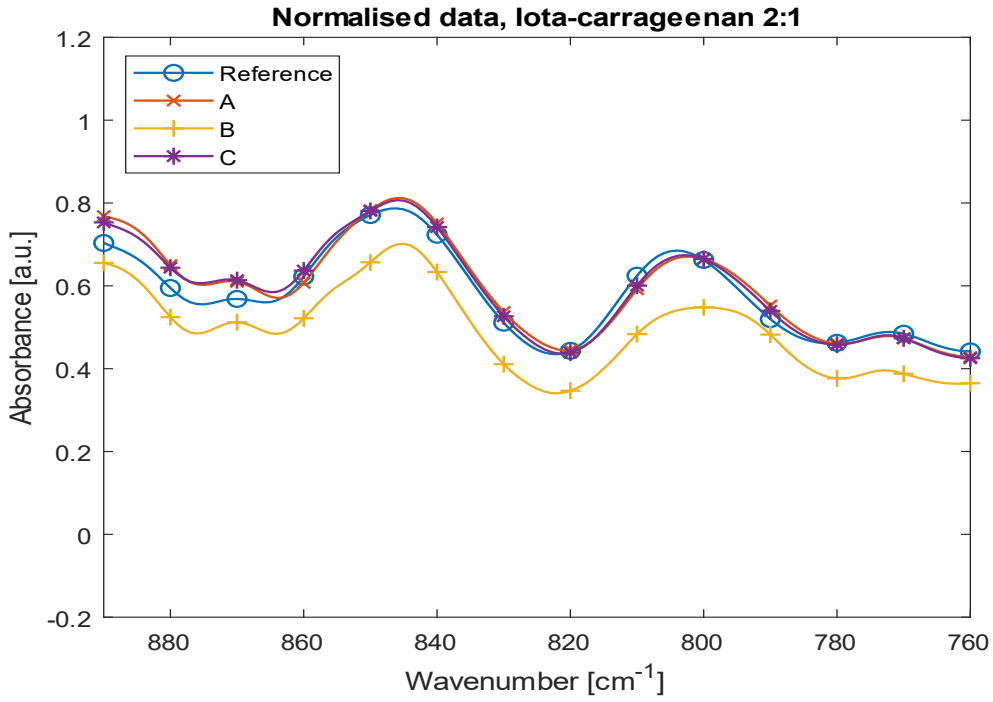


Figure 7 FTIR spectra of iota-carrageenan with added a hydrophobic compound in 2:1 ratio. The spectra are normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1).

Figure 8 and Figure 9 shows the FTIR results for the kappa-carrageenan samples. In kappa-carrageenan the C2-O-S bond is absent and consequently there should not be a peak at this frequency for any of the samples. Nevertheless, a small peak can be seen at this frequency in the reference sample. The reason for this peak can be due to impurities in the sample, which also has been observed by others (30). From Figure 8 and Figure 9 we can see that there is no change in frequency in the C4-O-S region. This implies that we cannot see that the hydrophobic compound has interacted with kappa-carrageenan.

