A!

Aalto University
School of Chemical
Engineering

Lauri Matikainen

NANOCELLULOSE AS BARRIER COATING DEPOSITED USING A LABORATORY ROD COATER

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Biomass refining

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 24th of April, 2017.

Supervisor   Professor Orlando J. Rojas

Instructor   PhD. Ilari Filpponen

A? Aalto University
School of Chemical
Engineering

Author Lauri Matikainen

Title of thesis Nanocellulose as barrier coating deposited by a laboratory rod coater

Department Department of Bioproducts and Biosystems

Major Biomass refining

Thesis supervisor Professor Orlando Rojas

Thesis advisor(s) / Thesis examiner(s) PhD. Ilari Filpponen

| **Date** 24.04.2017 | **Number of pages** 77 | **Language** English |

Abstract

Both nanocellulose and barrier coatings are topical subjects, as evidenced by the accelerated number of recent reports related to nanocellulose and packaging. This thesis aims to understand the flow behaviour of nanocellulose as a coating layer deposited on paper by using a laboratory rod coater.

The experimental efforts cover tests related to the rod-coating parameters and the properties of the deposited nanocellulose. Associated properties were explored with respect to nanocellulose pre-treatment, substrate type, heat treatment, as well as the effect of added soy proteins. The latter relied on the effect of this inexpensive biomolecule to facilitate layer cohesion. The main target was to investigate the response of the end-use properties on both the device parameters and the properties of the coated material. In terms of liquid packaging, the main properties studied included barrier effects, which in this thesis were assessed by measurements of air permeability, water and oil absorption. In addition, the tensile strength and fracture toughness were determined. Moreover, the relation between the rod coater parameters, the properties of the coating layer, coat weight and coating thickness were investigated.

Heat treatment and binding with soy protein were identified as suitable strategies to reduce water absorption by nanocellulose. In addition, a connection between rod metering speed, air permeability and oil absorption was found. The effect was also based on rod gap size which regulated the amount of coating. Water transfer from the coating layer to the substrate and reduced coat weight were possible causes of a relatively high air permeability and oil absorption. However, the rheology of the layer and fibril agglomeration also played a role. Finally, nanocellulose percolation was found to decrease the fracture toughness as a function of coating solids.

Keywords CNF, nanocellulose, rod coater, coating, barrier

Aalto-yliopisto
Kemian tekniikan
korkeakoulu

Tekijä Lauri Matikainen	
Työn nimi Nanoselluloosa barrier-päällysteenä sauvapäällystimellä applikoitaessa	
Laitos Puunjalostustekniikan laitos	
Pääaine Biomassan jalostus	
Työn valvoja Professori Orlando J. Rojas	
Työn ohjaaja(t)/Työn tarkastaja(t) PhD. Ilari Filpponen	
Päivämäärä 24.4.2017 **Sivumäärä** 77 **Kieli** Englanti	

Tiivistelmä

Nanoselluloosa ja barrier-päällysteet ovat ajankohtainen aihe, mikä on selvästi havaittavissa tieteellisten julkaisujen määrästä. Tämän diplomityön keskeisimpiä tavoitteita on tarkastella nanoselluloosan virtauskäyttäytymistä laboratoriomittakaavan sauvapäällystimellä päällystettäessä.

Kokeellinen osuus kattaa sekä laiteparametrien että päällystekomposiitin käyttäytymisen testausta. Käyttäytymistä tarkasteltiin liittyen pohjapaperiin, esikäsittelyyn, lämpökäsittelyyn, sekä ristisilloittamiseen, jossa perustettiin soijaproteiinin ja ristisilloittajan yhteisvaikutukseen. Kokeellisen osuuden päätavoite oli tutkia loppukäyttöominaisuuksien vastetta, sekä laiteparametrien suhteen että päällystekomposiitin käyttäytymisen suhteen. Nestepakkauksissa loppukäyttöominaisuudet kattavat ennen kaikkea barrier-ominaisuudet, joita tässä työssä edustivat ilmanläpäisy, veden absorptio ja öljyn absorptio. Lisäksi mekaanisia loppukäyttöominaisuuksia eli vetolujuutta ja murtositkeyttä tutkittiin vähäisissä määrin, kuten myös päällysteen nk. paksuuntumis-ilmiötä. Laiteparametrien, päällystekomposiitin käyttäytymisen ja loppukäyttöominaisuuksien välinen suhde käsitti päällystemäärän ja päällysteen paksuuden tutkimisen.

Veden adsorptiota nanoselluloosaan onnistuttiin vähentämään sekä lämpökäsittelyn että ristisilloitetun soijaproteiinin avulla. Lisäksi havaittiin yhteys sauvan päällystysnopeuden, ilmanläpäisyn ja öljyn absorption välillä. Toisaalta laiteparametreja testatessa ilmeni epäselvyyttä tulosten tulkinnassa. Kyse oli siitä, olivatko veden imeytyminen päällysteestä pohjapaperiin ja alhainen päällystemäärä yksiselitteisiä syitä osittain korkeisiin ilmanläpäisevyyksiin ja öljyn absorptiolukuihin, vai vaikuttivatko myös fibrillien agglomeraatio tai erilaiset reologiset ilmiöt, kuten hydrodynaamiset voimat. Nanoselluloosan perkolaatiokäyttäytymisen havaittiin vaikuttavan murtositkeyden heikkenemiseen päällysteen kiintoainepitoisuuden funktiona.

Avainsanat CNF, nanoselluloosa, sauvapäällystin, päällystys, barrier

Acknowledgements

Contents

Abbreviations

BC = Bacterial cellulose

BNC = Bacterial cellulose nanocrystals

CLC = Cylindrical laboratory coater

CNC = Cellulose nanocrystals

CNF = Cellulose nanofibrils

CTMP = Chemi-thermomechanical pulp

EMC = Equilibrium moisture content

FBB = Folding boxboard

GW = Groundwood pulp

HDPE = High-density polyethylene

LDPE = Low-density polyethylene

LLDPE = Linear low-density polyethylene

LPB = Liquid packaging board

MAP = Modified Atmosphere Packaging

MD = Machine direction

MFC = Microfibrillated cellulose

MNFC = Microfibrillated and nanofibrillated cellulose

MSW = Municipal solid waste

OP = Oxygen permeability

OTR = Oxygen transmission rate

PE = Polyethylene

PEr = Polyethylene Raw Cupboard

PET = Polyethylene terephthalate

PP = Polypropylene

PS = Polystyrene

RH = Relative humidity [%]

SBB = Solid bleached board

SUB = Solid unbleached board

TMP = Thermomechanical pulp

UD = Uncoated Duplex

WLC = White-lined chipboard

WVP = Water vapor permeability

WVTR = Water vapor transmission rate

1. Introduction

1.1. Motivation

The accumulation of municipal solid waste (MSW) is a global problem, which is a consequence of the usage of plastic in many consumer products, such as packages. Packaging materials are used throughout the world to protect a package against physical, biochemical and microbiological deterioration (Nair et al., 2014). Nowadays, the common packaging materials consumed can be classified into four main groups by their raw-material: Paper and board, plastic, metal, and glass packages. The two most dominant packaging materials nowadays include both paper and board as well as stiff plastics (Sjöholm 2010), especially those utilized as flexible films and rigid containers. On the contrary, the plastic materials, being petrochemical-based, are in practice non-degradable. (Doroudgarian 2011) Meanwhile, the development of bio-based barrier materials to replace petrochemical-based polymers in food packaging has received limited attention: Until today, the role of barrier materials is mostly delegated to both plastics, such as LDPE, as well as metal films, such as aluminum and silica (Karvo et al. 2009). As an abundant naturally occurring mineral, Silica is one example of an inorganic alternative for bio-based polymers (Sjöholm 2010; Tuominen and Lahtinen, 2008). Likewise, in packaging, the most applied polymers are polyethylene (HDPE and LDPE), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS) (Kaila 2008) and it appears that the high ductility of thermoplastic polymers by regulating the amount of catalyst or temperature during processing makes them very challenging to displace by bio-based alternatives. Moreover, the protection requirements of a product can rarely be achieved by only one material: usually the films for packaging are laminates, which have two or more substances combined as thin layers. Although non-coated paper protects well from light, it does not offer protection against the diffusion of gas, water and aromas. In case the paper requires high barrier properties, by conventional standards it would be coated, or laminated, with aluminum or plastic. (Kaila 2008) However, due to environmental issues such as problems with disposal, bio-based, biodegradable alternatives could offer a simple solution to the demanded replacement of plastics and some metals (Nair et al. 2014). In **Figure 1**, the global packaging consumption in today's industry is displayed.
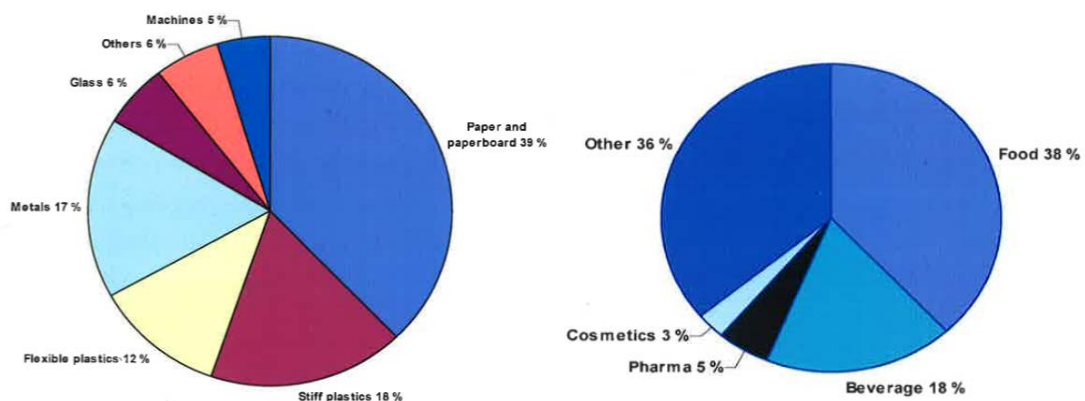

Figure 1. The global package consumption of year 2009 divided by raw material (left) and by end-use (right). (Sjöholm 2010)

1.2. Objectives

The coating industry today covers three different coating processes: Dispersion coating and extrusion coating are dedicated for the preparation of barrier coated film composites, and paper coating for pigment coated film composites. The sub processes within these coating processes are broad among various alternatives, not to forget that also the coating compositions between these coating processes differ considerably from each other. Therefore, no extensive comparison was made between the sub processes of these coating processes nor comparison between the varying behavior of different coating components of the coating processes. Instead, the behavior of nanocellulose in terms of laboratory scale rod coating was interpreted to the best of available knowledge with the objective of achieving the best possible barrier properties.

The target was to investigate the capability of nanocellulose to act as barrier coating on top of a substrate a.k.a. base sheet, which was herein selected to be of paperboard. In literature, barrier properties are basically represented by oxygen transmission rate (OTR), water vapor transmission rate (WVTR) and oil absorption. Due to availability restrictions, the tested barrier properties were narrowed in this thesis into air permeability and water absorption on behalf of OTR and WVTR, since these properties represent OTR and WVTR to a satisfactory extent. In terms of the coated paper, the coated film composite, the target was to apply the film by using a continuous method instead of the film formation methods presented typically in nanocellulose-related publications till date. The drawback of these methods is their inconveniently long duration in respect of industrial operation, as the film formation typically requires waiting overnight.

In practice, the research was carried out by preparing coated film composites out of paperboard substrates by using a laboratory rod coater. Afterwards, the coated films were examined by testing their barrier properties. The barrier properties were tested by means of a crosslinking test, pretreatment and substrate test, heat treatment test, and two parameter tests to investigate the common effect of rod coater parameters, namely, the rod gap size and rod speed. The rod gap size and the rod speed were suspected to be responsible for many attributes that govern the barrier properties, such as the flow behavior of the nanocellulose coating. Finally, the optimum rod coating parameters were selected based on background knowledge and some hypotheses. In addition, some future development ideas were presented.

2. Barrier properties

Barrier properties are the end-use properties that are required from a liquid packaging film. Barrier films in liquid packaging are intended to mitigate both the absorption and desorption of liquids as well as the diffusion of both gases and liquids from outside to inside and from the inside to the outside of the package. In addition to liquid, they should protect the insides from the impact of water vapor as well as from an unfavorable relative composition of permanent gases. These gases exist in air, covering mainly oxygen, nitrogen and carbon dioxide. (Karvo et al. 2009) By definition, a decent barrier film should protect the foodstuff from drying, breakdown, change in temperature, light, oxygen, odors and evaporation of aromas (Kaila 2008). Inside a food package there are chemical, biochemical, physical and

2

microbiological changes which take place through time. As these phenomena are deteriorative to the food package content, the intention of a barrier film is to maintain these changes within a reasonable level. This will consequently increase the product shelf life. (Doroudgarian 2011) (Nair et al. 2014)

Tortuosity and material density

As a total, the whole transmitting process which describes the movement of gases and water inside, entering and leaving a material, includes the following physical phenomena: absorption, dissolution, diffusion, and desorption. Basically, improved barrier properties are normally related to an increase in material density, which can be assumed to be proportional to tortuosity. By definition, tortuosity is intended to describe the effort a permeant on average experiences while transmitting through the blocking material. As in **Equation 1**, the tortuosity factor represents the degree of tortuosity. It is defined as the relation between two alternate molecule paths, as illustrated in **Figure 2**. The illustration resembles a material of nanoparticles, such as nanocellulose. (Karvo et al., 2009) Tortuosity is increased by fibril entanglement, as a consequence of higher aspect ratio for instance after mechanical fibrillation.

$$\tau = \frac{Dm}{D} \qquad\qquad (1)$$

where τ is the tortuosity factor, while D and D_m represent the shortest and the longest possible molecular path, respectively.
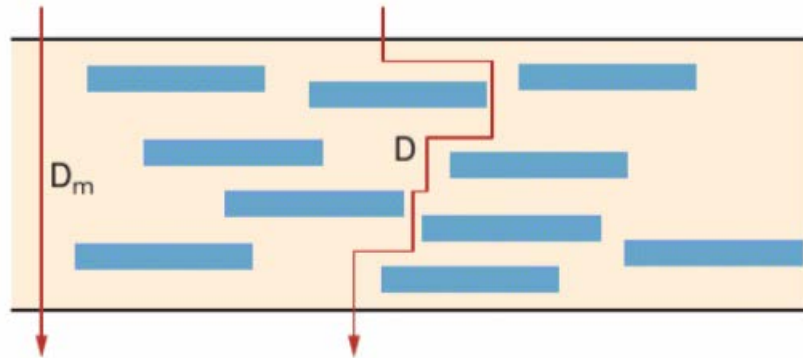
Figure 2. The two alternate paths of diffusing molecules. (Dufresne 2013)

Impact of crystallinity

However, in addition to tortuosity, gas and water transmission is affected by the degree of crystallinity, as crystalline phases block more transmission than amorphous phases (Dufresne 2013). In general, there are numerous reports from literature that the greater the degree of crystallinity, the higher the barrier properties (Sjöholm 2010). Crystallinity requires perfect packing of polymer chains during the drying stage of a polymer coating. In the case of being able to pack perfectly, the polymer chains form a concise structure that is practically impermeable to penetrating molecules. This means that the polymer chains have transformed to crystallites (Auvinen and Lahtinen, 2008).

3

2.1. Air and gas barrier

Gas permeability is a common term for the permeability of the most common permanent gases occurring in air: oxygen, carbon dioxide, and nitrogen. Out of these gases, the prevention of excessive oxygen transmission into the food package is of utmost importance, because oxygen is the most reactive. Exposition to excessive amounts of oxygen causes permanent changes in food quality as well as shelf-life decrease of the food product. (Nygårds 2011) The target of gas barrier films is to maintain a constant relative composition of gases inside a package. In the foodstuff industry, a typical food package barrier film protects against a deteriorative relative composition of carbon dioxide, nitrogen and oxygen which occurs in the ambient air, while conserving a proper relative composition of the respective permanent gases inside the package. Some products require more specific gas compositions than others, while others even require vacuum packing (Doroudgarian 2011).

Polarity and barrier properties

The resistance to diffusion of a material originates from a very low solubility of gas into the material. In microscale, a very low solubility means that there is a substantial difference in factors such as hydrogen bonding between the permeating gas and the blocking material. For instance, oxygen and nitrogen are both non-polar compounds, implicating that their mutual hydrogen bonding is relatively poor due to little OH-groups. On the contrary, cellulose contains a multitude of OH-groups which are prone to hydrogen bonding, making it a polar material. Finally, this conformity to law regarding polarity and the tendency to diffuse can be expressed as a rule of thumb, which states that *like dissolves like*. In addition to the difference in polarity, another key factor relating to the resistance to diffusion was noted by Lagaron et al. (2004). This was a high cohesive energy, which is, as similar to polarity, attributed to hydrogen bonding (Auvinen and Lahtinen, 2008; Hubbe et al. 2017).

Main equations of gas transmission

The gas transmission of any permeating molecule is affected by Fick's first and second law of diffusion as well as Henry's law of solubility. When looking in microscale, the molecules vibrate to random directions and deflect from one spot to another. However, in a larger scale the direction of the diffusing molecules is not random. Instead, it is governed by the tendency to equalize the chemical potential of the diffusing molecule between the opposing edges of the film material, the distance in between being the film thickness, as resembled by **Equation 2**. This chemical potential is typically expressed by concentration and pressure. However, before or after diffusion the molecules permeate to or from the film material. While penetrating into the film material the permeating molecules follow Henry's law, as resembled by **Equation 3**. In contrast, during their diffusion, now inside the material, the respective molecules follow Fick's law. Fick's first law states, that "the speed of activated diffusion is proportional to the gradient of penetrant's concentration":

$$J = -D\frac{dc}{dx}$$

(2)

where

D = Diffusion coefficient
c = concentration of the transmitting material

x = distance of the sight level from the film's surface

while the Henry's law states, that:

$$P = D*S \tag{3}$$

D = Diffusion coefficient
S = Solubility coefficient
P = Partial pressure of the penetrant

In addition, there exists Fick's second law, which is an integral form of Fick's first law. By combining Fick's second law and Henry's law, partial pressure of the penetrant can be used in calculation instead of its concentration. Indeed, it is often the case that the known constant is the partial pressure of the penetrant instead of its concentration. Moreover, the diffusion coefficient, D, indicates the speed of molecules passing through a film material, whereas the solubility coefficient, S, is a measure of the amount of molecules passing through the film material. (Auvinen and Lahtinen, 2008)

2.2. Moisture barrier

In general, the transmission of water molecules through a material can be expressed as liquid water or water vapor, namely, water absorption or water vapor transmission. However, regarding the latter expression, there are two quantities used, namely, water vapor permeability (WVP) and water vapor transmission rate (WVTR). Out of these, the WVTR is more commonly used. (Dufresne, 2013) According to Dufresne (2013), "the WVTR corresponds to the quantity of water which penetrates a surface unit sample of defined thickness during 24 hours under specified temperature controlled RH and under a vapor pressure difference". Water vapor transmission rate is an important quantity to recognize within food packaging, as the absence of water vapor improves both the shelf life of the food package as well as the product stability of its content (Saxena et al. 2011). Principally, a tendency to form strong and dense hydrogen bonding enhances barrier properties (Nair et al. 2014). However, since water is hydrophilic as well as its hydrogen constituents, the hydrogen bonds tend to absorb water. This rule of thumb which states that like dissolves like, meaning polar components dissolve into polar materials and vice versa, is demonstrated in practice in **Table 1** (Auvinen and Lahtinen, 2008).