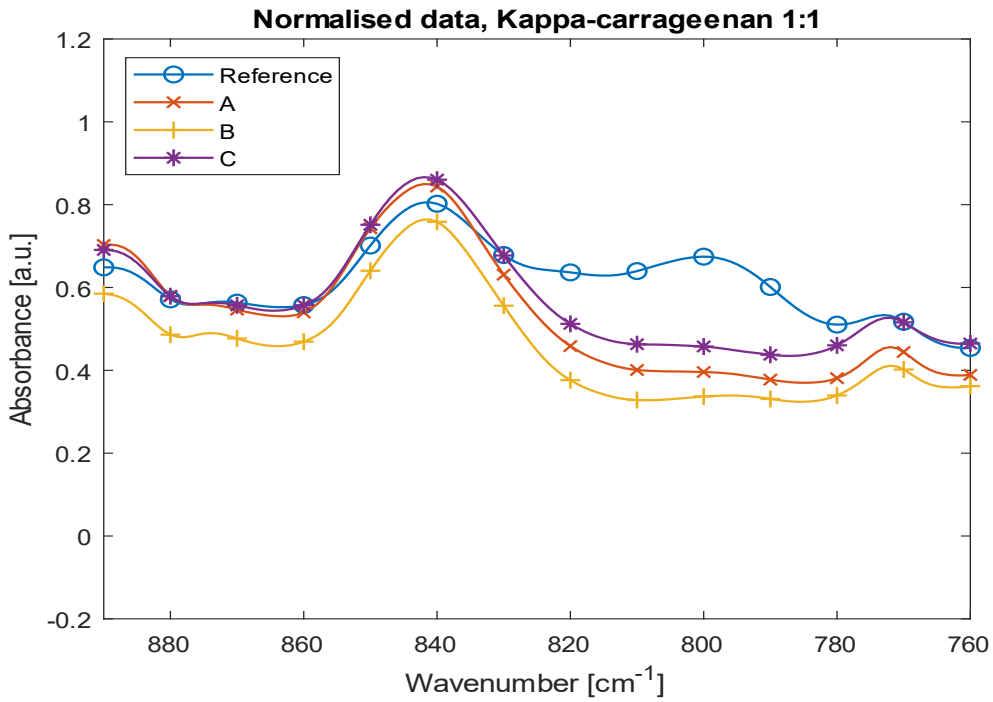


Figure 8 FTIR spectra of kappa-carrageenan with added a hydrophobic compound in 2:1 ratio. The spectra are normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1).

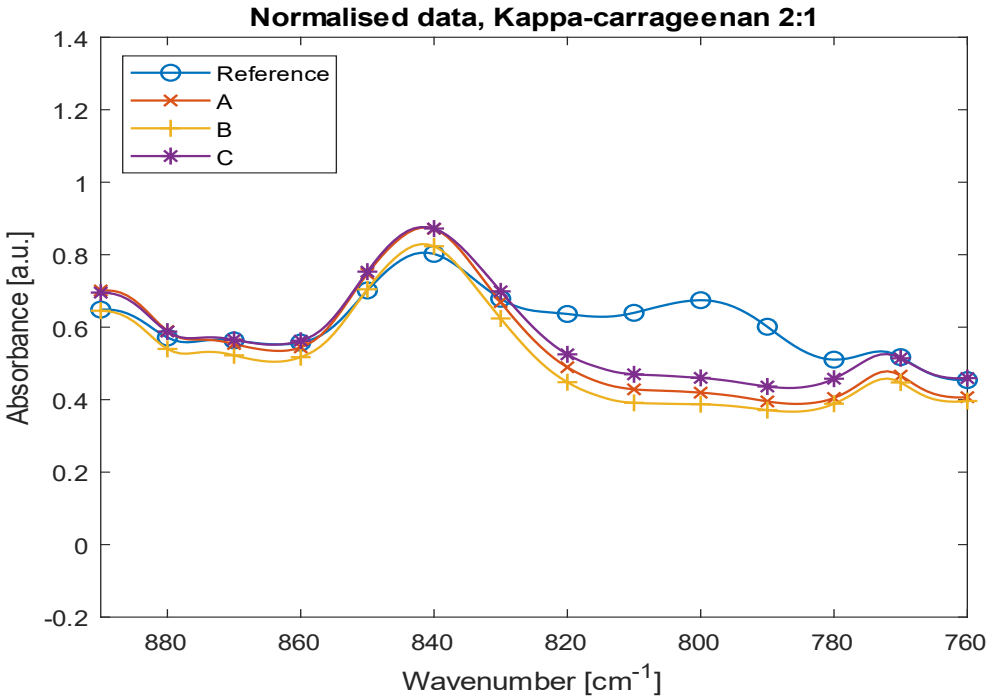


Figure 9 FTIR spectra of kappa-carrageenan with added a hydrophobic compound in 1:1 ratio. The spectra are normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1).

4.2 Water contact angle

4.2.1 Kappa- and iota-carrageenan films with added hydrophobic compound

In Table 3 results from the samples functionalised with the hydrophobic compound are presented. Overall, the films based on iota-carrageenan seem to exhibit a higher hydrophobicity than the kappa-carrageenan films. The hydrophobicity of all kappa-carrageenan films does not reach the cut-off value of 65° after 60s.

Sample Kappa	**CA [°] (0s)**	**CA [°] (30s)**	**CA [°] (60s)**
Reference	*81,93*	*40,37*	*42,38*
A (1:1)	67,42	43,60	38,62
A (2:1)	58,01	39,92	36,12
B (1:1)	60,00	56,66	52,94
B (2:1)	60,46	52,59	51,25
C (1:1)	59,78	47,40	63,23
C (2:1)	84,52	62,86	64,98

Table 3 Results from water contact angle measurements on kappa-carrageenan films functionalised with a hydrophobic compound

Regarding the iota-carrageenan films each hydrophobic compound seems to increase the hydrophobicity compared to the reference (Table 4). All films exhibit a rather stable hydrophobicity during the studied time interval. B seems to have the most stable hydrophobicity of all the hydrophobic compounds. Additionally, the B film seems to exhibit the highest contact angle in the molar ratio 1:1, highlighted in red in Table 4. However, B did not dissolve entirely so the film formed an uneven surface with bubbles (see Figure 10) which could contribute to a misleading result because of the water contact angle measurement being sensitive to uneven surfaces. The two other compounds A and C show that they are over the cut-off value and formed transparent films.

Sample Iota	**CA [°] (0s)**	**CA [°] (30s)**	**CA [°] (60s)**
Reference	*89,91*	*65,17*	*55,38*
A (1:1)	98,72	88,19	83,20
A (2:1)	89,91	82,99	87,12
B (1:1)	**99.46**	**98,62**	**93,32**
B (2:1)	71,22	66,58	64,04
C (1:1)	95,74	74,33	77,24
C (2:1)	98,09	76,16	66,79

Table 4 Results from water contact angle measurements on iota-carrageenan films functionalised with a hydrophobic compound. Highlighted in red is the results of the film functionalised with B *with a molar ratio 1:1 which showed the best result.*

Figure 10 Picture of iota-carrageenan film functionalised with hydrophobic compound B.

4.2.2 Kappa- and iota-carrageenan films with added plasticiser

The contact angle results from the addition of plasticisers are shown in Table 5. For the kappa-carrageenan films only one film met the contact angle cut-off value namely the film with a concentration of 20 wt% glycerol. Regarding the iota-carrageenan films, they all exhibit a surprisingly good hydrophobicity as they all fulfil the cut-off value of 65°. The iota film with 45 wt% added sorbitol seems to decrease the least in water contact angle over the time span of 60s, while the iota film with 20 wt% sorbitol demonstrates to be more hydrophobic at the initial measurement but becomes rapidly less hydrophobic after 60s.

Sample	**CA [°] (0sec)**	**CA [°] (30sec)**	**CA [°] (60sec)**
Kappa reference	*81,93*	*40,37*	*42,38*
Kappa Glycerol 45%	48,37	39,62	39,34
Kappa Glycerol 20%	106,99	82,20	72,43
Kappa Sorbitol 45%	68,50	42,61	37,30
Kappa Sorbitol 20%	72,58	58,33	44,12
Iota reference	*89,91*	*65,17*	*55,38*
Iota Glycerol 45%	91,68	76,00	73,16
Iota Glycerol 20%	93,73	88,23	83,10
Iota Sorbitol 45%	87,96	84,44	83,61
Iota Sorbitol 20%	108,33	89,48	82,18

Table 5 Results of water contact angle measurements of carrageenan films with added plasticisers. Kappa-and-iota reference are the films without addition of plasticiser.

From the results, both glycerol and sorbitol seem to increase the hydrophobicity when comparing to the carrageenan films without any added plasticiser. This can be due to the formation of double helices which are formed during the film formation. These double helices can then align with each other and this could possibly lead to stronger hydrogen bonds to the plasticiser than to the water resulting in the films becoming more water repellent (19).

4.2.3 Iota-carrageenan films with added hydrophobic compound and plasticiser

Table 6 presents the results of iota-carrageenan films with the addition of A and the plasticiser. The only films that meet the contact angle cut-off requirement is shown upon addition of 45 wt% glycerol or 20 wt% sorbitol. This is interesting since the glycerol in this case seems to work best at a higher concentration and sorbitol at the lower concentration. However, if we compare these to the A iota-reference film the hydrophobicity is lower in both cases of addition of plasticiser.