Polymer	Oxygen permeability (cm^3-mil/m^2-day-atm)*	
	0% RH	100% RH
PVOH	0,16	388
Cellophane	2,02	3100
PA-6	15,5	77,5
PVAc	853	2325
PET	109	93
HDPE	1705	1705

Table 1. Effect of moisture on barrier of non-polar, moderately polar, and highly polar polymers at 23°C. (Auvinen and Lahtinen, 2008)

Regarding nanocellulose films, even though the oxygen barrier of nanocellulose films is very competitive with petrochemical-based polymers used today, their moisture resistance is too low to compete with petrochemical-based polymers (Sjöholm 2010). This is due to the strong hydrophilic nature of nanocellulose hydroxyl side groups. In microscale, a hydrophilic nature attracts water, a tendency which arises typically with hydroxyl and amide groups. Consequently, materials which have lots of hydroxyl and amide groups, some of which are synthetic such as ethyl vinyl alcohol (EVOH) and polyacrylate (PA) exhibit modest barrier properties in humid environment. Similarly, the functional groups of polymers with only a moderate polarity are less disturbed, such as those of polyethylene terephthalate (PET). (Andersson et al. 2002) In order to address the water sensitivity of hydrophobic polymers, various chemical modification methods have been applied. (Nair et al. 2014) Finally, these hydrophobic polymers could improve the water vapor barrier of the resultant nanocellulose composite. (Siró and Plackett, 2010)

Sensitivity to moisture is a major obstacle for many potential applications of nanocellulose-based barrier films. The cause of the deterioration of oxygen barrier at high humidity conditions has been evidenced by many researchers, and as such is confirmed to be a consequence of the plasticizing effect of water in the amorphous parts of nanocellulose, as illustrated in **Figure 3**. More exactly, this relates to a weakened film cohesion and a consequent acceleration of the rate of gas diffusion. (Hubbe et al. 2017)
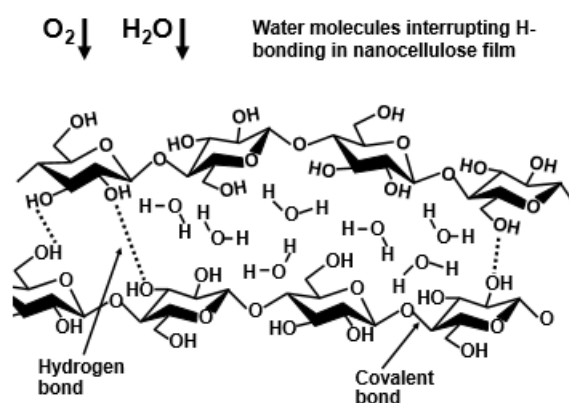
Figure 3. The water molecules interrupting the inter-chain hydrogen bonding between adjacent glucose molecules. (Hubbe et al. 2017)

As a good example of the moisture sensitivity of microfibrillated and nanofibrillated cellulose (MNFC), Gustafsson (2011) reported an abrupt, over ten-fold increase in air permeability of microfibrillated cellulose coating at about 70% relative humidity. Aulin et al. (2010) have reported oxygen permeability to be non-linearly correlative with the absolute moisture content of film material: Oxygen permeability was reported to increase abruptly when the absolute moisture content of the used film exceeds the limit of 15 wt%. (Gustafsson 2011) However, the exact film material was left unspecified. On the contrary, while increasing MNFC coat weight by adding multiple layers, the water absorbency of MNFC coating first drops abruptly although the drop in water absorption decelerates later on (Gustafsson 2011). Furthermore, the relation between nanocellulose and petrochemical-based plastics used today is presented in **Table 2**.

Material	WVTR	[g/m2 day]	Coating thickness	[µm]	Conditions
CNF	234,0		42,0		50% RH
CNF (0,5h acetylation)	167,0		46,0		50% RH
PVdC	3,1		12,7		100% RH
Polyethylene (PE)	16,8		18,3		100% RH
Plasticized PVC	118,6		12,7		100% RH

Table 2. Comparison of water vapor transmission between nanocellulose and petrochemical-based plastics. The petrochemical-based plastics exhibit a much higher water vapor barrier despite a roughly four times lower thickness and a double times higher relative humidity. (Nair et al. 2014)

2.3. Oil and grease barrier

Considering the measurement of oil and grease, there appear to be several terms to describe a similar concept: oil resistance, oil absorption, oil barrier, grease resistance, and grease permeability either mean the same or are reciprocals of the same measurement. However, the unit of measurement can be different, ranging from g/m^2 as according to the Cobb-Ungern test, to Kit-number with values 0-12 as according to the Kit test (Lavoine et al. 2014). Oil resistance is important for food products that typically contain fats and other oil-based substances. Finally, in addition to preventing the leakage of the insides of a greasy product through the food package, e.g. in a cake package, oil resistance is an esthetic requirement of such packages. (Kirwan 2005)

Oil, fat or grease, is a non-polar substance composed mainly of triglycerides, which are esters of glycerol and fatty acids. The fatty acids possess a main chain of varying length in terms of the amount of carbon atoms. The length varies between 4 and 24 carbon atoms. Interestingly enough, the amount of fat or oil permeation is stated to be governed to a large extent by the carbon chain length of the fat or oil in question. In addition, some other attributes of the material in question also have an influence to one way or another on the final amount of fat or oil permeation. These attributes include crosslinking amount, crystallinity, the amount of air-filled spaces, etc., not to forget the polarity of the material. As usually in chemistry, non-polar material absorbs the non-polar fat or oil more than a polar material. Regarding the plastics that nowadays are commonly used in food packaging as grease blocking material, non-polarity has an essential role. These non-polar plastics are resembled by polyolefins, for instance by polyethylene (PE). In contrast, polar plastics include for instance polyesters. Nevertheless, polarity affects grease permeability also indirectly. This means, that in case the blocking material is hydrophilic, it will allow more grease to permeate if exposed to moisture than if it was dry. Subsequently, as a consequence of earlier moisture exposition, the additional penetrated grease deteriorates the barrier properties of the package wall even more. (Auvinen and Lahtinen, 2008)

The porosity of the substrate appears to have an increasing impact on oil absorption. Such behavior was reported by Aulin et al. (2010): While surface coating MFC onto a base paper, carboxymethylated microfibrillated cellulose (MFC) alleviated the porosity of the base paper, thus resulting to improved oil resistance. In addition, Aulin et al. (2010) presented that grease permeability is usually directly proportional to air or gas permeability (Sjöholm 2010). In

7

contrast to porosity, crosslinking as well as possibly also crystallinity to a minor extent appear to have a reducing impact on oil absorption: Doroudgarian (2011) tested oil resistance of xylan coatings with and without a 5 % content of cellulose nanocrystals, as well as with and without crosslinking. In summary, the results indicated that oil resistance improved with increased crosslinking, while it either improved or decreased by the addition of cellulose nanocrystals. This would indicate that the crosslinking was more significant in terms of oil resistance than the structure of the nanocellulose coating. (Auvinen and Lahtinen, 2008)

2.4. Other

The disappearance of odors and volatile flavors is a concern regarding foodstuff packages. This is due to diffusion through the package wall, and can occur in either direction: from the package insides to outside, or vice versa. (Doroudgarian 2011) Some food products are also sensitive to light, which is why they are often conserved in a package of aluminum coating. In addition, substances can blend to each other as solids in direct physical contact. This kind of behavior is known as migration.

2.4.1. Odor, taste and UV-light

Odor and taste barrier

Considering odor and taste properties, flavorings and vitamins could be added to make a food package tastier in addition to making it more nutritious. These could be added for instance to dispersions containing soy protein, being used as edible films (Wang et al. 2013). Nevertheless, odors can also be a problem: For instance, it is important to avoid extended oxidation during extrusion coating in order to prevent malicious odor and taste from developing into the coating. This example relates to the oxidation treatment used to improve substrate adhesion during extrusion coating (Tuominen et al. 2008). In practice, the light barrier material is usually made of aluminum foil. (Kirwan 2005)

UV-light barrier

UV-light can harm the package content by causing oxidative rancidity. Especially fat-containing products tend to deteriorate in sunlight. Even though deterioration can undergo also under other types of light exposition than ultraviolet, a light barrier, meaning a high-opacity barrier, is required for such packages. In today's industry, the UV-light barrier can be enhanced the most by coating with aluminum foil, which provides a highly opaque light barrier. (Kirwan 2005) However, the opacity of e.g. nanocellulose can also be decreased by e.g. TEMPO oxidation or by increasing the amount of passes through a fluidizer (Gustafsson 2011).

2.4.2. Migration

Migration is a phenomenon that occurs in direct contact between the inside wall of a package and the package content, namely, the food. Therefore, the package should also prevent or inhibit migration between the package insides and the preserved food. Depending on the type of component being migrated, migration is considered somewhat detrimental to the safety and quality of the food. Migration occurs usually in direct contact

between the package wall and the food, although can also occur if the package contains volatile gases, for instance in the form of odors and taints. Attributes which affect the extent of migration cover the content of the migrant in the packaging material, mobility of compounds in the packaging materials, contact between packaging material and food, composition of food, conditions during contact, and duration of contact. (Castle, 2001; Robertson, 1993) Furthermore, migration is classified into overall migration and specific migration. When measuring overall migration, the precise component that causes the migration between the package and the food is unknown. Conversely, when measuring specific migration, the migrating component has been identified. Migration can be problematic for instance when a petrochemical-based material is in direct contact with the food it preserves. Considering plastics, the migrating, harmful substances have been added into the plastics during their processing. These include for instance residual monomers, plasticizers, solvents, or other additives. (Brown and Williams, 2003; Auvinen and Lahtinen, 2008)

3. Food package requirements

Types of foodstuff

Barrier coatings can be utilized in multiple applications, a large share of which classify as food products. These food products are often categorized according to their storing temperature. These include ambient foods that are meant to be stored in ambient temperatures, chilled foods that are meant to be stored in refrigerated temperatures, and frozen foods that are stored in frozen temperatures. Examples of frozen foods include frozen food cartons and disposables, which have stringent requirements regarding water and water vapor barrier. Likewise to storage temperature regarding ambient, chilled and frozen foodstuffs, food packages can be classified according to relative humidity, such as dry foodstuffs. (Andersson et al. 2002; Auvinen and Lahtinen, 2008; Kimpimäki and Savolainen, 2015) In **Figure 4 a**, some characteristic barrier requirements for some typical dry foods and beverages are displayed. The beverages are typically packed into layers according to the standards of liquid packaging, as displayed in **Figure 4 b**.
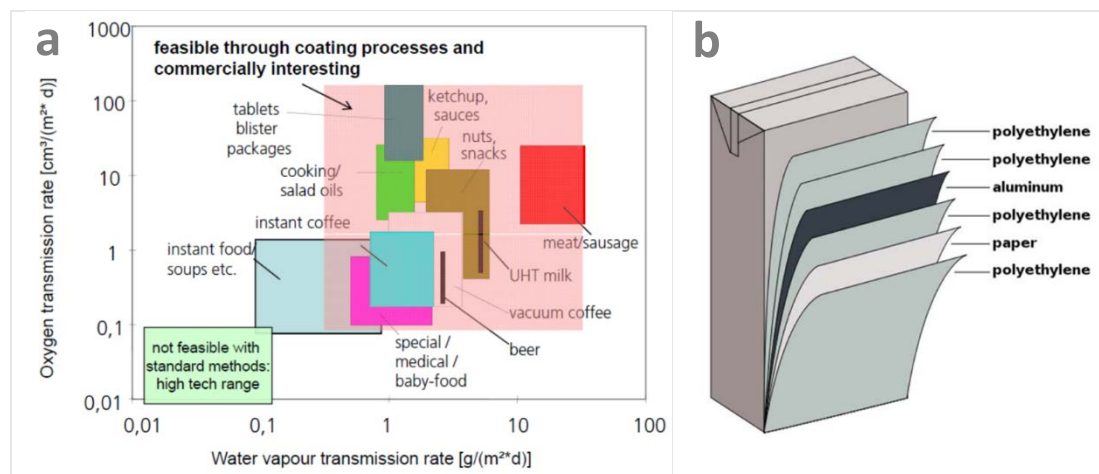

Figure 4. a) The OTR and WVTR restrictions for different end-use products in food industry. **b)** A Tetra-Pak packaging layer sequence, typical for liquid packaging. (Doroudgarian 2011)

Dried and moisture sensitive foods

Dried and moisture sensitive foods require drying of the food before packaging. The target behind the reduction of water by drying is to inhibit the growth of micro-organisms. The drying will also inhibit biochemical and enzymatic changes in food. In general, the equilibrium moisture content (EMC) of a product appears to govern the water-resistance requirements and water vapor barrier requirements of the product's intended food package, because the optimum EMC of the product designates the required relative humidity of the package insides, and finally the requirements to block moisture from the environment. Products that require a low equilibrium relative humidity (RH) typically have a low equilibrium moisture content. Thereafter, these products are typically more sensitive to quality changes as a consequence of moisture gain inside the package. As a result, these products require packing by using materials with high water vapor barrier properties. Similarly, the final moisture content affects the food product shelf life. (Auvinen and Lahtinen, 2008)

Aseptic packaging

Aseptic packaging includes sterilized products and also ultra-high temperature (UHT) products, the latter of which involves a treatment of few seconds in a relatively high temperature, typically around 140 ℃, in order to disable the activity of bacteria and micro-organisms. Subsequently, the product is packed into a protective atmosphere, or vacuum. Aseptic packaging is generally used to pack liquid foods. These involve dairy products such as milk, as well as beverages and soups. The most common packaging material nowadays in aseptic packaging is the liquid packaging board (LPB). It is a type of paperboard that is usually coated by co-extrusion or laminated by aluminum foil in order to achieve the barrier property requirements of liquid packaging. (Auvinen and Lahtinen, 2008)

Modified Atmosphere Packaging and oxidative deterioration

In order to maintain a convenient relative gaseous composition inside a food package that is specific for different foodstuffs, a technique referred to as Modified Atmosphere Packaging (MAP) has been developed. The MAP technology is a wide spread technology intended to pack perishable products. The target of this technique is to inhibit chemical, physical or microbiological activity related to the existence of permanent gases that might in disadvantageous relative compositions lead to a decrease of food quality or safety. The relative compositions, in turn, depend on not only the gas behavior itself but also on the behavior of the food product: Each gas behaves a bit differently regarding the packed foodstuff. The gases regulated in this technique cover the permanent gases. These gases exist in air, and mainly comprise oxygen, nitrogen and carbon dioxide. These gases impose a varying chemical or physical behavior that depends not only on the gas itself but also on the food product they are interacting with. One of the gases to be regulated is, undoubtedly, oxygen. The need for regulating oxygen originates from its tendency to cause deteriorative reactions. These reactions lead to food spoilage due to aerobic microbes or oxidative reactions of, for instance, fatty constituents. Subsequently, these lead to some unwanted food quality and safety issues, such as the growth of anaerobic bacteria or unfavorable color changes in packed red meat. Likewise to oxygen, carbon dioxide needs to be regulated. In food packaging, carbon dioxide is used as a MAP gas to increase pH and thereafter to mitigate the growth of microbes. The third more common MAP gas is nitrogen. Being relatively inert, nitrogen can be perfectly used to displace environmental oxygen. As such, it can be used to

prevent the growth of aerobic microbes, although by only displacing oxygen it will have no effect on the growth of anaerobic microbes. (Auvinen and Lahtinen, 2008)

4. Coated film composite

Coating can be done a single time or several times, the latter method being known as a layer-by-layer process (Hubbe et al. 2017). The coating, while forming several layers on top of each other, is referred to as multilayer coating. In extrusion lamination, multilayered structures are built when two or more films are laminated together by using molten plastic as adhesive. Herein, the adhesive is often coated as a continuous film, the procedure being referred to as web coating. (McKeen 2012) Furthermore, to-date there exist various coating methods, some of which are not applied in industrial scale. In addition to size press, they include for example spray coating, spin coating, curtain coating, rod coating a.k.a. bar coating, cylindrical laboratory coating a.k.a. CLC-coating, immersion coating a.k.a. dip coating, roll coating, etc. The ones which are also used industrially in paper coating, dispersion coating and extrusion coating, include for example blade coating, air-knife coating, rod coating, dip coating and roll coating. Moreover, it is ambiguous which coating method is the most suitable for barrier properties. Some methods, like blade coating, tend to coat an even film surface while others, like air-knife coating, tend to conform the base sheet morphology, the latter of which usually results into better barrier properties than the former. Similarly, rod coating produces a surface that is somewhere between an even coating and even surface. In **Section 5.2.2**, the differences in the two surfaces is displayed in **Figure 23**. (Kimpimäki et al. 2008) Moreover, spraying might also be a good way of improving barrier properties. In metallizing, the deposited film is very thin and thus needs to be deposited very evenly by vaporizing (Kirwan 2005). While using the CLC-coater, Gustafsson (2011) reported spray coating to result into better barrier properties than rod coating, based on earlier results by Sjöholm (2010) regarding the rod coater.