Sample	CA [°] (0sec)	CA [°] (30sec)	CA [°] (60sec)
A iota reference	*98,72*	*88,19*	*83,20*
A Glycerol 45%	81,80	72,27	74,87
A Glycerol 20%	81,34	43,96	40,89
A Sorbitol 45%	46,18	34,69	33,51
A Sorbitol 20%	95,94	90,33	76,21

Table 6 Results of water contact angle from iota films functionalised with A and added plasticisers.

Regarding the result from the samples functionalised with B and added plasticiser (Table 7) the hydrophobicity seems to have decreased generally when compared to the B iota-reference film. Addition of 20wt% glycerol or 45wt% sorbitol are the only samples that meet the requirement.

Sample	CA [°] (0sec)	CA [°] (30sec)	CA [°] (60sec)
B iota reference	*99.46*	*98,62*	*93,32*
B Glycerol 45%	74,42	66,27	55,20
B Glycerol 20%	76,73	70,22	66,37
B Sorbitol 45%	72,05	70,09	69,08
B Sorbitol 20%	51,35	47,43	45,55

Table 7 Results of water contact angle from iota films functionalised with B and added plasticisers.

The results of the films functionalised with C and added plasticiser are presented in Table 8. The addition of 45wt% glycerol has the highest hydrophobicity, but it also decreases the fastest over the time span of 60s. Addition of sorbitol 45 wt% was the only film that did not meet the requirement of 65°.

Sample	CA [°] (0sec)	CA [°] (30sec)	CA [°] (60sec)
C iota reference	*95,74*	*74,33*	*77,24*
C Glycerol 45%	111,10	82,96	76,03
C Glycerol 20%	80,71	88,22	71,31
C Sorbitol 45%	79,62	62,03	56,98
C Sorbitol 20%	89,42	80,37	74,29

Table 8 Results of water contact angle from iota films functionalised with C and added plasticisers.

4.3 Ocular inspection of films

All samples modified with the hydrophobic compounds formed films, however not whole films were formed. The overall impression was that they were brittle, uneven, and difficult to remove from the plastic petri dishes. The ocular film properties were the same for the two reference samples consisting of only carrageenan and water. However, the iota-carrageenan films modified with A and C seemed to have the best film properties as these were not as brittle.

The addition of plasticisers to the carrageenan films without a hydrophobic compound seemed to improve the ocular film properties in terms of durability and elasticity (see Figure 11). The majority of the films were easier to remove from the plastic petri dish and intact films were formed. The kappa-carrageenan films seemed to have slightly better mechanical properties than iota-carrageenan films with the plasticisers, but this has to be further evaluated using tensile testing.

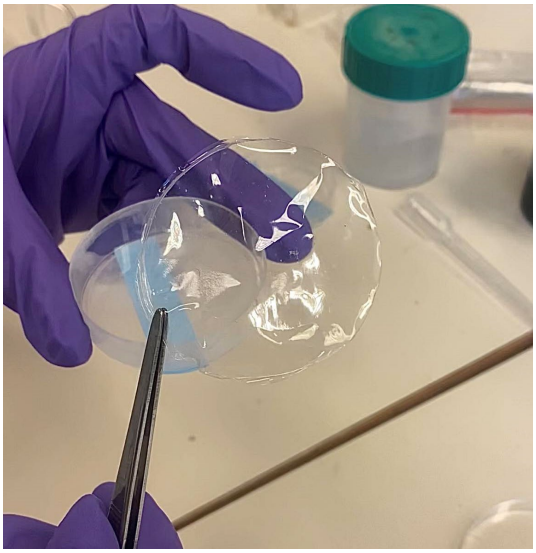


Figure 11 Example how one of the films looked with added plasticiser, namely iota-carrageenan with 20 wt% added sorbitol.

Although the addition of plasticiser to iota-carrageenan films seemed to improve the mechanical properties, the addition of a hydrophobic compound to these films did not seem to have the same apparent effect. Some of the films could have had increased mechanical properties but not evidently, again this change has to be evaluated further using tensile testing to be sure that the mechanical properties have increased. Furthermore, to ensure that the plasticisers did not interfere with the interaction of iota-carrageenan and the hydrophobic compound, FTIR was performed on these films (see Appendix). The FTIR spectra shows the same indication of

interaction, hence no conflict between the hydrophobic compound and the added plasticisers were observed using this method. This is the opposite of what was observed for many of the contact angle measurements were the addition of a plasticiser seemed to decrease the hydrophobic effect obtained by the modification.

4.4 Six minutes functional water-resistant evaluation

Since the catheter is used within six minutes after activation it is important that the films can provide a water barrier for this time interval. Based on previous results on the water contact angle measurements and the ocular inspection we decided to evaluate all kappa- and iota-carrageenan films with added plasticiser as well as the iota-carrageenan films functionalised with a hydrophobic compound and added plasticiser. However, iota-carrageenan films functionalised with B and added sorbitol did not form good enough films to be evaluated in this assessment. In Table 9 the functional testing results of the kappa- and iota-carrageenan films with added plasticiser are shown. The films that provided a water barrier for six minutes is marked in green, and films that did not uphold a water barrier are marked with red. In Table 10 the results of the functional water-resistant evaluation of the iota-carrageenan films functionalised with a hydrophobic compound and added plasticiser is shown in the same way.

Sample	**Upholds water barrier**
Kappa Glycerol 45%	
Kappa Glycerol 20%	
Kappa Sorbitol 45%	
Kappa Sorbitol 20%	
Iota Glycerol 45%	
Iota Glycerol 20%	
Iota Sorbitol 45%	
Iota Sorbitol 20%	

Table 9 Results for the final water barrier evaluation for kappa-and iota-carrageenan films with added plasticiser. The films that could uphold a water barrier for six minutes is marked with green and the films that could not is marked with red.

Sample	Upholds water barrier
A Glycerol 45%	
A Glycerol 20%	
A Sorbitol 45%	
A Sorbitol 20%	
B Glycerol 45%	
B Glycerol 20%	
C Glycerol 45%	
C Glycerol 20%	
C Sorbitol 45%	
C Sorbitol 20%	

Table 10 Results for the final water barrier evaluation of iota-carrageenan films functionalised with a hydrophobic compound and added plasticiser. The films that could uphold a water barrier for six minutes is marked with green and the films that could not is marked in red.

It is interesting that some of the films did not manage to reach the cut-off value of 65° in the water contact angle measurement but upheld a water barrier for six minutes. One possible reason for this could be due to the water contact angle measurement being very sensitive and the surface of film could be uneven resulting in different results depending on where the drop is placed. Additionally, a possible wetness of the sample surface during the contact angle measurement could also be an explanation for this deviation (9). It is also stated in literature that surface properties of polysaccharides, such as carrageenan, are challenging to analyse and therefore further analysing methods of the property is preferable (9).

5. Conclusion

The aim of this thesis was to create a hydrophobic barrier using carrageenan for a female intermittent urinary catheter packaging. The approach to make the films hydrophobic was to functionalise carrageenan with three different hydrophobic compounds. FTIR-spectroscopy of the carrageenan films functionalised with the different hydrophobic compounds indicated that the compounds interact with iota-carrageenan but not with kappa-carrageenan. Furthermore, only modified iota-carrageenan met the requirement for hydrophobicity with a contact angle above 65°. Out of the three hydrophobic compounds, the iota-film modified with B had the best hydrophobic properties. However, the compound did not dissolve entirely when mixed with carrageenan and water which resulted in an uneven film. Therefore, the two other compounds that formed even films and which also reached the contact angle requirement of 65° for hydrophobicity, might be a better choice for further studies.

Plasticisers were added to improve the mechanical properties of the films. The plasticisers worked best with the kappa-carrageenan films but an overall improvement of the films for both carrageenan types could be observed. A positive feature was that the hydrophobicity of the films was improved with the addition of plasticisers compared to the films without plasticiser.

The compatibility of plasticisers and iota-carrageenan modified with a hydrophobic compound were also studied. This showed a small indication of improved mechanical properties but needs to be investigated further. The water contact angle measurements seem to decrease compared to films functionalised with the hydrophobic compound without plasticiser. However, several films still met the contact angle requirement of 65°.

The *six minutes functional water-resistant evaluation* that was performed showed interesting results. Out of the iota- and kappa-carrageenan films with added plasticiser only three films upheld a sufficient water barrier for six minutes. The iota-carrageenan films functionalised with the hydrophobic compounds and added plasticiser showed deviation from the water contact angle results. The majority of these films were able to maintain a water barrier for six minutes.