Application method of nanocellulose on paper

There appears to be various opinions about the method that makes the most use of nanocellulose qualitative properties as a packaging material. These cover the possibility of adding nanocellulose as a thickener into paper slurry (Richmond et al. 2012; Sjöholm 2010) or as a coating layer on top of paper. In this thesis, nanocellulose was used as the primary component of the intended barrier dispersion a.k.a. coating. Nanocellulose was selected to be coated rather onto a reinforcing substrate than prepared as a self-standing film or mixed to paper as "nanopaper". Sjöholm (2010) reported that the use of nanocellulose as nanopaper, having nanocellulose mixed into fiber network, was more beneficial than applying nanocellulose as a coating, in terms of both mechanical and barrier properties. On the contrary, Charani et al. (2013) found that the coating of microfibrillated cellulose (MFC) reduced air permeability more than the addition of MFC to a fiber slurry (Hubbe et al. 2017). Likewise, Kirwan (2005) states that considering the addition of additional functions to paper, coating is the simplest method. Moreover, it appears likely that while existing as a separate layer, nanocellulose is able to form a more concise structure than as a component in paper slurry. Consequently, the more concise structure would indicate as higher barrier properties. On the contrary, Sjöholm reported that nanocellulose enhanced the barrier properties of a laboratory sheet only until a certain consistency, after which the addition of nanocellulose

slowly deteriorated the barrier properties. Nevertheless, in the near future a self-standing nanofilm could also serve as a barrier film. Indeed, according to a research project by Bessonoff and Paltakari (2015) there was established a feasible method for continuous CNF membrane production. However, although in the project a production rate was decreased from 60 seconds to only two seconds, this rate was claimed slow for applications in the area of e.g. food packaging products. However, it is still a big increase in the rate of nanocellulose film preparation when comparing to what was reported a few years earlier by Sehaqui et al. (2010) as the fastest preparation method of NFC films using a Rapid Köthen equipment (Österberg et al. 2013). Furthermore, several factors affect a barrier dispersion coated product. These factors can be categorized into three main variables, namely, the coating, the substrate and the coating process and circumstances. (Kimpimäki and Savolainen, 2015)

4.1. Coating composition

The main components of a pigment coating suspension include the coating color, a binder, co-binder, a filler and a thickener. In extrusion coating, the coating itself is relatively homogeneous. In dispersion coating, the composition is pretty much the same as in pigment coating except for the components which in pigment coating base on achieving enhanced optical properties or printability. Bio-based coatings, that will likely be added into dispersion coatings along with the development of improved substrates for barrier dispersions, are actual today whilst they cover a broad area of options. In this section, a few of them are subsequently covered.

4.1.1. Nanocellulose

The investigation considering microscale and nanoscale cellulose has recently opened up an alternative for the coating of plastics and inorganics. In general, this appears to originate from the research of MFC as a coating slurry for paper and paperboard. (Lavoine et al. 2014) As stated in the introduction of the coating section, the possible use of nanocellulose as a barrier film reinforcement is not only as a coating but also as a component of a paper coating formulation, in which nanocellulose has been suggested to act either as a co-binder or thickener. (Richmond et al. 2014) However, there are varying insights on whether coating or impregnation of nanocellulose directly into a fiber slurry is a more efficient method in order to take the most advantage of nanocellulose usage. Sjöholm (2010) summarized that nanocellulose is better used as a component in fiber slurry, whereas Hubbe et al. (2017) relied more on the coating method. In addition, the type of nanocellulose is undoubtedly an issue to consider regarding barrier properties.

Plant-based nanocellulose

Nanocellulose is a broad concept and can be classified into three subcategories. These include nanofibrillar cellulose (CNF), nanocrystalline cellulose (CNC) and bacterial cellulose (BC). Their preparation method as well as their properties differ remarkably from each other, the two previous being plant-based and the latter being bacterial based. As reported by Nair et al. (2014), mechanical fibrillation was found to improve barrier properties: Even though crystallinity primarily increases barrier properties by providing a more rigid network with more tortuosity, the higher fibril entanglement enhanced by mechanical fibrillation caused

CNF to exhibit better oxygen barrier than CNC even though CNC is more crystalline. Furthermore, the size and shape of nanofibrillar cellulose depend largely on the preparation method used and also the cytological source (Virtanen 2015). This could also suggest, that the barrier properties also depend on such aspects. Indeed, aspect ratio increases fibril entanglement, both of which are increased by mechanical fibrillation. Consequently, the higher fibril entanglement increases oxygen barrier.

Comparison of CNF and CNF

The higher air barrier of CNF compared to CNC was evidenced by Belbekhouche et al. (2011) (Hubbe et al. 2017). Still, although surpassed by CNF in air barrier, CNC appears to exhibit relatively good moisture barrier properties. In a study considering the barrier properties of xylan films, a 74% reduction in water transmission properties was achieved by adding 10% of CNC onto a xylan matrix, when compared to a xylan film without CNC reinforcement. In addition, a 362% reduction was obtained in water transmission properties compared to a film of xylan and 10% softwood kraft fibers. (Nair et al. 2014) The high moisture barrier of CNC relates to its high crystallinity.

Bacterial cellulose

In contrast to CNF and CNC, bacterial cellulose (BC) a.k.a. bacterial nanocellulose (BNC) is not considered plant-based at all. Instead, it grows by the aid of certain species of bacteria, and is produced as a hydrated and relatively pure cellulose membrane. Consequently, there is no need for chemical treatments to purify BC from lignin and hemicellulose, as is the case with plant-based cellulose, which saves in energy costs. The only species of bacteria that is considered to produce BC at a rate which is sufficient for commercial scale, is denominated as *Gluconacetobacter xylinus*. Within BC, the degree of crystallinity is the highest among the three types of nanocelluloses, being practically 100% since the bacteria produce only pure cellulose. The extremely high crystallinity can be considered an advantage regarding the potential usage of BC as barrier material, for instance in barrier coatings. However, the consequent rigidity might be another issue to be confronted. Moreover, BC has an outstanding oxygen barrier at a low relative humidity, although the oxygen barrier is drastically weakened around 70% relative humidity. However, Ifuku et al. (2007) reported that acetylation, while also improving transparency, reduced the hygroscopicity a.k.a. hydrophilicity of BC/acrylic resin composite materials. The condition therein was to conduct the acetylation procedure only to a certain limit, since excessive acetylation reduced hygroscopicity. (Nair et al. 2014; Siró and Plackett, 2010)

4.1.2. Other bio-based materials

Today, many biopolymers are investigated with the interest of applying them as paper coating materials. These biopolymers include for example whey, proteins, chitosan, starch or alginates. (Lavoine et al. 2014) A biopolymer is a biodegradable polymer, which typically occurs in nature. However, bio-based polymers cover biopolymers that exist in nature and also man-made bio-based polymers, in which synthetic means "man-made". To the former group one can account the ones directly extracted from biomass and the polymers which are directly produced by organisms. To the latter group one can count the polymers synthesized of bio-derived monomers. The categorization is illustrated more profoundly in **Figure 5**.

13
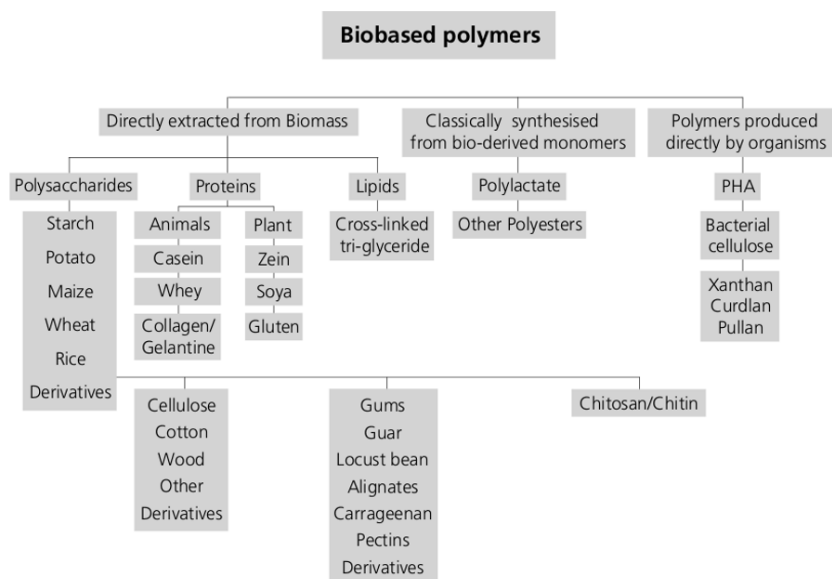
Figure 5. The three biopolymer groups and their subgroups. The only man-made bio-based polymers are "classically synthesized from bio-derived monomers", of which PLA is a known representative. (Doroudgarian 2011)

Starch

Starch is nowadays one of the cheapest biodegradable materials available in markets. It can be easily chemically modified, although its high viscosity, film brittleness and moisture sensitivity are its main drawbacks. Starch consists of glucose monomers and its properties vary to a minor extent depending on its cytological source. Prior to usage, starch should be modified by functionalizing or by modifying its rheological properties in order to use it in coating and surface sizing. In addition, starch should be boiled in order to make it soluble. However, starch reacts readily with water due to its free hydroxyl groups at its surface, although its moisture resistance can be enhanced by a crosslinker. When coated, its surface charge affects its behavior with the base paper as well as with other coating components. (Gustafsson 2011)

Chitosan

Chitosan can be produced from chitin by partial deacetylation. Hosokawa et al. (1990, 1991) reported a mixture of chitosan and MFC which exhibits a high oxygen barrier. However, although insoluble to water, the mixture was hydrophilic and thereafter exhibited a limited water vapor barrier. (Siró and Plackett, 2010) Further, chitosan has been reported to exhibit high antibacterial properties (Karvo et al. 2009). Chitosan was also mixed with beeswax in a study by Zhang et al. (2014) in order to yield an enhanced water vapor barrier and grease resistance.

Polylactic acid

Polylactic acid is one of the most studied biodegradable materials. This originates from its extraordinary properties which are relatively unique among other bio-based materials, the unique properties being likely a consequence of its synthetic nature. By its nature it is a

14

thermoplastic polymer that is hydrophobic, aliphatic and crystalline, with a high melting point. These properties enable the production of PLA via extrusion, which is apparently rare for a bio-based material although common for plastics such as polyethylene, as explained later in Petrochemical-based materials. In addition, it exhibits very good mechanical properties, although it is very light. One clear aspect that differs PLA from plant-based nanocellulose is its cytological source: Instead of wood, it is made from renewable agricultural raw materials. In addition, it is degraded by enzymatic hydrolysis, which however can also be used for nanocellulose preparation. Nevertheless, there are undoubtedly also some drawbacks. These include low thermal stability, which is contradictory to nanocellulose. Others include poor impact strength and a narrow processing window, the latter of which likely means that it is not easily e.g. surface modified. Therefore, it ought to be recommendable to further investigate the behavior of these drawback properties while incorporating various nanoscale materials into the PLA matrix and observing whether or not they improve some of the poor properties of PLA. (Sjöholm 2010)

Lignin

The addition of lignin appears not to affect water vapor barrier, although it increases hydrophobicity: according to Spence et al. (2010), the presence of lignin hinders hydrogen bonding while creating more hydrophobic pores. In practice, the pores absorb more water which inhibits the otherwise hydrophobic impact of lignin addition. Moreover, it remains yet unclear whether the creation of the pores was a consequence of decreased hydrogen bonding. (Spence et al. 2010; Nair et al. 2014) In contrast to water vapor barrier, the addition of lignin appears to increase oxygen barrier. This is a consequence of increased material density, suggesting an increased tortuosity. (Rojo et al. 2015) Considering the hydrolysate extracted as a pretreatment of dissolving pulp within kraft pulp production, Yaich et al. (2015) reported that the presence of lignin in the hydrolysate of kraft pulp increased the oxygen barrier of the films finally prepared from the hydrolysate.

Hemicelluloses

While cellulose as solely its original form is being utilized in many applications, hemicelluloses are released to the liquid stream of for instance a conventional pulping process as organic waste. This treatment originates primarily from their complicated molecular structure, which causes hemicelluloses to behave in a more complicated way than cellulose. Likewise, in contrast to cellulose, the chain length of hemicelluloses is only around 200, which is much lower and implies that they dissolve more readily than cellulose. The relative content of polysaccharides in a fiber slurry, such as hemicelluloses, depends essentially on the cytological source. Typically, hardwoods contain more hemicelluloses and less lignin than softwoods. For instance, birch pulp contains about 20 % of the most common type of hemicellulose, xylan, whereas softwoods are richer in mannan. Moreover, although both mannan and xylan exhibit low moisture barrier as typical for biopolymers, they both demonstrate high oxygen barrier. Both mannans and xylans have reportedly been successfully used in packaging film preparation. (Doroudgarian 2011)

Soy protein

Soy protein, usually delivered in the solid form as soy protein isolate (SPI), is a well-known biopolymer that is used throughout the world. It is commonly utilized in the development of edible materials for a multitude of applications, and also used as a bio-based co-binder for

paper coatings. Soy protein films, likewise to many other edible films, are able to control moisture, flavor and aroma transfer as well as oxygen and carbon dioxide transfer which occurs typically between food components and the environment (Wang et al. 2013). When excluding the hull, the composition of soybean is mainly protein (40%), carbohydrate (32%), and oil (20%). As typical for proteins, soy protein contains 20 amino groups. Eight of these are hydrophobic, and can be activated for crosslinking purposes by the aid of denaturation a.k.a. unfolding. As important for co-binders in paper coating, soy protein possesses a good water holding capacity. However, the utilization of soy protein in different applications has been limited by their modest mechanical properties as well as their water sensitivity: as similar to starch, water easily breaks up the structure. This might originate from the free hydroxyls on the surface of soy protein (Wang et al. 2013), which readily attract water molecules. Regarding rheology, soy protein typically exhibits a pseudoplastic-thixotropic behavior, as does nanocellulose. (Hanciogullari 2009) This should promote the applicability of soy protein as a coating component.

4.1.3. Petrochemical-based materials

Petrochemical-based materials, which cover most plastics, can be classified into two groups based on thermal behavior: Thermoplastics and thermosets, the former of which is much more common in industry than the latter. In essence, the definition of plastic material mean materials that can be made soft and malleable to be able to mold or shape, after which they can be fixed by heating, by some chemical reaction, or by cooling. (Sjöholm 2010)

Polyethylene

In principle, it appears that a petrochemical-based plastic, such as polyethylene (PE), is very challenging to displace in global markets: despite its simple chemical structure, amending the amount of catalyst as well as temperature and pressure conditions allow to regulate and specify the end-use properties of PE for a multitude of end-use products, such as food packages. Indeed, the prosperity of PE bases on its diverse grade options which cover a broad amount of high-quality properties. Consequently, PE is joinable to characteristics that are ideal for an infinitude of applications. Being discovered in 1933, PE is the largest volume polymer consumed in the world. Thus, it is also the most commonly used thermoplastic polymer. Polyethylene has been developed into two forms. Namely, low-density polyethylene (LDPE) and high-density polyethylene (HDPE). LDPE is more branched than HDPE, while HDPE is more concise. While HDPE exhibits better mechanical properties, LDPE is better in flexibility and e.g. moisture resistance. Today, the innovations in packaging technology for paperboard coating and paper and foil composite structures support the growth of LDPE usage in its second largest application segment, the extrusion coating of paper and paperboard. To this segment belong also the end-use products of the liquid packaging sector. Altogether, 17 % of LDPE and its forms are produced by extrusion coating, the majority (59 %) being used as film. Although not considering food packaging, the film segment is declining due to the displacement of LDPE by linear low-density polyethylene (LLDPE), which exhibits a lower thickness more suitable for some end-use products. (Vasile and Pascu, 2005)

Latex

The term synthetic latex covers a set of polymers which target as a component in paper coatings and dispersion coatings is to decrease viscosity and make the coating more Newtonian (Roper 2009). Although the term latex is very broad as latex also exists in nature, herein latex was decided to be reviewed among other petrochemical-based products, because latex typically occurs today in coatings as petrochemical-based synthetic latex. Furthermore, barrier coating latexes, being present in dispersion coatings, are usually polymers or co-polymers of styrene, acrylate, metacrylate, butadiene or vinyl acetate, which means the latexes in barrier coatings are mainly the same as latexes in pigment coatings (Andersson et al. 2002). However, there exists also renewable latex, which is fully biodegradable: One example of such latex is starch. By definition, latex can be either of natural or synthetic origin: In nature, latex exists in the insides of 10 % of all flowering plants as a milky fluid, which consist of proteins, alkaloids, starches, sugars, oils, tannins, resins, and gums. In fact, the word latex originates from a Latin verb that means "to milk" (Kimpimäki et al. 2008). Moreover, the natural latex is typically secreted after tissue injury to protect against herbivorous insects. Structurally, it is a stable dispersion or emulsion of polymer microparticles in an aqueous medium, which coagulates after being exposed to air. In addition to the latex found in flowering plants, there is an individual term used for natural latex rubber. Likewise, latex can also be prepared synthetically by polymerization of a monomer previously emulsified with surfactants. Examples of synthetic latex polymers are polyvinyl chloride (PVC), polyvinyl acetate (PVAc), waterborne epoxy, and waterborne polyurethane (WPU). (Dufresne, 2013). The synthetic latex is commonly used in paper coatings to regulate viscosity by a principle illustrated in **Figure 6**.
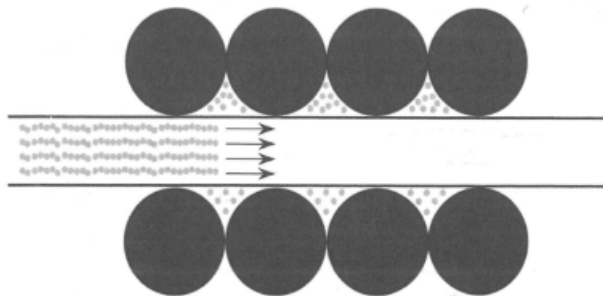
Figure 6. The mechanism by which latex plasticizes and modifies the suspension more Newtonian. (Roper 2009)

Particle size is an essential parameter of lattices. In paper coatings, the small latex particles smoothen the flow between other coating components by penetrating in between. By definition, this is how latex reduces viscosity. The lowered viscosity consequently increases coating runnability, which in turn improves efficiency. (Roper 2009)

4.1.4. Minerals

Inorganics, which typically comprise of clays and layered silicates such as montmorillonite, saponite, and hectorite, are clay minerals that appear as fine fragments of rocks or soils, and can therefore be easily located. They have typically a high aspect ratio and a large surface area. (Sjöholm 2010) Inorganics, e.g. silicon oxide, could be considered an alternative

solution for bio-based materials regarding barrier coatings. Besides, the usage of many inorganics is principally environmentally justified, since they occur naturally in environment. This applies e.g. for silicon oxide, which in nature is as common as sand. (Tuominen and Lahtinen, 2008) In a study by Nygårds (2011) it was reported that the oxygen barrier did not improve as a result of mineral addition. The mineral used was Barrisurf LX, which is of kaolin that can principally be used as barrier material due to its plate-like particle shape. In spite of no improvement in oxygen permeability, the Barrisurf LX minerals proved to decrease coating viscosity in a cost-effective manner. This suggests, that such minerals like the kaolin Barrisurf LX could be in demand for nanocellulose coatings in the future. However, many inorganics do present good barrier properties. The plate-like structure of kaolin, for instance, can be used to block gas transmission and thus can be used as a decent oxygen barrier. In addition, montmorillonite clay or related materials have been reported to exhibit high water-resistant properties when used together with cellulose nanomaterials. Likewise, while incorporating vermiculite nanoparticles into CNF films, Aulin et al. (2012) noticed a good oxygen resistance at a relatively high humidity. (Hubbe et al. 2017) In addition, Sjöholm (2010) aimed to improve barrier properties by incorporating kaolin into a laboratory sheet. However, the content was considered too low in order to obtain a collective network structure.