Interesting future work would be to test more parameters in the laboratory work such as temperature, time for heating and different concentrations of carrageenan. For instance, to see

how these parameters affect film thickness and solubility of the compounds. It would also be interesting to continue investigating if it is enough to create hydrophobic carrageenan films by only adding plasticiser, and further testing the compatibility of other plasticisers in carrageenan films. Further interesting future work would be to test the carrageenan polysaccharide hydrophobicity using other methods than water contact angle due to the sensitivity of this method and due the surface properties of carrageenan which is challenging to determine.

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Appendix

FTIR spectras of iota-carrageenan functionalised with the hydrophobic compounds and added plasticiser.

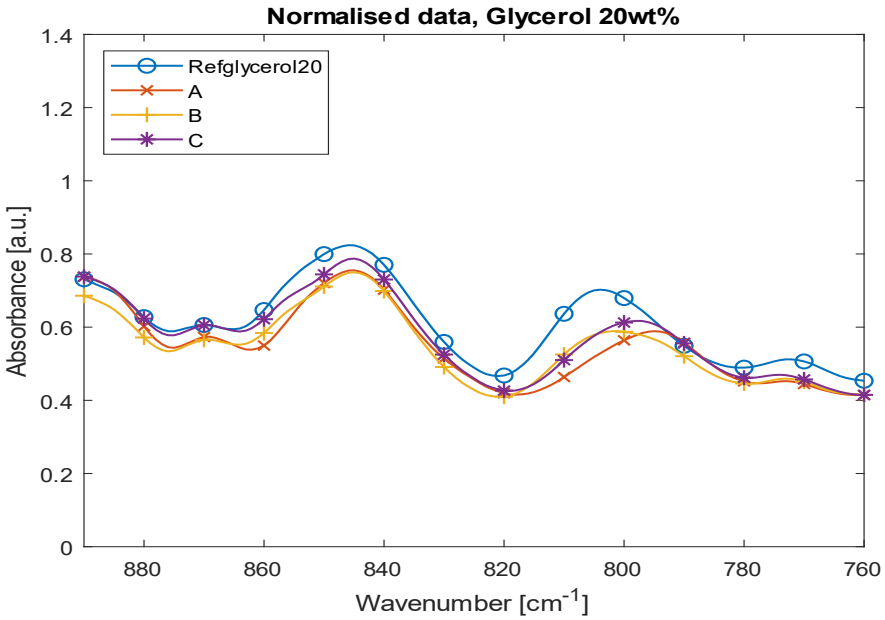

Figure 12 FTIR spectra of iota-carrageenan with added a hydrophobic compound and 20% glycerol. The spectra is normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1)

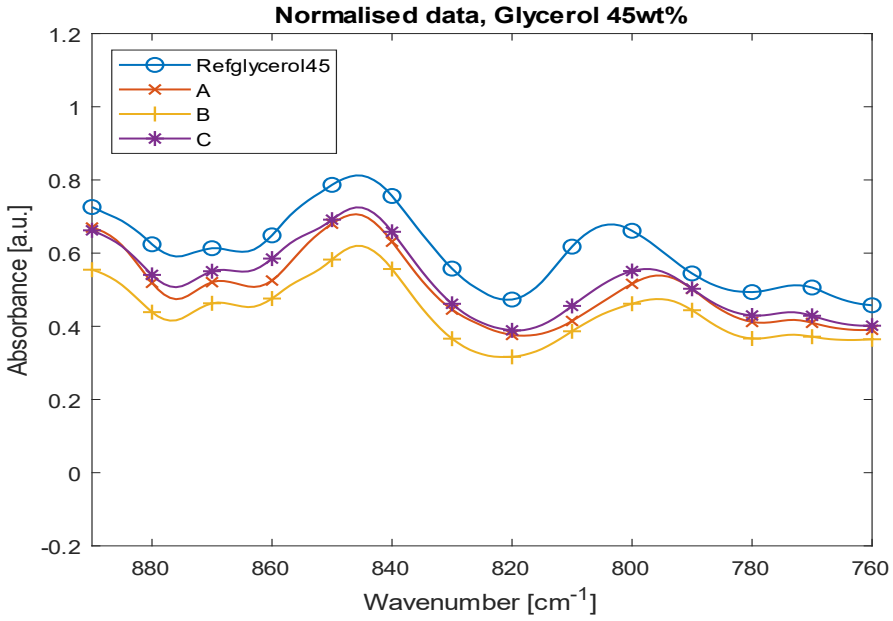

Figure 13 FTIR spectra of iota-carrageenan with added a hydrophobic compound and 45% glycerol. The spectra is normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1)