4.1.5. Crosslinking agents

When there are fluctuations in the free volume of a polymer, penetrating molecules generally diffuse. Fluctuations in the free volume tend to facilitate the penetration of molecules. However, crosslinking reduces polymer chain mobility, meaning it reduces fluctuations in the free volume. Consequently, this reduces the diffusion of permeants. Crosslinking affects barrier properties the more the bigger the size of the permeating molecules in question. (Auvinen and Lahtinen, 2008) The addition of crosslinking agent onto a MFC coating suspension was reported by Gustafsson (2011) to level the base paper surface, although not by smoothening the surface of the MFC coated paper. In general, crosslinking agents tend to improve the bonding of MNFC coating into the base paper as well as to other MNFC fibrils. Some common crosslinking agents cover aldehydes, such as glutaraldehyde and glyceraldehyde (Wang et al. 2012).

4.2. Base paper

Only in paper coating, there are a few different terms used to describe a substrate. These include e.g. "base paper", "base sheet", and "base board". A substrate is a common term for a type of base or constitution, a reinforcing matrix for some other material which properties are primarily in demand regarding the final product. Herein, the final product is a food package. The role of a food package is both to provide protection as well as to work as a barrier. The raw material of the substrate can be out of paper, board, plastic or even glass, depending on the final product desired (Kimpimäki et al. 2008). It is postulated, that the substrate a.k.a. base paper is likely the most important factor of a coated film composite, as 50-80 % of its total properties are said to depend on the properties of the base paper (Forsström 2009). However, while paperboards exhibit good mechanical properties and flexibility, they lack barrier properties (Nygårds 2011). Nevertheless, being

most commonly a paperboard, the substrate offers mechanical strength and flexibility to the final package. The four most essential attributes of a substrate are based on its roughness, porosity, sizing, and stiffness (Kimpimäki et al. 2008). Moreover, it is a fundamental rule of thumb, that the less the substrate absorbs the aqueous phase of the coating, the better the barrier properties of the coated film composite (Forsström 2009). However, slight water penetration is only advantageous for the base paper, as explained more in **Section 4.2.2**.

4.2.1. Cartonboard grades

As illustrated in **Figure 7**, there exist three main types of paperboard: cartonboards, containerboards, and specialty boards. Out of these board types, cartonboard has been specialized for consumer board use. In practice, consumer board applications mean applications such as food, cigarettes, pharmaceuticals, milk, and yoghurts. The common divisor of these applications is that they accept recycled pulp, which is the primary ingredient of cartonboards. In addition, the pulp of cartonboard is usually of chemical pulp, as either bleached or unbleached. In either case, it provides usually higher mechanical properties than mechanical pulp, which is why chemical pulp is commonly used as raw-material for packaging papers. Besides the coatings, different additives provide special attributes to the packaging papers. (Sjöholm 2010)
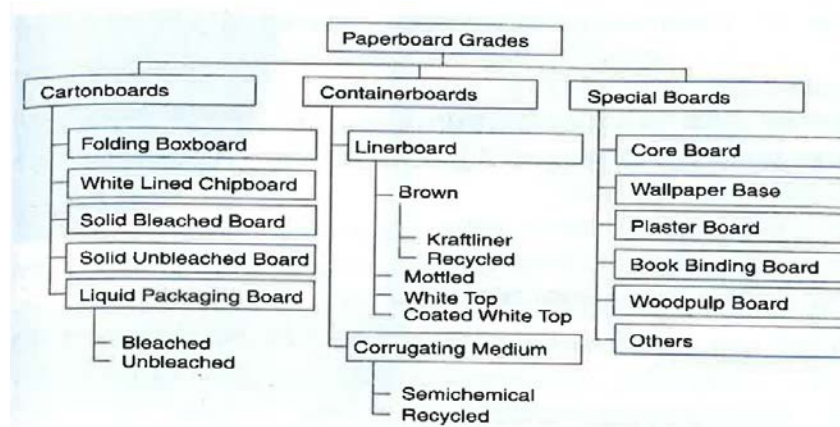
Figure 7. Classification of different packaging grades. (Sjöholm 2010)

Comparison between solid bleached board and solid unbleached board

Solid bleached board (SBB) is a type of paperboard that is prepared using primary quality fibers a.k.a. virgin fibers. As only bleached chemical pulp is used, SBB is of pure cellulose. In addition, SBB usually contains a mineral pigment coated top surface, while some grades are also coated on the back. Its grammage ranges between 170 and 380 g/m^2. It is a good choice for packaging of aroma and flavor sensitive products, since being made out of primary chemical pulp it provides a good barrier against odor or taint. Some examples of the use of solid bleached board include chocolate packaging, frozen, chilled and reheatable products, tea, coffee, liquid packaging and non-foods. SBB possesses good surface characteristics while exhibiting a high barrier against moisture. Further, another similar type of paperboard is referred to as solid unbleached board (SUB), which exhibits a grammage typically over 300 g/m^2. Likewise to SBB, it is made exclusively from unbleached chemical pulp, which means it has a significantly higher content of hemicelluloses and lignin. As such, the base board of SUB

19

is brown in color. What distinguishes SUB from SBB in addition to bleaching is that SUB has a high puncture and tear resistance, as well as good wet strength, the latter making SUB a decent base for liquid packaging. (Kirwan 2005; Sjöholm 2010) Moreover, the wet strength of nanocellulose films was improved by a hot press technique, as reported by Österberg et al. (2013). In general, the composition of the different cartonboard grades can be summarized into three layers, as indicated in **Table 3**.

	FBB	WLC	LPB	SBB / SUB
Top layer	Chemical pulp with pigment coating	Woodfree waste or chemical pulp	Polymer coating	Chemical pulp
Middle layer	Mechanical pulp	Mixed paper	Chemical pulp	Chemical pulp
Bottom layer	Chemical pulp	Woodfree waste or chemical pulp	Polymer coating	Chemical pulp

Table 3. Composition of the layers of different cartonboard grades. In contrast to the other cartonboard grades, WLC typically consists of more than three layers. (Kirwan 2005)

Folding boxboard

In addition to SBB and SUB, folding boxboard (FBB), white lined chipboard (WLC) and liquid packaging board (LPB) are other cartonboards which are commonly used in food packaging. In FBB, the middle layers are of mechanical pulp whereas the outer layers are of bleached chemical pulp. This combination creates high stiffness to the paperboard. The fully coated grades of FBB have a smooth surface with good printing characteristics. As a primary product, meaning that it is made of virgin fibers, the FBB possesses a consistent purity which is evident for food package safety and suitable for the packing of aroma and flavor sensitive products. Moreover, FBB is suitable for a variety of products, covering foodstuff as well as cosmetics and healthcare products. (Kirwan 2005) In extrusion coating today, LPB is used inside a film laminate of several functional layers (LDPE and aluminum), as displayed in **Figure 8**.
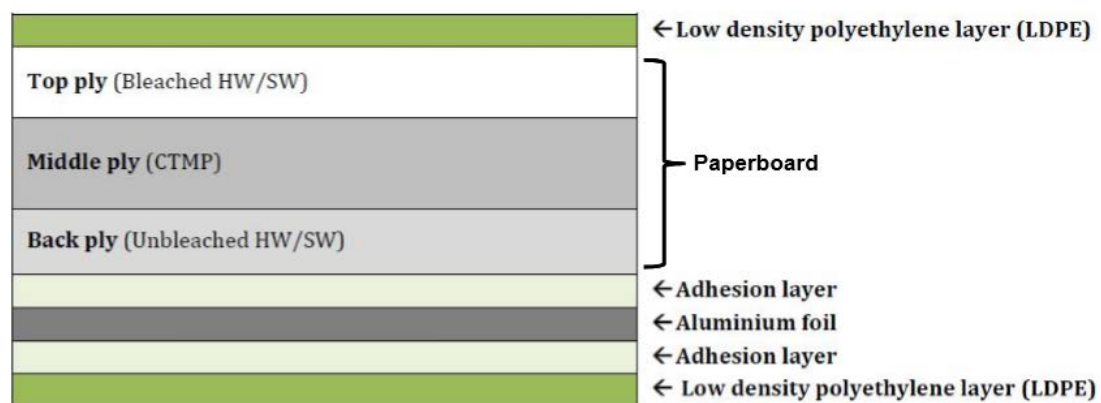
Figure 8. A typical laminate for liquid packaging. The indicated paperboard comprise the three-layered structure of the liquid packaging board (LPB). (Kuusipalo et al. 2008)

Comparison between white-lined chipboard and liquid packaging board

Another cartonboard applied in food packaging industry are both the white lined chipboard (WLC) as well as liquid packaging board (LPB). WLC consists of several layers, LPB consists of only three. Considering WLC, the top layer is conventionally made of white, woodfree

(without mechanical pulp) waste or chemical pulp, while the middle layer consists of mixed paper. On the contrary, within LPB both layers are often extrusion coated to obtain the required barrier properties of liquid packaging, while also lamination by a thin layer of aluminum is neither rare. Thence, a good example of LPB layers is provided in **Figure 8**. Although both consist mainly of chemical pulp, WLC uses recycled fiber while LPB uses virgin fiber. For LPB, virgin fiber is a requirement due to the sensitivity of its liquid applications to impurities. Likewise, the usage of recycled fiber limits the usage of WLC regarding some more sensitive food products. On the contrary, LPB is used for various food packaging applications that cover for example milk and juice packaging. In general, liquid packages are classified into two types. There is the two-sided low density polyethylene coated paperboard, and also a high barrier coated paperboard. The former is used for milk products, while the latter is used for other dairy products, vitamins, etc. Finally, WLC and LPB have a similar grammage, although for WLC the variation is larger, namely, between 200 and 450 g/m^2 versus that of LPB, which is about 300 g/m^2. (Kirwan 2005; Sjöholm 2010)

4.2.2. Base sheet behavior

Base paper impact

In general, the base paper has an impact on both the final properties of the coating layer as well as to the behavior of the deposited coating layer during application, metering and drying. On the contrary, the applied coating method has an impact on the properties which are required from the base paper. Basically, there are a few factors which are demanded from a high-quality base paper: "A good and equal stiffness, no flaws or impurities, and a uniform z-directional structure." (Gustafsson 2011)

Water retention

The water retention of a coating is essential in order to maintain an intact structure of the coated film composite. A too low water retention of the coating means that the water phase will penetrate into the base sheet in excessive amounts, causing drying shrinkage and fiber roughening. Likewise, a too high water retention can also be a problem for the coating, as the consequently too low water penetration can lead into too small interfacial adhesion between the coating and the base sheet. In addition, there might consequently occur problems in drying. Therefore, the target for the liquid is to penetrate in limited, controlled amounts to the base sheet. (Gustafsson 2011) For nanocellulose, the water retention value is typically rather high. In principle, this could be understood to cause low interfacial adhesion between nanocellulose and base paper, although this should be investigated more.

The interaction between water and the fiber network

While water-based dispersion is applied onto the base paper, there are principally two alternative methods by which a base paper can absorb the coating: "The base paper can either absorb the whole coating suspension, or separate the water phase from the solid particles." When the base paper separates the water phase from the solid particles of the coating, the solid particles remain, or deposit, on the surface of the base paper. Consequently, this forms a coating layer. Essentially, the dimensions of pores in the base paper and the dimensions of the particles in the coating suspension eventually determine, which of these alternative methods is prevalent. In addition, the pressure during the

21

absorption of the coating can affect the result. (Gustafsson 2011) Moreover, there are a few theories in the area of wetting and adhesion, namely the theories of adhesion, some of which describe the interaction between the coating and the base sheet. In addition to mechanical interlocking, these theories include the diffusion theory, thermodynamic absorption theory, weak boundary layer theory and the penetration of liquid into porous material. (Kuusipalo and Avellan, 2008) Herein focus will be drawn on the penetration of liquid into porous material, namely the base sheet. In practice, the base sheet absorbs the liquid phase of the coating suspension, which is water in water-based suspensions, to a varying extent depending on the type of paperboard or cartonboard in question, as observable from **Figure 9.** Constituting of fibers, the base paper experiences fiber network deformation, or expansion of fiber network, as a consequence of water interacting with the fibers in the sheet. The extent of fiber network deformation most likely depends on the amount of the liquid phase being penetrated. The behavior which in response to water penetration from coating eventually leads to drying shrinkage of the coated sheet and also to an increase in paper grammage and paper thickness, was reported by Manninen et al. (2011) (Gustafsson 2011). Moreover, fiber network deformation is classified into both intra-fiber deformation and inter-fiber deformation. Intra-fiber deformation includes fiber swelling, while inter-fiber deformation covers de-bonding and stress relaxation, both of which are irreversible changes. More exactly, de-bonding means fiber-to-fiber bond breakage while stress relaxation means internal stress redistribution. The pores in the sheet absorb the liquid phase, which is called inter-fiber sorption, and also by the fibers themselves, called fiber sorption. Finally, the consequent fiber swelling roughens the paper by expanding the fiber network. (Forsström 2009)
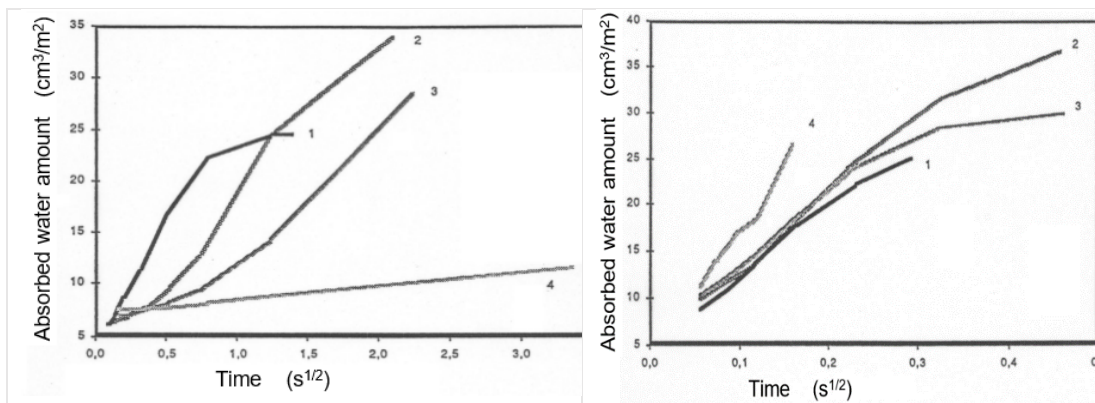
Figure 9. The water absorption rate of a few different paperboard grades in normal pressure (left) and 1,5 bar pressure, meaning 0,5 bar pressure difference to improve absorption (right). (Kuusipalo 2008)

The numbers are:

1) LWC base paper containing refiner pulp
2) SC-paper (supercalendered paper)
3) LWC base paper containing groundwood pulp
4) Hydrophobe sized woodfree paper

The impact of pulp production method in the mill

The preparation method of the fiber in the substrate structure has a considerable impact on the substrate's performance. For instance, groundwood pulp (GW) contains more fines and

shorter fibers than thermomechanical pulp (TMP). As a result, GW provides a denser structure than TMP. (Forsström 2009) Although TMP containing base paper is not displayed in **Figure 9**, the GW content theoretically provides a better water resistance than TMP. Consequently, the substrate structure should remain more uniform after an exposure to moisture, than with TMP. Another example of affecting the substrate's structure is the impact of refining on the base paper structure. The refining of chemical pulp breaks up the structure and surface as well as the fragments of the fiber wall, while simultaneously also increasing fines content. As a consequence of refining, the density as well as the average pore size of the substrate made from chemical pulp is reduced. Therefore, it can be concluded in regard of wood-free paper grades, that a high amount of refining is beneficial in terms of the substrate's water resistance.

Comparison between chemical and mechanical pulp

Regarding the interaction between the base paper and the coating layer, the selection of fiber raw material is essential. In practice, this selection should be carried out with the target to minimize fiber network deformation, and to avoid non-uniformity in the substrate which is one fundamental cause of decreased barrier properties. It was reported, that "swelling was faster for paper containing mechanical pulp than for papers containing a large amount of chemical pulp". Thus, it can be estimated that chemical pulp is less deteriorative to base paper uniformity. Besides, a tendency for spontaneous fiber collapse has been reported with mechanical pulps after pre-calendering. (Linnonmaa and Trefz, 2009) This consecutively suggests, that it would be more beneficial to use a substrate with as much chemical pulp as possible to avoid fiber swelling and thereafter maintain coating uniformity also after applying the coating.

4.3. Pretreatment of nanocellulose

Due to high aspect ratio, branching, and flexibility, micro- and nanofibrillated cellulose (MNFC) fibrils present a high water holding capacity which allows them to form a gel at low concentrations. (Dimic-Misic et al. 2013) The effect of establishing the gel phase is referred to as gelation. In contrast to CNF, CNC does not occur as gel in any concentration. Instead, it occurs as a colloidal dispersion, and eventually as a liquid crystalline material when the concentration of CNC is lowered. This also means that CNF and CNC perform in a remarkably different way considering their rheological behavior. As CNF is used more in liquid state, in this section attention will be drawn solely on CNF or MNFC, which is a combination of microfibrillated and nanofibrillated cellulose.

The purpose of pretreatment

There are two primary ways of producing CNFs: Either by sole mechanical disintegration, or by a combination of chemical or enzymatic pretreatment and the subsequent mechanical disintegration. Homogenization, micro-fluidization and refining are typical mechanical treatments of nanofibrillar cellulose. (Liljeström 2016) As an individual process, the mechanical fibrillation of cellulose fibers to CNFs consumes vast amounts of energy, the values ranging between 4500 and 10 000 kWh/tonne (Nair et al. 2014). Therefore, more economically feasible ways of preparing micro- and nanofibrillated cellulose (MNFC) have been developed. These pretreatments are classified to chemical and biochemical

pretreatments. The two commonly used chemical pretreatments for MNFC are carboxymethylation and TEMPO-mediated oxidation. Likewise, the biochemical pretreatment which is usually used is the enzymatic pretreatment. According to a comparison by Nygårds (2011), it appears that a chemical pretreatment gives higher barrier properties than an enzymatic treatment. This will be covered further in this section. However, in contrast to chemical pretreatments, enzymatic pretreatment has advantages from environmental perspective, since it bases on enzymatic decomposition (Liljeström 2016). This is highlighted by the report, that the two most common pretreatments reported in literature regarding pulp pretreatment, the TEMPO-mediated oxidation and the acid hydrolysis, are considered harmful both to the environment as well as to the worker's health (Tolbert et al. 2016).

TEMPO-oxidation

By definition, TEMPO-mediated oxidation as well as carboxymethylation is an oxidation reaction that introduces carboxyl groups. Thereafter, the carboxyl groups interact with the hydroxyl groups of nanocellulose which are responsible for the inter-fibrillar linkages. Consequently, the linkages are weakened, which indicates as facilitated mechanical fibrillation. (Virtanen 2015; Liljeström 2016) The TEMPO-mediated oxidation also renders the fibril suspension negatively charged (Hubbe et al. 2017). As a result of TEMPO-oxidation, the formed carboxyl groups on cellulose obtain an anionic charge and repel each other. These carboxylic groups also render TEMPO-oxidated nanocellulose even more hydrophilic, while increasing water retention even more (Sjöholm 2010). Furthermore, it is proven that high ionic strength with a sufficient amount of exposure to shear causes severe aggregation in pulp suspensions, leading to an abrupt reduction in barrier properties (Karppinen et al. 2012). By definition, it is likely that TEMPO-oxidation causes severe aggregation to nanofibers, because TEMPO-pretreatment causes high ionic strength to the pulp fibers and nanofibers. Moreover, the side groups used with TEMPO-oxidation appear to have an impact on at least oxygen permeability: the coating of TEMPO-oxidized CNFs with sodium carboxyl groups appears to enhance the oxygen barrier more than with ordinary carboxyl groups. This study by Fujisawa et al. (2011) was conducted by using polyethylene terephthalate (PET) films as substrates. (Nair et al. 2014)

Comparison between carboxymethylated and enzyme pretreated MFC

Both carboxymethylation as well as TEMPO-oxidation, displayed in **Figure 10**, introduce carboxylic groups to MNFC. The air permeability of MFC prepared by two pretreatments, carboxymethylation and the enzymatic pretreatment, were compared as illustrated in **Figure 11**. The study revealed that carboxymethylation decreases air permeability much more than enzymatic treatment. The higher viscosity of carboxymethylated MFC caused that the lowest air permeability was measured within a higher solids content than with the enzymatically pretreated MFC which had a lower viscosity. Nygårds (2011) reported that when the viscosity of a dispersion is too high, the coating coverage usually worsens. This usually also worsens barrier properties. The superior barrier performance of carboxymethylated CNF was most likely linked to the carboxymethylated highly charged nanofibrils, as presented by Nygårds (2011). This originated likely from the high ionic charge or surface repulsion of the carboxyl groups, which maintains the fibrils more apart, thus keeping aggregates from being formed. Likewise, Nygårds (2011) presents that the smaller fibril size of carboxymethylated CNF can explain the higher barrier performance, as compared to enzymatically pretreated CNF.

24

Indeed, the higher barrier would likely be a cause of a lower tendency of the fibrils to aggregate due to lower fibril entanglement, which is in relation with lower fibril aspect ratio. Herein it is assumed that by the term smaller fibril size a reduced aspect ratio has been meant.

Figure 10. TEMPO-pretreated CNF (left) and carboxymethylated CNF (right). (Virtanen 2015)
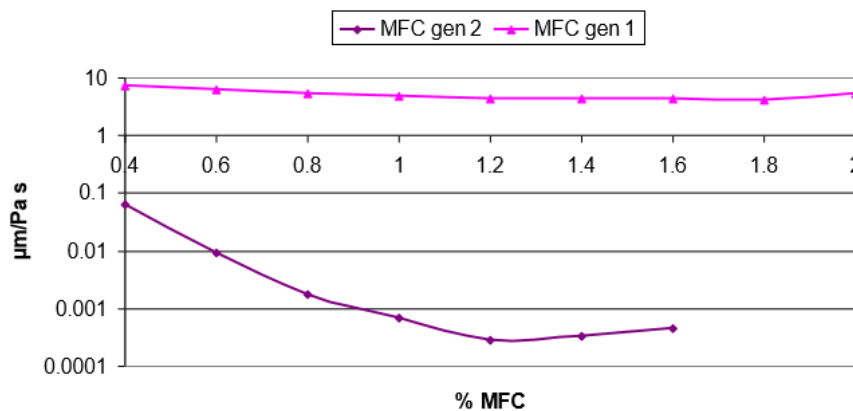
Figure 11. The relation between the air permeability of enzymatic pretreated (generation 1) and carboxymethylated (generation 2) MFC. (Nygårds 2011)

Ionic strength

Ionic strength, which is achieved by chemical treatment such as carboxymethylation and TEMPO-mediated oxidation, causes surface repulsion between fibers. After the fibrils have been fibrillated as a consequence of mechanical fibrillation, the fibrils are still charged because of the chemical treatment. As such, the ionic strength which is obtained, maintains repulsion between fibrils and thus affects to the yield stress which is lowered as a consequence of ionic charge. Therefore, the fibrils need less yield stress to start to flow, also understood as a lower limit of fibril network collapse. However, due to the ionic charge, the fibrils will experience permanent aggregation at some level of shear rate. The greater the ionic strength, the lower the shear rate limit of permanent aggregation. As a consequence of permanent aggregation, the fibril suspension loses its barrier properties to a large extent. (Saarikoski et al. 2012) Conclusively, ionic strength is beneficial in case the shear can be maintained within a low level. At higher levels, the risk of permanent aggregation might be too significant.

4.4. Coating rheology

Rheology is the science of flow and deformation. It is of relevance to understand the flow behavior a.k.a. rheology of the nanocellulose suspension, as the flow properties affect considerably its final quality. In case the rheology before solidification of for example a polymer dispersion coating is in question, rheology is about the flow of colloidal liquid. Likewise, if the rheology of a solid is considered, for instance during the drying phase of a polymer dispersion, rheology is about the deformation of the polymer particles. (Roper 2009) Moreover, in contrast to dispersion coating, both pigment coating and extrusion coating enjoy a broad know-how in terms of their coating rheology, as they have been practiced industrially for decades.

Rheology of microfibrillar and nanofibrillar cellulose suspensions

When talking about degraded cellulose, both nanofibrillar cellulose (CNF) and microfibrillar cellulose (MFC) are commonly being referred to. The difference between the two is rather negligible in terms of their flow behavior, considering primarily the width of their respective fibrils, which for MFC are thicker than for NFC. However, by rheological means both are commonly referred to as microfibrillar and nanofibrillar cellulose (MNFC), most likely in order to highlight the indifference between the two in terms of their flow behavior. Further, for MNFC coating dispersions the viscosity can be a problem already at relatively low volume fractions of nanocellulose (Richmond et al. 2014) and low shear rates. This inherently high viscosity is a challenge in terms of the future industrial implementation of nanocellulose (Lindström and Aulin, 2014). This is explained by the fact that a typical viscosity range for coating dispersions within industrial dispersion coating is between 500 and 1000 mPa*s (Kimpimäki et al. 2008). In practice, high viscosity makes spreading, or the metering, of the coating more difficult. Consequently, the coating might easily result less uniform (Richmond et al. 2014). Therefore, it might prove unavoidable not to reduce the coating solids to achieve sufficient flow properties. (Hubbe et al. 2017) Simple methods of regulating viscosity include the addition of water or centrifugation, since these regulate the solids content, which is directly proportional to viscosity (Grön et al. 2009). In addition, viscosity is inversely affected by temperature (Kimpimäki et al. 2008) and directly by the amount of passes through a refining unit during the preparation of MNFC, as displayed in **Figure 12 a** and **b**.
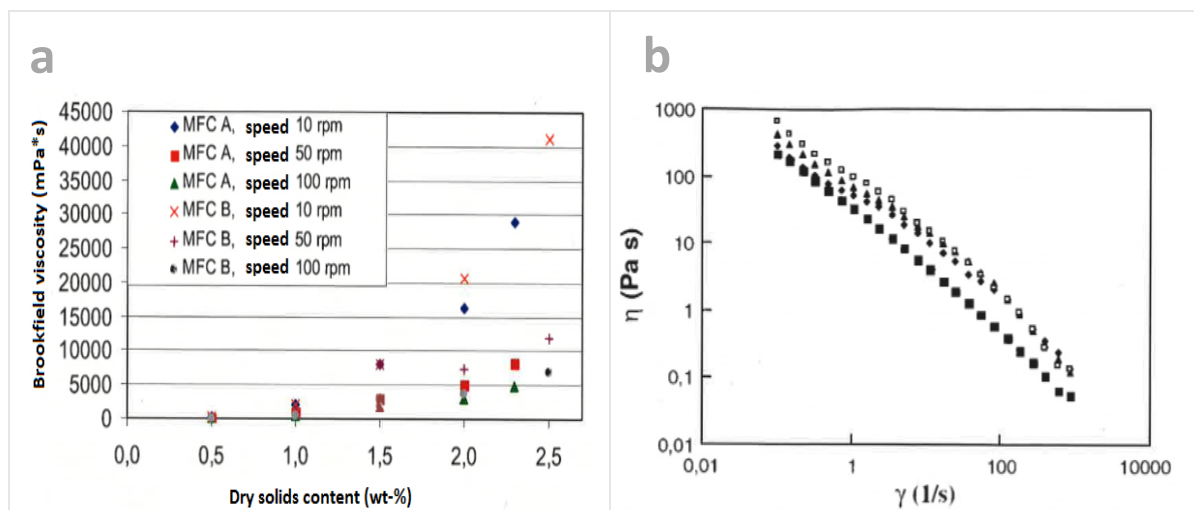
Figure 12. **a)** The dry solids content a.k.a. consistency of the MFC coating was intrinsically relatively high for a typical barrier dispersion coating, while showing a relatively steady increase along with viscosity. **b)** In addition, viscosity was increased by the amount of passes through a refining stage. (Gustafsson 2011)

As displayed in **Figure 12 a**, Gustafsson (2011) evidenced the increase of coating viscosity along with the increase in MFC coating solids content. However, these are very low concentrations when compared to typical solids content of paper coating which can be easily above 50 wt%. Likewise, dispersion coatings have a concentration which is normally between 25 wt% and 70 wt% (Kimpimäki et al. 2008).

Analogy between macroscale and microscale fiber suspensions

It appears relatively ambiguous how well the flow behavior of a pulp suspension that consists of macroscale fibers is analogous to micro and nanoscale fibril suspensions. While comparing the behavior of MFC suspension with pulp suspension, the floc structure is similar, although MFC fibers possess a considerably higher aspect ratio than pulp fibers. An essential similarity between the suspensions is that in both the individual floc size of the fibers/fibrils decreases by increasing shear rate. This is a clear indication that the decomposition of MFC water-suspensions follow the general behavior of macroscale pulp suspensions. (Saarikoski et al. 2012)

Pseudoplasticity

Pseudoplasticity or shear-thinning behavior is common in many coatings and affects coating runnability (Roper 2009). Nanofibrillar cellulose is a water-suspension of nanofibrils. As characteristic for pseudoplastic fluids, the fluid particles, namely, nanofibrils, align or orientate towards the direction of flow. The orientation is the more intense the higher the shear rate. Consequently, when the fibrils are more aligned, the flow is facilitated, as evidenced by the pseudoplastic behavior demonstrated in **Figure 13**. (Gustafsson 2011)
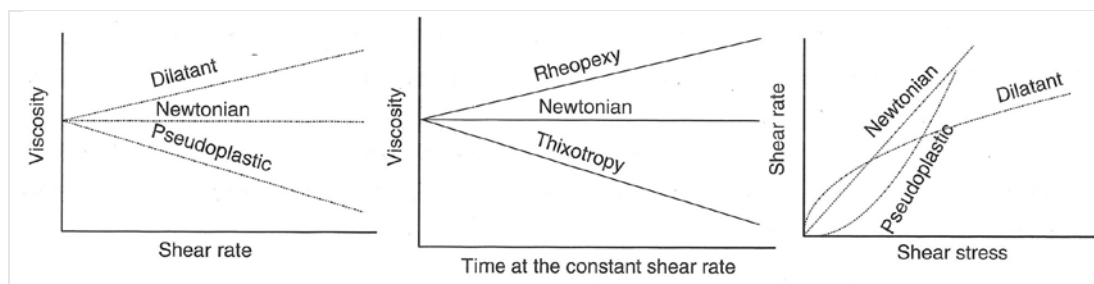
27

Figure 13. Comparison between different types of typical flow behavior. (Roper 2009)

The pseudoplastic nature is basically an advantage for a coating, essentially because the coating should to be applied and metered at high web speeds. For the application and metering to succeed, a high viscosity is preferable. (Roper 2009) Conversely, a dilatant behavior would cause the coating to clog into the pumping system as well as to consume much more energy. Due to pseudoplasticity and the intrinsically high viscosity of nanocellulose, within industrial scale the solids content of nanocellulose suspension should not exceed about 2 wt% in order to avoid clogging of pumping systems (Dufresne 2013), as well as to avoid a challenge with standard equipment when coating at high web speeds (Richmond et al. 2014). Moreover, apart from pseudoplastic MNFC suspensions are also thixotropic. A thixotropic fluid exhibits a decreasing viscosity as a function of time within constant shear rate. However, it appears unclear whether thixotropic behavior has any benefit in terms of coating dispersions.

Viscoelasticity of nanocellulose

Nanocellulose suspensions are elastically dominated at rest and in the low shear rate range, between 0 and 1000 s^{-1}. The relation between storage modulus G' and loss modulus G'' (CONFIRM) is a good indicator of viscoelasticity: when the ratio is in favor of storage modulus, the suspension is elastically dominated, and vice versa. In microscale, the fibrils are interlocked in such a way that they respond elastically to induced shear. In terms of MFC suspensions, whenever their solids content is above the gel point (above about 0,5 wt%), they form a gel at rest. When sheared, this network structure first deforms elastically. In practice, this means that the loosened flocs start to flow in chain-like formation. However, at this stage the flow behavior is yet elastically dominated (Karppinen et al. 2012). When shear rate is increased even more, the flocs, having formed at rest, break apart from each other into smaller and smaller flocs along with increasing shear rate. (Saarikoski et al. 2012) Simultaneously, the viscosity decreases although so does elasticity.

Yield stress

The strength of a nanofibrillar network can be referred to as the yield stress. It depends on the relation of local volume fraction and the gel point of a fibril suspension (Dimic-Misic 2015). The idea of yield stress is easier to understand by an example of for instance a ketchup bottle: when holding the bottle upside down and letting the content flow to the opened die, the ketchup suspension does not drip out until a certain amount of ketchup is forced out by squeezing the bottle enough. Likewise, the yield stress of a fibril network maintains the fibril suspension at rest until the induced shear reaches the yield point. At this point, the fibril network collapses from its weakest point, presumably between the flocs that form the network. Simultaneously, weak forces are overcome by hydrodynamic forces typically

occurring during flow. (Virtanen 2015) This leads into an elastically dominated flow behavior. The fibrillar network bonding before and after network collapse is illustrated in **Figure 14**.
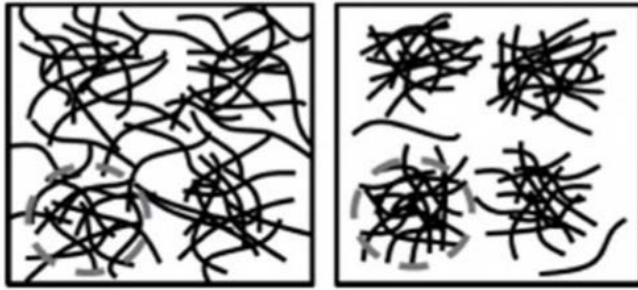
Figure 14. a) Fibril network at rest. **b)** A collapsed fibril network with flocs flowing freely after exceeding the yield stress limit while achieving a specific shear rate. (Karppinen 2014)

Agglomeration of fibrils

By agglomeration, one describes the phenomenon of fibers or fibrils to entangle, which produces small bundles of these fibers or fibrils. In general, these bundles are referred to as agglomerates. The content and size of agglomerates depend on shear rate and solids content. If the agglomerate is capable to disentangle, this agglomerate can be called a floc, being a consequence of flocculation, which is a reversible effect. In contrast, if the agglomerate is irreversible then it is called an aggregate, being a consequence of aggregation which implies the fibrils cannot disentangle. At times, the irreversible nature of aggregation is highlighted by referring to permanent aggregation. (Saarikoski et al. 2012; Dimic-Misic 2015) Furthermore, while the fibril network collapses, it produces flocs which are displayed both as increased floc diameter and shear stress as a function of shear rate. This trend is displayed in **Figure 15**.
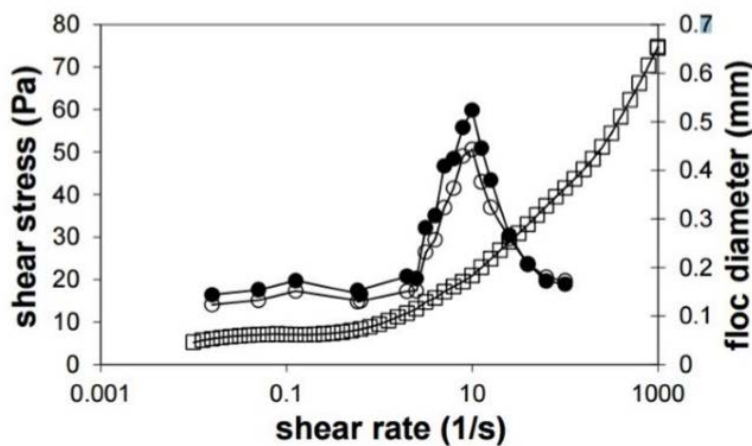
Figure 15. The effect of flocculation on shear rate and floc diameter displays as a momentarily increased floc size and shear stress, while increasing shear rate. The flocculation effect occurs typically right after the fibril network collapse when exceeding the yield stress limit. (Saarikoski et al. 2012)