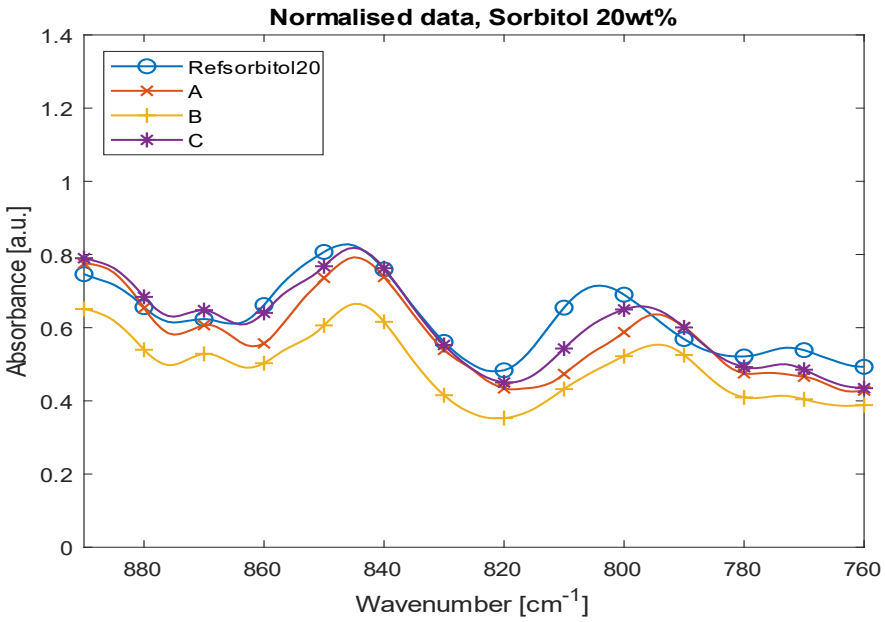

Figure 14 FTIR spectra of iota-carrageenan with added a hydrophobic compound and 20% sorbitol. The spectra is normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1)

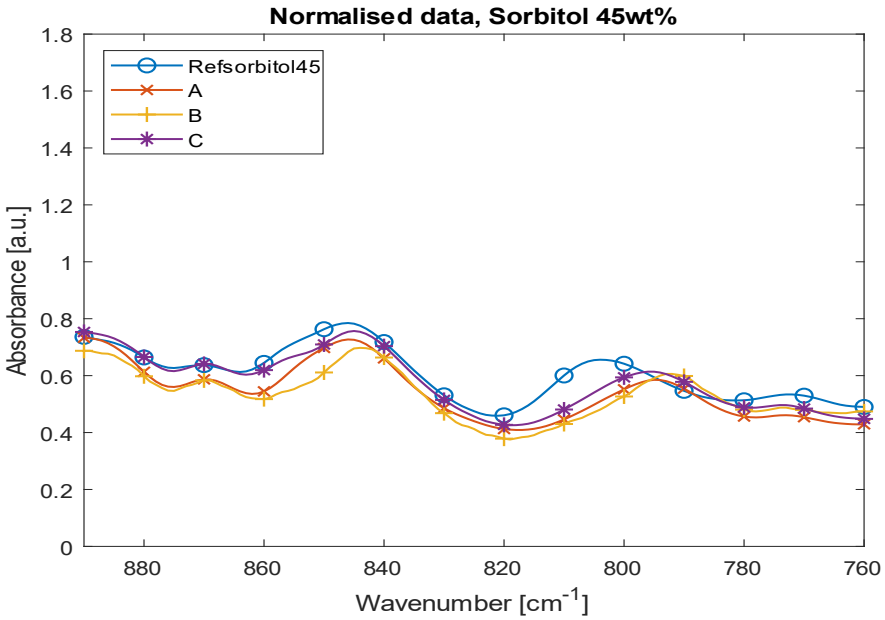

Figure 15 FTIR spectra of iota-carrageenan with added a hydrophobic compound and 45% sorbitol. The spectra is normalised to the peak of maximum absorbance (in the peak range 1024-1035cm-1)