Compression and voids

While increasing shear rate, the fibril suspension experiences compression, which consequently induces voids (Saarikoski et al. 2012). Further, according to Richmond et al. (2014), nanocellulose dewatering rate increases with increased solids content. Moreover, the increased dewatering rate could be explained by more voids occurring while increasing solids content. However, this hypothesis would presume that an increase in solids content provides more internal compression inside the suspension, which is unconfirmed to my knowledge. In **Figure 16**, the effect of compressive stress into an individual fibril is demonstrated. For comparison, a fibril experiencing tensile stress is also illustrated (Dimic-Misic 2015).
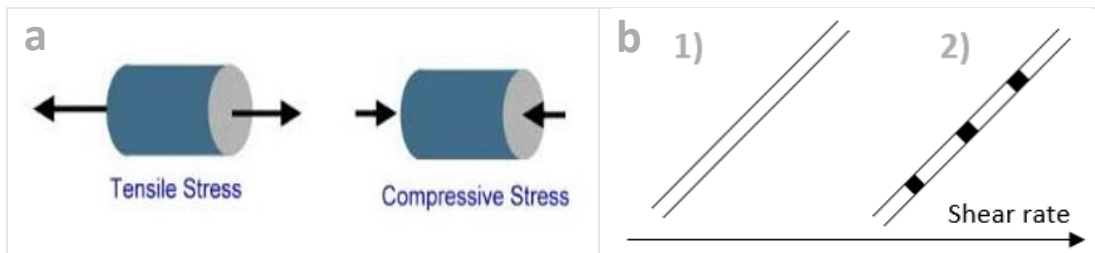
Figure 16. a) The impact of tensile stress (left) and compressive stress (right) into a fibril. (Dimic-Misic 2015) **b)** The presumed impact of compressive stress into a polymer chain with low shear rate (1) and increased shear rate (2). The black areas resemble voids that emerge parallel to the direction of greatest compression, when the fibril is "being pulled" more. The direction of greatest compression is parallel to the polymer chain. (Saarikoski et al. 2012)

Extensional viscosity

Whenever there is a sudden change in geometry, extensional viscosity has an impact on the fluid flow. In practice, it extends the polymers of the suspension exposed. (Roper 2009) In regard of the rod coater, the wire wounds form gaps in between each other in such a way, that they create cross-sections that allow the coating to pass through. During the passage through the limited inlet, extensional viscosity can be suspected to occur. In addition, polymer chains in the suspension are expanded in the suspension during extensional viscosity (Sjöholm 2010). This is illustrated in **Figure 17**.
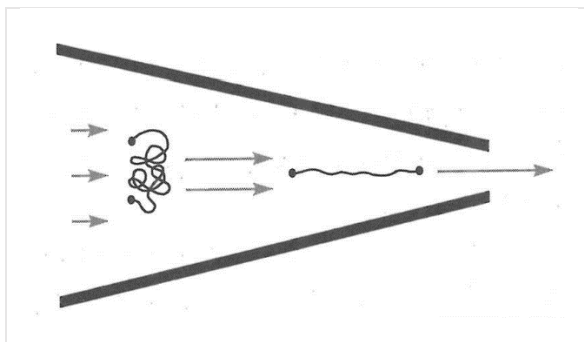
Figure 17. In this example, the converging nip is forcing the fluid to experience extensional viscosity, as indicated by the motion arrows and the extended polymer chains. (Roper 2009)

5. Coating process

In addition to the coating and the substrate variables, the third factor that defines a coating procedure entails the coating method/process and the coating circumstances. All the three factors have an impact on the final barrier, release and sealing properties of the final end-use product. The coating process involves the application of a coating suspension onto a porous surface in such a way, that the coating solids will convert into a film that adheres to the surface, meaning the substrate beneath. (Kimpimäki and Savolainen, 2015)

5.1. Industrial coating

Coating methods today – Plastic, metals and glass

Industrial packaging today includes mainly the usage of plastics, such as PE, metals and glass. There exist mainly three different metals which are more commonly used: Steel, tin and aluminum. Aluminum is commonly applied as coating for many esoteric food products that require high barrier protection. Indeed, aluminum offers not only high barrier but "total protection" against such effects as sunlight, moisture, temperature variations, high pressure, gas and grease, which consecutively provide aluminum packages very long shelf-lives. Likewise to aluminum, glass is commonly used for the conservation of beverages. In addition, glass also provides total protection for most of the abovementioned effects. However, both glass and aluminum have the drawback of high energy consumption during their manufacture, which is not considered environmentally friendly. (Sjöholm 2010)

Two alternative production line setups

There exist both on-line a.k.a. in-line, and off-line coating methods. The terms indicate the formation by which the process devices have been joined together within a process line. Both of these schemes have their advantages and disadvantages. Eventually, the decision of the more suitable one depends on the desired production rate and quality: In case production rate is more important, the on-line coating method is preferable, whereas in case production quality is more important, the off-line coating method is more convenient. Even though production rate is highly appreciated, in the coating industry the off-line coating method is nowadays more common. (Kimpimäki et al. 2008)

5.1.1. Dispersion coating

Dispersion coating is a relatively novel area of coating methods, which still today finds relatively small use, although projects such as that of Kotkamills® ought to be changing the situation. Nevertheless, the demand considering e.g. the barrier performance of dispersion coatings is increasing due to improved environmental awareness, more stringent environmental legislation, and also enhanced barrier properties of upgraded fiber-based packages. The applications in which preparation dispersion coated film composites can be used include many disposable products, such as wrappings, sacks, food and nonfood packages, and bakery products, to name a few. (Sjöholm 2010) In brief, dispersion coating bases normally on the application of a latex onto the surface of a base paper or base board, after which the coating is applied and metered. Styrene butadiene and acrylates are the most common synthetic polymers used for barrier coating (Kimpimäki et al. 2008). It is also

31

common in the coating stage to coat two thin layers instead of one thick layer. Subsequently, a non-porous layer exhibiting high barrier properties is formed as a consequence of water evaporation during the drying stage.

Comparison to paper coating

Although very similar to paper coating a.k.a. pigment coating in regard of its applied technology, the main difference between pigment coating and dispersion coating is the intention. In pigment coating, "the smoothness and stiffness of the surface are improved, the absorption of ink and dusting is reduced and gloss, opacity and possibly also lightness increase". In contrast, in dispersion coating as well as in extrusion coating the target is rather to block or prevent different materials of penetrating through. (Sjöholm 2010) Furthermore, a typical coat weight of dispersion coatings is between 4 and 15 g/m^2, whereas a typical solids content is between 25 wt% and 70 wt% before the drying stage. The viscosity of a typical dispersion coating is between 500 and 1000 mPa*s and the density is roughly 1 kg/dm^3 in case no fillers are added. Nevertheless, clay, talc or calcium carbonate might be added to enhance both optical properties, barrier properties as well as coating runnability and thereafter also cost effectiveness (Andersson et al. 2002). (Kimpimäki et al. 2008) On the contrary, in pigment coatings, the flow properties are controlled by adding fillers in amounts well above the critical pigment volume concentration (CPVC), whereas in barrier dispersions the amount of fillers added is well below this level. The CPVC is "the point where the binder concentration is just sufficient to fill the interstitial voids between pigment particles." Moreover, investments on dispersion coating are promising in regard of environmental awareness, although the use of biopolymers in dispersion coatings has not been implemented to date to my knowledge. The problem with many biopolymers are their relatively low moisture barrier properties compared to the already existing polymers, such as LDPE. In addition, biopolymers usually have a high price. However, possible applications for dispersion coated biopolymers could include liquid and aseptic packages, where the dispersion coatings would function as a primary layer. (Sjöholm 2010)

Comparison to extrusion coating

Regarding the comparison to extrusion coating, dispersion coating has a few advantages. One is that neither the operational speed nor operational width is limited. This is due to the usage of an on-line coating method instead of an off-line coating method, which requires a separate coating unit. Another advantage in the favor of dispersion coating is the environmental aspect: The price difference between dispersion coatings and extrusion coated polyethylene has been reduced, such as that of low-density polyethylene (LDPE), as a consequence of environmental fees of these plastics. However, barrier dispersions are yet much more expensive than polyolefin resins, not to forget that the latter are highly amenable for different end-uses. (Kimpimäki et al. 2008)

5.1.2. Pigment coating

Pigment coating, a.k.a. paper coating, is principally very similar to dispersion coating: The only remarkable difference is in the target (Kimpimäki et al. 2008). Therefore, pigment coating will be covered herein only briefly. In pigment coating, the demanded properties relate usually somehow to the outlook of the coating, such as printability, gloss, etc., while with barrier dispersions the demanded properties cover the functionality, which means the

blocking capability or the barrier properties of the polymer film. The functional properties require good uniformity and coating coverage, which are related to a diversity of other properties, such as adhesion and wetting. Furthermore, the main component in paper coating is the coating color. The amount of water it should contain is restricted based on the flow property requirements. In a coating color, the dry content can reach as high as 70 wt%. (Lehtinen et al. 2009) In addition to coating color, synthetic co-binders and thickeners are typical for paper coatings, and are used to adjust rheological properties and water retention. The rheological properties are modified in order to fulfil the final performance requirements, and the flow behavior is governed by both the internal attributes of paper coatings which are defined already early in the coating preparation, and also by the attributes which are brought to paper coatings by rheology-modifiers, such as co-binders and thickeners. Nevertheless, the effect is often different for low-shear viscosity and high-shear viscosity. In addition, co-binders and thickeners have a varying effect on water retention. (Hanciogullari 2009) One example of a bio-based co-binder for paper and paperboard coatings is soy protein, which was covered more in Section 3.1.2. Furthermore, the drying phenomena of pigment coatings can be suspected to be relatively different from those of nanocellulose coatings due to many different characteristics.

5.1.3. Extrusion

Extrusion coating

Since 1950s, extrusion coating has expanded to the packaging field, although it was not until the 1960s when extrusion coating expanded to the liquid packaging sector. Before that, the liquid packaging sector was handled by an earlier method, namely, the wax-impregnating method. In extrusion coating, molecular weight regulates viscosity, which is an essential factor distinguishing extrusion coating from paper coating and dispersion coating. In addition, the extrusion coaters use a broader range of polymers than dispersion coaters. These polymers include many polyolefins such as LDPE, copolymers, barrier polymers such as EVOH, etc. Besides, glass transition temperature, melting temperature and degradation temperature are important. Nonetheless, as in dispersion coating, the target is to produce a coating with high liquid and gas barrier properties. In brief, the basic mechanism of extrusion coating is the transfer of a thermoplastic polymer from a solid to a melted state, and secondly the compression against a substrate or web. This is illustrated in **Figure 18**. The compression against the substrate is achieved by using a high pressure in the die. (Kuusipalo et al. 2008)
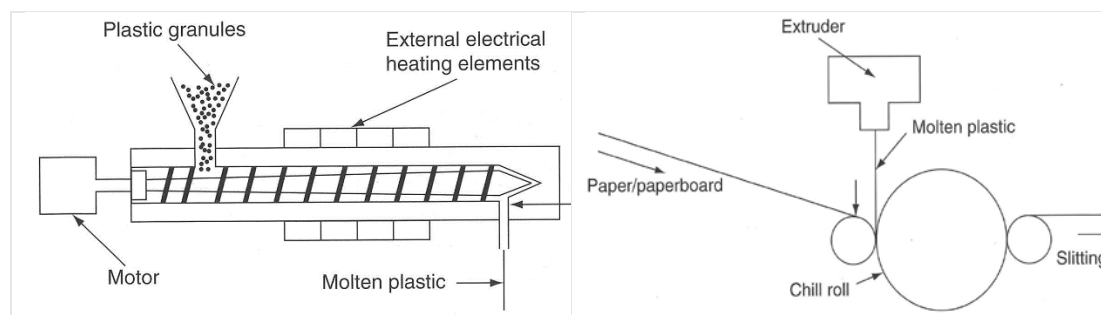

Figure 18. Plastic extruder (left) and extrusion coating of paper or paperboard (right). (Kirwan 2005)

Extrusion lamination

Extrusion lamination is similar to extrusion coating. Whereas in extrusion coating only one web is used, in extrusion lamination two webs of substrate, usually paperboard, are adhered together by molten plastic. This follows the basic criteria of a laminate, meaning the convention of joining together two functional layers with an adhesive. In practice, the laminator nip presses together the two separate webs and the molten plastic film. (Kuusipalo et al. 2008)

5.2. Coating methods

The coating operation forms perhaps the most essential sub process of the coating process. In addition to the subsequent drying, it primarily includes two essential unit operations: Application and metering. However, in some coating operations the metering of the coating can also be carried out prior to the application of the coating, in the case of which the referred unit operation would be "pre-metering" (Forsström 2009). In industrial scale dispersion coating, the objective is to produce a uniform film with an even coating thickness on top of a paper substrate. Hence, after unwinding the paper web, the industrial coater unit must be able to conduct several sequential unit operations: Apply the coating, meter and dry the coating, and finally quench the coating to avoid sticking onto the paper before rewinding the coated paper web, as shown in **Figure 19**.
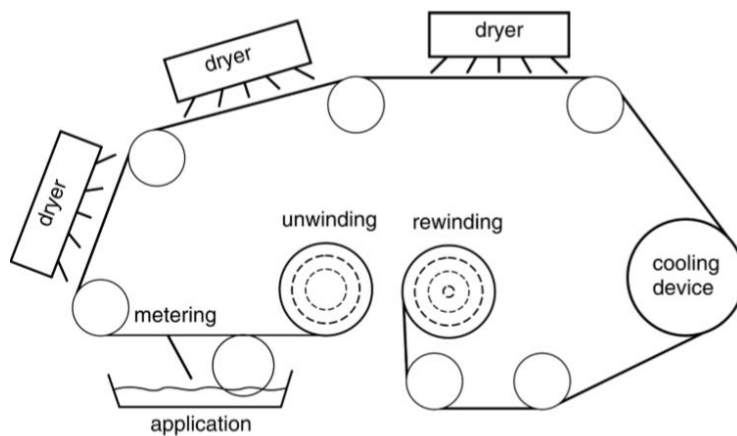
Figure 19. In industry, the coating operation is a sub process consisting of several sequential unit operations. an industrial dispersion coating line. (Kimpimäki et al. 2008)

Rod coating

Rod coating, a.k.a. bar coating, is principally similar to blade coating: Instead of a blade, the metering unit is a rod a.k.a. a bar. In principle, the rotating rod, being held in a plastic holder, wipes off the excess coating from the web surface similarly as with a blade coater. By definition, the wiping off is denominated as metering. While touching the surface of the web being rolled, the rod meters the shortly applied coating onto the web. While in contact with the web, the rod meters a coating with a coat weight that is proportional to the cross-sectional area of the grooves circulating the rod (Kimpimäki et al. 2008). In addition to the groove cross-section, which can also be indicated by the wire diameter, also other parameters affect the final coating quality: The rod metering speed has a varying impact on

coat weight, while rod pressure has a decreasing impact on coat weight. More exactly, the rod speed effect on coat weight depends on the diameter of the grooves, or the wire circulating the rod. In case the diameter is small, the rod will not induce much hydrodynamic forces, while with large groove diameters the grooves will create notable hydrodynamic forces in the coating suspension during rod movement. In essence, the hydrodynamic principle is used to operate a smooth rod. (Linnonmaa and Trefz, 2009)

Blade coating and air-knife coating

Blade coating produces a web with a coating with an even surface: The coating itself is very smooth. However, the web beneath is usually a bit rougher, which is why the coating thickness will most likely result uneven. In blade coating, the principle is to meter the coating by using either of the two optional metering devices, the bent blade or the beveled blade. Having an adjustable angle, the bent blade is more adjustable according to desired specifications relating to coating thickness. In contrast, the angle of the beveled blade is fixed, thus making the beveled blade less adjustable to specifications. Moreover, the bent blade is more suitable to high coating thicknesses, while the beveled blade is more suitable to low coating thicknesses, most likely since the low thickness results more even with the beveled blade. The air-knife, a.k.a. air doctor, is a metering unit floating slightly above the web which is intended to coat. The uniform coating produced by the floating air-knife is optimal as a barrier coating: While the blade coating method produces an even surface, the air-knife produces an even coating. The difference between the two concepts is explained in **Figure 22**. The *air-knife coating* method is ideal for products which need to be coated without any contact with the coating device, due to for instance the corrosiveness of the product. The air-knife produces typically a coating which can very accurately conform the rough surface of the web. (Kimpimäki et al. 2008)

5.2.1. Curing of nanocellulose

Some method involving heating and drying is often useful in order to enhance some desired properties of the end-use product containing nanocellulose. These methods also form the final step in the preparation of a nanocellulose film. In terms of nanocellulose, the methods of heating and drying appear to be commonly known as *curing*. Some curing steps include *heating* or photo-initiation, with the target of initiating chemical reactions which cure the films. For example, while applying heat treatment, Österberg et al. (2013) reported an increase in water-resistance of films prepared from nanofibrillated cellulose. It was noted therein that wet strength of the NFC films improved by heating. This effect could have originated from coalescence of adjacent cellulosic surfaces, an effect sometimes termed "aggregation" of the nanocellulose fibrils. (Hubbe et al. 2017) This is also similar to the drting behavior of polymer particles in dispersion coating: At higher temperatures, polymer particles pack more tightly due to deformation induced by heat, which eventually leads to improved barrier properties (Kimpimäki et al. 2008). Heat treatment, implicating the procedure of drying in elevated temperature, has reportedly had a beneficial effect on both oxygen barrier, water barrier and water vapor barrier of nanocellulose films (Nair et al. 2014). The reducing effect of drying in elevated temperature on water vapor transmission is also reported by Kimpimäki et al. (2008) when considering polymer particles of a dispersion coating. The behavior is displayed more in detail in **Figure 19**.
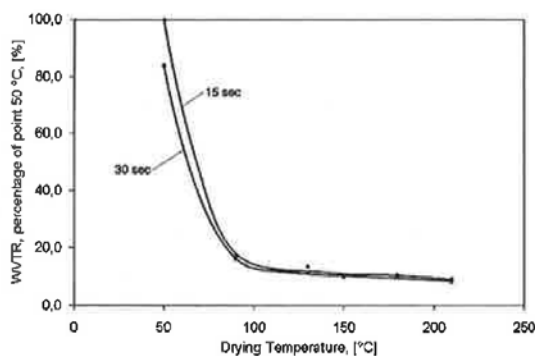
Figure 19. The effect of drying temperature on WVTR while heat treating the polymer dispersion coated film composite while using very short exposure times. (Kimpimäki et al. 2008)

As displayed in **Figure 19**, the WVTR of the exposed polymer dispersion coated films decreased considerably by only a very short exposure to elevated temperature (Kimpimäki et al. 2008). Likewise, in a study by Sharma et al. (2014) the water vapor permeability of CNF films was reduced by 50% as a consequence of heat treatment at 175℃ for 3 hours, as compared to untreated CNF films. Nonetheless, it was also found that wax coating further enhanced the obtained water-resistance. Moreover, the usage of UV-light to cure nanocellulose is described by patents by Bai et al. (2015a,b) and Schade et al. (2015), not to forget also gamma radiation employed by Fernandez et al. (2008). (Hubbe et al. 2017) All of these treatments, the heat treatment and the light treatments, are already used in the drying stage of paper coating processes, although therein infrared light is usually used instead of UV-light or gamma radiation (Linnonmaa and Trefz, 2009).

Drying shrinkage and fiber roughening

Drying shrinkage, which is typical for nanocellulose as it exhibits a very high swelling capability, is an unwanted phenomenon in terms of coating. According to Gustafsson (2011), drying shrinkage, and to a lesser extent also fiber roughening, are responsible for fiber network deformation causing a loss of dimensional stability. Manninen et al. (2011) stated that drying shrinkage is the cause of fiber expansion which appears as increase in coat weight along with increase in the amount of applied water. In addition, this effect appearing as coat weight increase is even more apparent with high water contents. Consequently, the expansion shows as increased paper thickness and apparent coat weight. The coat weight is apparent, because the increase in coat weight is mostly due to the water increasing paper grammage instead of the actual dry solids of the coating in question. (Gustafsson 2011) By comparing **Figure 20** with **Figure 21**, it is observable that in the research by Gustafsson, coating by MFC actually decreases the additional weight caused by water expanding the fiber dimensions of the base sheet. However, there ought to be still impact from penetrated water that increases the actual coat weight of MFC dry solids.
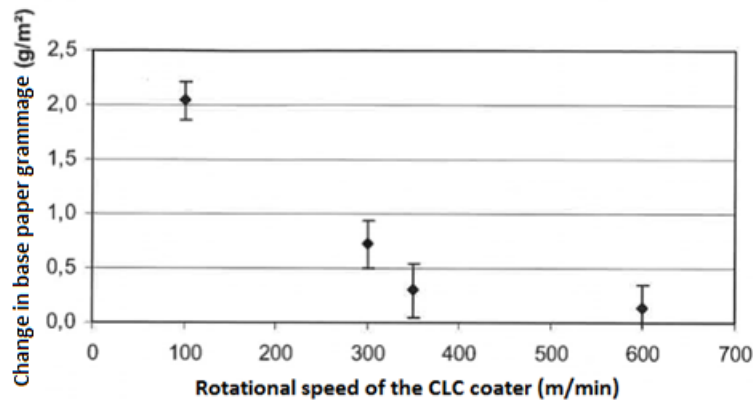
Figure 20. The grammage difference to the original base paper dimensions after applying pure water with different rotational speeds of the cylindrical laboratory coater. The test already indicated a considerable increase in the base paper grammage induced by water. (Gustafsson 2011)
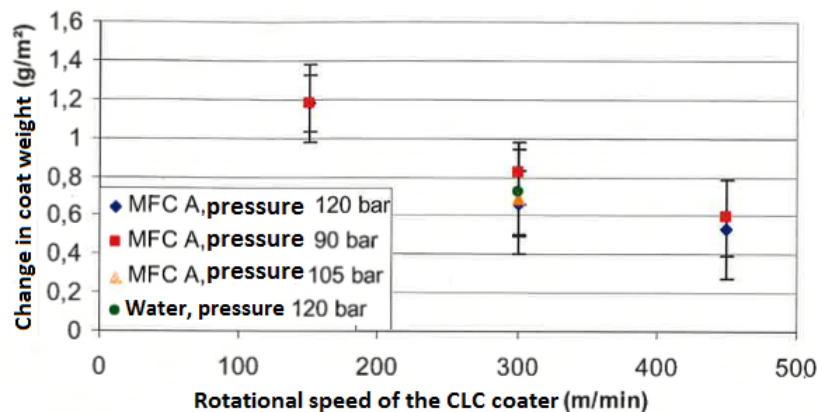
Figure 21. Application of 2,5 wt% MFC coating suspension reduced the difference in paper grammage when compared to the effect of applying pure water, most likely because the MFC fibrils restricted the effect of drying shrinkage and fiber roughening. (Gustafsson 2011)

5.2.2. Advantageous and deteriorative properties

There are a few fundamentally advantageous properties regarding a coated film composite that are beneficial to be controlled or monitored during the coating process. There appear to exist some flaws that might occur either during the coating process or during the storage of the final product.

Glass transition temperature

The glass transition temperature is the temperature of a polymer where a phase change occurs from hard and brittle (glassy state) to soft and ductile (rubbery state). It is probably one of the most important characteristics of a polymer, as it has connections to several other properties. (Dufresne 2013) Regarding coatings, the glass transition temperature has an impact on the minimum film formation temperature (MFFT) of thermoplastics, as well as to heat sealing and blocking. Polymers used in barrier dispersions typically have a glass transition temperature between 10°C and 40°C. The carboxylation degree and the monomer

ratio of a polymer dispersion change the glass transition temperature. (Kimpimäki et al. 2008) According to Lagaron et al. (2004), glass transition has a connection to gas permeation through a solid film. Herein, a high T_g value represents an immobile nature of molecular segments. Thus, a high glass transition temperature would provide hint of a good gas barrier. (Hubbe et al. 2017)

Runnability

Two advantageous as well as very fundamental properties related to the coating process cover the coating runnability and the coating uniformity. Runnability is a property which describes the ease of web progression. In each coating process, the web is the base paper or base board which proceeds from pre-metering to post-metering and to coating consolidation. Runnability covers many attributes, the product of which the runnability is. In practice, good coating runnability requires a low-shear viscosity between a specific range in order to enable pumping, a convenient high-shear viscosity to regulate the coat weight by metering and also to ensure adequate water retention of the coating. (Forsström 2009) As stated previously, there are many ways to regulate coating viscosity which depend on the coating method used. However, the addition of latex appears to be often a good way to regulate coating viscosity and thereafter the coating runnability.

Uniformity

Likewise to runnability, the uniformity of a coating appears to be a holistic concept that could for example mean an equal thickness between the surface of the substrate and the surface of the coating, as well as many other things which finally derive from the homogeneousness of the coating and the smoothness of the base sheet underneath. Moreover, usually a good coating uniformity goes in hand with a good coating holdout. At low coat weights, a good coating holdout means that the coating is distributed throughout the base sheet, whereas at high coat weights it means that the mass distribution of the coating on top of the base sheet is uniform. One example of the significance of uniformity relies on the z-direction of the base paper. By definition, the z-direction determines, together with the surface properties of the base paper, the coating holdout and the coat weight variation or coat weight uniformity of the subsequently coated film. (Forsström 2009) In contrast to uniformity, *evenness* appears a more precise quantity. Basically it means the flatness of a coating surface, as illustrated in **Figure 22**. This could as well be understood as coating distribution or coating coverage. However, evenness can also be expressed in even more ways.
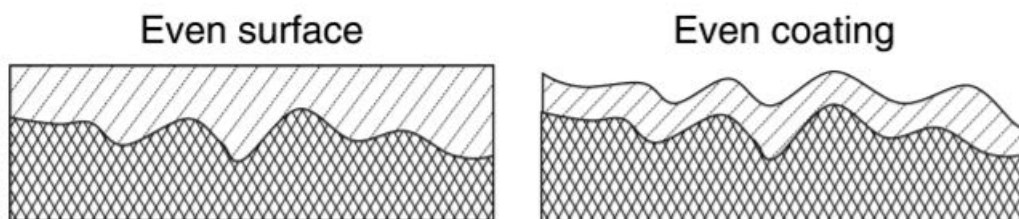

Figure 22. An even surface is a flat surface which leaves the coating thickness uneven in case the substrate is not completely flat and evenly absorbent. However, an even coating means an even thickness. The former is a typical result of blade metering, the latter of air-knife metering. (Kimpimäki et al. 2008)

Pinholes

Pinholes are small holes that have propagated through or almost through a film. In the case of coatings, the risk of pinholes most likely concerns only the coating film itself, that is, not taking the reinforcing substrate into account. Nonetheless, defects of the coating layer should be enough to deteriorate the barrier properties of the coated paper as a total, because the base paper or base substrate usually provides rather modest barrier properties, thus allowing leakage to occur. Leakage, consecutively, is "the rate at which a gas or vapor passes through a film by using defects, such as pinholes, or cracks". Likewise, in addition to pinholes, defects can be considered as "small cracks or channels on a microscopic scale". In addition, the flow through pinholes can be much higher than the diffusion flow. Furthermore, in laboratory scale, the amount of pinholes can be tested for instance by "applying a thin layer of test liquid on a sheet of paper and counting the marked spots after a specific time", as presented by Andersson et al. (2002). This could be useful in predicting the occurrence of pinholes already in laboratory scale or pilot scale testing, before proceeding to industrial scale. (Kuusipalo et al. 2008)

Blocking

Besides pinholes, another deteriorative property which occurs typically within the coating process is referred to as blocking. In practice, it is the effect of a coating surface adhering to the back side of the adjoining substrate layer. This implies that it usually occurs when the web is winded. Blocking is recognizable from a faint cracking noise it produces. It should be avoided as it is an irreversible effect which might destroy the coating, reduce its barrier properties and harm the subsequent unwinding of the coated web in question. Moreover, although the level of blocking depends on exposure time, blocking can occur at any time after winding within a time scale from a moment till weeks. A late occurrence of blocking is more probable if the coated rolls or sheets are exposed to unfavorable conditions regarding temperature, pressure and humidity during transportation and storage. However, blocking is possible to prevent by using minerals or plastic pigments. Nevertheless, these materials are often primarily used to enhance gluability or printability of the coated products. (Kuusipalo et al. 2008)

6. Disposal

In general, biodegradability is referred to as the capability of material to decompose totally by natural organism (Doroudgarian 2011). The decomposing natural organisms mostly entail bacteria, fungi, yeasts and algae. That is, these organisms return the material to the carbon cycle after their consumption of the material. (Plackett 2011) In contrast, a degradable polymer is referred to as decomposable in virtually any way; by either chemical, physical or biological means. The rate of material decomposition is affected by both chemical and also mechanical characteristics of the respective material. For instance, a larger surface area as well as exposure to correct enzymes can accelerate degradation (Doroudgarian 2011). A simple way of measuring biodegradability is by hydrolysis using enzymes. (Seppälä 2005)

Barrier dispersion coatings can be fully recycled. This is the baseline behind their development. (Kimpimäki and Savolainen, 2015) However, it is challenging to provide such a bio-based material that possesses sufficient mechanical properties to withstand storage and

use, yet being capable to biodegrade within a reasonable time scale after use. Likewise, "Degradability can on one hand constrain biopolymer applications to short term use, while on the other hand facilitate composting of spoiled food." (Doroudgarian 2011) Regarding polymer dispersion coatings, the most probable ways of disposal would be either to incinerate or to dispose them in a landfill. The benefit of incineration is, that the biodegradable content can be combusted as energy, although burning is not recommended if the barrier dispersion contains chlorine in any form (Kimpimäki and Savolainen, 2015). In contrast, traditional disposal in a landfill does not offer any additional value regarding recyclability. Moreover, dispersion coated barrier products are in general "more easily re-used than typical extrusion coated applications" (Kimpimäki and Savolainen, 2015). This originates from their more facile re-pulping compared to plastic, such as extrusion coated LDPE. In contrast, plastic film coated products do not repulp easily because of the accumulation of small pieces of plastic. Besides, plastic film coated products neither are compostable. (Kimpimäki et al. 2008)

In terms of recycling, there exist distinct opinions about the repulping capability of polymer dispersion-coatings: about whether they should be recycled or not by returning them to the pulping process, after which they would be utilized as fiber raw material. The undergoing debate is due to perceptions about some deleterious effects the recycling might cause to the wet-end chemistry of kraft paper processing. However, there has been no prove for such flaws to actually occur. (Kimpimäki et al. 2008) This could suggest, that the repulping capability of polymer dispersion coatings is sufficient. In addition to recycling, incineration and simple landfilling, composting is another form of disposal. Considering the biochemical conditions during composting, it is essential to expose the material to the correct enzymes which can selectively biodegrade the respective material. In microscale, the degradation reaction requires a close contact between the enzyme and the main chain of the degradable polymer. (Doroudgarian 2011)

7. Summary

On the surfaces of bio-based polymers there typically exist a high content of free hydroxyls, which make these polymers polar. As a rule of thumb, like dissolves like. This means that bio-based polymers are typically good air and gas barriers, although their moisture resistance is typically only within a satisfactory level.

There is a remarkable challenge while heading towards what could be referred to as a paradigm change of packaging films, which calls for the replacement of oil-based polymers, possessing an unparalleled moisture barrier, with bio-based polymers which exhibit only a modest moisture barrier. Besides, the high quality-grade of oil-based polymers ought to provide additional challenge in their displacement, or the implementation of this paradigm change. Nevertheless, there are several ways to reduce the difference in moisture barrier, or to prevent water or water vapor from deteriorating barrier properties of a bio-based polymer coating. These methods include chemical modification of the surface of the coating, such as acetylation (Nair et al. 2014), or sizing by either a surface size or by a hydrophobic internal size (Paltakari and Lehtinen, 2009). Water resistance is important not only in terms of the coating itself but also in terms of the base paper, which dimensions expand while experiencing structural deformation as a consequence of water penetration

from the coating (Forsström 2009). As reported by Manninen et al. (2011), this kind of water exposure demonstrates as a higher grammage and thickness of the base paper. However, water retention of a coating suspension can also be too high, which would indicate as insufficient adhesion into the base paper (Gustafsson 2011). Nevertheless, the base paper quality has an essential role on how much water gets penetrated into the paper. In addition to the amount of size, the base paper quality mainly derives from the relation between virgin and recycled fiber, the relation between chemical and mechanical pulp, the fiber aspect ratio or the relation between hardwood and softwood as well as the degree of pulp refining.

In contrast to water molecules, bio-based polymers typically repel permanent gases existing in air, because the gases are non-polar and thereafter do not bond with the free hydroxyls on the surface of bio-based polymers. Therefore, the air and gas barrier of bio-based polymers is typically much more competitive while comparing to oil-based polymers. However, the modest moisture resistance of bio-based polymers tends to reduce their air and gas barrier rather abruptly in case the ambient relative humidity exceeds a certain limit. This considers evidently MFC, which oxygen permeability increases drastically around 70 % RH (Gustafsson 2011). Regarding the oil barrier, Aulin et al. (2010) presented that oil absorption is somewhat predictable from the behavior of oxygen permeability. This is reasonable also in terms of the polarity rule about like dissolving like, since oxygen as a permanent gas is nonpolar, as well as oil. Moreover, poor oil resistance and consequent leakage might easily deteriorate other barrier properties as well, not to forget mechanical properties.

A coated film composite consists of a coating and a base sheet which is typically of paper or board. In addition, a coating process combines the coating with the base sheet in a convenient way. The coating process includes the application and metering of the coating, and also the drying or consolidation of the coating, the latter of which in terms of nanocellulose is referred to as curing (Hubbe et al. 2017). Moreover, these unit operations and sub processes can be implemented in varying ways depending on the coating process. The options for a sub process appear to be constrained depending on whether extrusion, pigment or dispersion coating is used as the coating process. In addition, the process line can be either an on-line a.k.a. in-line process or an off-line process, depending on the desired quality-grade or cost-effectiveness.

The properties of nanocellulose coated film composite can be modified prior to the coating operation, after the coating operation, or during the coating operation. Considering modification prior to the coating operation, some options include 1) pretreatment of nanocellulose, 2) The selection of coating components, 3) surface sizing / hydrophobic internal sizing, 4) pre-calendering. Considering modification after the coating operation, some options include 1) drying in elevated temperature, 2) calendering, 3) hot-pressing, and 4) filtration using a wire.

- Prior to coating operation
    1) Regarding the pretreatment of MNFC, TEMPO-oxidation and carboxymethylation increase the surface ionic strength. Principally this leads to improved barrier properties as the fibrils are obliged to reorganize into a more intact network forced by their repelling charge. The drawback is that the charged fibrils are more exposed to permanent aggregation while increasing shear rate than non-charged fibrils

(Saarikoski et al. 2012). This could be an obstacle for the usage of MNFC in industrial production where the rod metering of the coating could momentarily expose to very high shear rates in the ultra-high shear range. Nevertheless, a third pretreatment option to enhance barrier properties could be the enzymatic pretreatment, which was reported by Nygårds (2011) to reduce air permeability while using MFC coating, although not nearly as much as carboxymethylation. However, the enzymatic pretreatment ought to be the most environmentally friendly alternative.

2) One can affect barrier property results also by the selection of coating components prior to coating. By definition, lignin, hemicelluloses and cellulose exhibit somewhat varying barrier properties. Considering pulp-derived coatings such as MNFC coating, the relative content of plant-based polysaccharides in pulp varies depending on the cytological source and the forest or agricultural processing operation (Doroudgarian 2011). This relative content of pulp polysaccharides most likely remains to some extent also after the subsequent processing to MNFC. Furthermore, crosslinking can be used to provide a more tortuous structure to the coating. In addition, viscosity and water retention can be increased for instance by adding cationic starch.

3) Surface sizing closes pores on the base paper surface while improving stiffness, whereas internal sizing adds overall hydrophobicity into the paper slurry.

4) Pre-calendering reduces surface porosity and roughness, whereas the density of the base sheet increases. It might also increase barrier properties.

- After the coating operation
  1) The MNFC coating can be modified after the coating operation by drying the coated film composite in elevated temperature instantly after coating. This is also referred to as heat treatment. Heat treatment has been reported to enhance both wet strength (Österberg et al. 2013) of a nanocellulose film as well as the WVTR of a polymer dispersion coating (Kimpimäki et al. 2008), both of which are essential for liquid packaging.

  2) Likewise to pre-calendering, calendering smoothens the surface of the coated film composite and makes it denser. In addition, it also decreases air and gas permeability. (Gustafsson 2011).

  3) Modification can also be carried out by hot pressing to enhance wet strength and interfacial adhesion (Österberg et al. 2013).

  4) In addition, filtration by using a wire could both enhance interfacial adhesion as well as reduce drying shrinkage of MNFC coating by pressurizing the fibrils in order to penetrate them thoroughly inside the fibrous structure of the base sheet.

8. Experimental

In addition to modifying nanocellulose properties prior to or after the coating operation, the properties can be modified during the coating operation. However, to my knowledge there are few publications available to-date about the behavior of barrier properties of MNFC coating in response to altering the rod coater parameters. Therefore, it was considered useful to test them in this thesis. In general, the rod coating parameters involve

1) the rod speed and 2) the rod gap size. In addition, there exists rod loading pressure, although it is most likely only used with smooth rods and thick coatings.

1) Rod speed
2) Rod gap size.

8.1. Materials

8.1.1. Rod coater

The laboratory rod coater, namely, the "K Control Coater" (**Figure 23**), was used as the device for coating nanocellulose on to the selected paperboard substrates. Several types of rods were available to be used for the deposition of coating suspension. These included the close wound rods, spirally wound rods and also smooth rods. By definition, the close wound rods are also referred to as small-diameter rods and large-diameter rods to distinguish between their wire diameter (not the cross-sectional diameter of the actual rod).

The rod coater has two parameters:

1) the rod metering speed
2) the rod wire diameter, a.k.a. the rod gap size.

Figure 23. Rod coater and the rods. (K Control coater user manual)

The lowest rod speed was measured about 1,5 cm/s and the highest about 19,2 cm/s, while the lowest wire diameter option was documented as 0,05 mm and the highest as 1,50 mm, as displayed in **Figure 25**. As explained in **Table 9** in **Section 8.3.1,** the rod speeds were calculated for the speed settings 2-10 of the rod coater (1-10 settings altogether). As evident by comparing the wet film thicknesses of **Figure 25 a** and **b**, the spirally wound rods displayed in **Figure 24 b** produce a deposit of higher thickness despite narrower wire diameters than the close wound rods displayed in **Figure 24 a**. This is due to the wire circulating more loosely, leaving considerably more space in between the cross-sectional spheres of the wires.
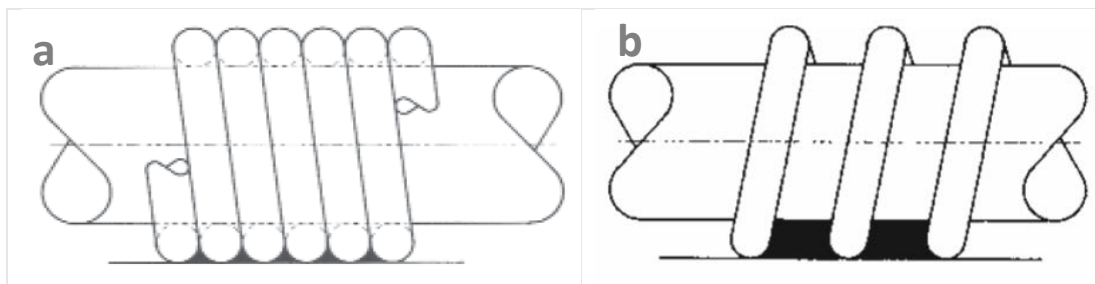

Figure 24. a) In a close wound rod (left), the winding wire circulates the rod by forming a closely wound, coil-like spiral of metal wire of uniform thickness. The dashed lines represent the cross-sectional spheres of the winding wire. **b)** In contrast, in a spirally wound rod (right) the wire is wounded more loosely, thereafter leaving wider gaps. (K Control User Manual)

The wire diameter is the diameter of a cross-sectional sphere formed by the wire. Hence, the wire diameter could also be denominated as the metal wire thickness. However, in order to avoid mixing up with coating thickness, only the term "wire diameter" is used in this thesis. The wire diameter is intended to demonstrate the gap size. However, the gap size appears to be less practical to use as a unit of measurement than wire diameter, because gap size is not reported in the table figures below (**Figure 25 a** and **b**), which are from the rod coater user manual. In addition, terms such as small-diameter rod and large-diameter rod are used e.g. in paper coating industry.

Figure 25. a) The rods of different colors represented different wire diameters. The selected rods are displayed as their corresponding colors. **b)** The spirally wound rods were not included in this thesis as they were originally designed to meter a coating which was considered both unnecessarily thick and also perceived impossible to coat with the solids content of nanocellulose coating of 1-2 wt%. (K Control Coater User Manual)

In addition to rod speed and rod wire diameter, another variable to regulate the coating properties is the rod loading pressure. The rod can be pressed against the cylinder, in industrial scale, or against the surface of the rod coater device in bench scale, by applying a specific pressure. A higher loading pressure enables a thinner coating with increased web speed of the coated web. (Linnonmaa and Trefz, 2009) This can be beneficial, because a thin coating is often more economical than a thicker one, although pressure is not normally used for other than smooth rods to regulate coat weight. However, if the solids content of the coating is high and a smooth rod is evident in order to avoid stripes that would otherwise result from wires, the regulation of loading pressure might prove as the only way to regulate coat weight in a convenient way.

8.1.2. Coating and base paper

Coating

The nanofibrillar cellulose (CNF) hydrogel was supplied by the faculty of Forest Products Technology of Aalto University, Espoo, Finland. As such, the preparation method was a standard by the faculty. The preparation method involved washing and refining by using a Voith refiner, after which the pulp was ran through a microfluidizer. Considering the nanocellulose used herein, the number of passes during its preparation was six, which yielded nanofibrillar cellulose hydrogel with a solids content typically between 1,5 wt% and 1,6 wt%. In practice, the number of passes refers to the number of times the slurry was ran through the microfluidizer. Nonetheless, by default, no pretreatments were applied prior to

the preparation of the nanocellulose hydrogel. Moreover, the nanofibrillar cellulose was produced from birch pulp and as such it contained a xylan concentration as high as about 20 wt%. Being totally amorphous, the xylan increased the originally very high water holding capacity of the nanocellulose suspension even higher.

Base paper

The paperboards used herein are referred to as Polyethylene Raw Cupboard, Uncoated Duplex, Pigment coated board, and Enso board. However, the usage of the two latter paperboards was rather limited and as such their content is considered negligible in terms of this thesis. This consideration was due to the fundamental difficulty to track the origin of the pulp compositions of the used paperboards. However, assumptions can be made that each of the used paperboards resembled a paperboard and were thus one of the paperboards presented in Cartonboard grades. However, considerable aspects that distinguish the two mainly used substrates, the Polyethylene Raw Cupboard from Uncoated Duplex, relate to their preparation: Differences exist in mass handling, the duration of refining and thereafter in their compactness, as well as in sizing, which appears to be stronger for Polyethylene raw cupboard than for Uncoated Duplex.

Polyethylene Raw Cupboard

The Polyethylene Raw Cupboard, which to simplify is in this thesis abbreviated as PEr, resembles a rather typical liquid packaging board (LPB) by its composition: It contains a three-layered structure which both outer layers are of bleached hardwood pulp while the middle layer is of chemi-thermomechanical pulp (CTMP). The bleached pulp is a guarantee that there is only a negligible amount of lignin. The pulp, both chemical pulp and CTMP, consist of virgin fiber, which is commonly perceived as a guarantee that the fiber should not contain impurities. In addition, the advantage of CTMP compared to other mechanical pulp is that the resin content is negligible.

Uncoated Duplex

The Uncoated Duplex board, which to simplify is in this thesis abbreviated as UD, resembles a rather typical linerboard by its composition: It contains two layers, one that is bleached and another that is non-bleached. Therefore, the Uncoated Duplex is of pale white color on one side and of brown color on the other side. In contrast to Polyethylene Raw Cupboard, Uncoated Duplex does not contain any mechanical mass.

8.2. Methods

In this section, brief explanations of the test methods as well as possible standards are being presented. Although some methods did not have a standard, they were still considered relevant enough in terms of the experimental procedure to be explained. Prior to measurement, the test pieces were conditioned in constant conditions in the paper lab, where the ambient temperature is 23°C and the ambient relative humidity is 50 %.

Application and metering

As displayed in **Figure 26,** the coating suspension was applied manually in front of the rod, by using a syringe. Depending on coating solids, which altogether varied between 1,1 wt% and 2,0 wt%, as well as the type of base paper, the amount of coating applied varied between 8 and 12 milliliters.

8.2.1. Test specifications

Two experimental arrangements, or test series, were performed in order to investigate the influence of the rod coater parameters on the coating deposition, namely, on coat weight and coating thickness. The target of *the first test series* was to investigate *the effect of rod speed and solids content* on coating deposition, and thereafter on barrier properties, such as air permeability and water absorption. In addition, a few more specific test arrangements were carried out. These covered a *heat treatment test*, *pretreatment and substrate test*, and a *crosslinking test of soy protein*.
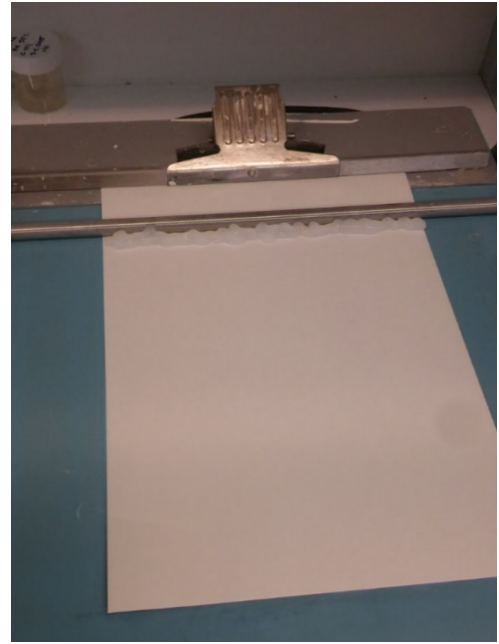
Figure 26. The rod coater is ready and set for metering after the application of CNF onto a PE Raw Cupboard.

Test series 1				
Substrate			*Coating*	
Type	*Specification*		*Specification*	
Paperboard	PE Raw Cupboard, 230 g/m2		CNF gel	
Paperboard	Enso board, 260 g/m2		Six passes	
			Non-pretreated	
Constants		*Variables*		
Device		*Device*	*Coating*	
Wire diameter:		Rod speed [cm/s]:	Solids content [wt%]:	
0,64 mm		1,5; 8,7; 17,2	1,10; 1,57; 2,00	
Tested combinations				
1 replicates x 3 combinations x 3 combinations = 9 sheets.				
Tested properties				
COBB water absorption				
COBB-Ungern oil absorption				
L&W Bendtsen air permeability				
Coating thickness and coat weight				

Table 4. Test series 1.

Application of coating

The application was conducted by inserting manually 8-12 milliliters of coating by using a syringe. The amount varied based on solids content: the lower solids content, the less the required amount of coating.

Modification of solids content

When received from the Department of Forest Products Technology, the nanocellulose coating had a solids content between 1,5 wt% and 1,6 wt%. The coating was possible to centrifuge into a higher solids content of 2,0 wt% or to dilute into a lower solids content of 1,1 wt%. Finally, the suspension of modified solids content was homogenized by an Ultra Turrax homogenizer.

Test series 2				
Substrate			**Coating**	
Type	*Specification*		*Specification*	
Paperboard	Uncoated Duplex, 260 g/m2		CNF gel	
			Six passes	
			Non-pretreated	
Constants		**Variables**		
Coating		*Device*		*Device*
- Solids content:		Rod speed [cm/s]:		Wire diameter [mm]:
1,57 wt%		1,5; 7,9; 15,2; 19,2		0,15; 0,64; 1,27
Tested combinations				
1 replicates x 3 combinations x 4 combinations = 12 sheets.				
Tested properties				
COBB water absorption				
COBB-Ungern oil absorption				
L&W Bendtsen air permeability				
Coating thickness and coat weight				

Table 5. Test series 2.

Crosslinking test				
Substrate			**Coating**	
Type	Specification		Specification	
Paperboard	Uncoated Duplex, 260 g/m2		CNF gel	
			Six passes	
Constants		**Variables**	Non-pretreated	
Device		Coating		
- Wire diameter		- Combinations of composition:		
0,64	mm	(CNF, CNF + Soy protein;		
- Rod speed		CNF + Glutaraldehyde;		
11,2	cm/s	CNF + Soy protein + Glutaraldehyde)		
(setting 6, 700 1/s)				
		Tested combinations		
Coating		1 replicate x 4 combinations = 4 sheets.		
- Solids content:				
1,57 wt%		**Tested properties**		
		COBB water absorption		
		COBB-Ungern oil absorption		
		Ambertec air permeability		

Table 6. Crosslinking test.

Preparation of the crosslinking test

Soy protein was denatured by heating at 80°C for 30 minutes. This unfolded the amino groups of soy protein to enable crosslinking. Consequently, the crosslinking agent, which was selected to be glutaraldehyde, affected the final properties of the soy protein coating. The relative proportions of each component was 7:3 of soy protein to nanocellulose and 3:1 of nanocellulose to glutaraldehyde. The relative amount of soy protein on water before denaturation was based on what was reported by Guerrero et al. (2010), namely, 7,5 grams of soy protein to 125 milliliters of distilled water. After the denaturation of soy protein, four suspensions of varying composition were established and thereafter coated onto an Uncoated Duplex paperboard. Finally, the extent of crosslinking established for the abovementioned suspensions was measured by the Cobb water absorption test, which was estimated to provide an indication of hydrophobic amide groups activated by the crosslinking agent, namely, glutaraldehyde. Similarly, also air permeability and oil absorption were measured for the suspensions.

Heat treatment test				
Substrate			**_Coating_**	
Type	_Specification_		_Specification_	
Paperboard	Pigment coated board, 210 g/m2		CNF gel	
			Six passes	
Constants		**_Variables_**	Non-pretreated	
Device		_Device_		
- Wire diameter		- Drying temperature		
0,64	mm	(Room temp. 23°C; 60°C;		
- Rod speed		80°C ; 105°C ; 130°C)		
11,2	cm/s			
(setting 6, 700 1/s)		**_Tested combinations_**		
		3 replicates x 5 combinations = 15 sheets.		
Coating				
- Solids content:		**_Tested properties_**		
1,48 wt%		COBB water absorption		
		COBB-Ungern oil absorption		
		Ambertec air permeability		
		Coating thickness and coat weight		

Table 7. Heat treatment test.

The heat treatment was carried out in an oven. During the transport from the coating laboratory to the oven, there was approximately a five-minute interval during which the test piece inevitably dried in room temperature of about 23 $^\circ$C. Nonetheless, curling occurred during drying, both in the elevated temperature inside the oven as well as in room temperature. In addition, the curling was accelerated right after insertion into the oven. The curling was understood to be a consequence of drying shrinkage.

Pretreatment and substrate test				
Substrate			**Coating**	
Type	Specification		Specification	
Paperboard	PE Raw Cupboard, 230 g/m2		CNF gel	
Paperboard	Uncoated Duplex, 260 g/m2		Six passes	
Constants		**Variables**		
Device		Coating		
- Wire diameter		- Pretreatment		
0,64	mm	(Non-pretreated; TEMPO-pretreated)		
- Rod speed		- Substrate		
11,2	cm/s	(PER/smoother substrate;		
(setting 6, 700 1/s)		UD/rougher substrate)		
Coating		**Tested combinations**		
- Solids content:		3 replicates x 4 combinations = 12 sheets.		
1,48 wt%				
		Tested properties		
		COBB water absorption		
		COBB-Ungern oil absorption		
		Ambertec air permeability		

Table 8. Pretreatment and substrate test.

8.2.2. Measurements

Air permeability (Bendtsen)

Air permeability (Bendtsen) (ml/min) was measured according to the standard SCAN-P 60:87. The air permeability was measured with L&W Bendtsen Tester, with the air flow direction towards the uncoated side of the sheet, by keeping the sheet as the coated side upwards during measurement. Seven measurements were made for each sample: Three from both side edges of the sheet and one from the bottom edge, each measurement as far inwards to the coated area as possible with the device. The accuracy was selected to be between 0 and 300 ml/min.

Air permeability (Ambertec)

In contrast to the Bendtsen tester, the air permeability of the Ambertec-device (relative unit) was a non-standardized method. Compared to the L&W Bendtsen air permeability, the values of the Ambertec air permeability and L&W air permeability device provided results with a similar relation. This was evidenced by a similar graph profile obtained from both Ambertec and L&W Bendtsen tester from the same test. However, the anomalies between data points were higher with Ambertec than with L&W Bendtsen tester. This was understood to be both due to higher accuracy of data points as well as a higher amount of replicates than the manually operated L&W Bendtsen tester. Furthermore, the utilized accuracy was that of barrier dispersions (10cm x 10cm). In contrast to L&W Bendtsen tester, the coated paper was

inserted with the coated side on the bottom side. This provided a direct air flow from the device to the coated side, which was considered beneficial in terms of the measurement. Moreover, the device provided air flow values both inbound and outbound the coated paper. However, for simplification the documented values represented air flow inbound the sheet, as they appeared to also indicate more considerable variation.

Water absorption measurement

Water absorption (Cobb method) (g/m^2) was measured according to the standard ISO 535. In addition, the 60 second Cobb-method was selected for the measurements.

Oil absorption measurement

Oil absorption (Cobb-Ungern method) (g/m^2). The Cobb-Ungern oil absorption test was conducted as according to the SCAN-P 37:77 standard. The method describes the amount of castor oil being absorbed onto a unit of paper surface area. As according to the standard, with extremely porous papers, such as thin newspapers, the CU_6 method is used instead of CU_{10}. In contrast, with very dense papers the CU_{30} method is typically used. In the tests herein, the CU_6 method was used for the drying test. However, for the rest of the oil tests it was decided that with CU_{10} the results will be more distinguishable and accurate.

Mechanical property measurements

Both the tensile strength and the fracture toughness were measured using the Lorentz & Wettre Tensile tester device. The values were measured in machine direction (MD) considering both tensile strength and fracture toughness. The measurements were carried out according to the standard ISO-1924-2.

Coat weight measurement

Coat weight measurement (g/m^2), which is a non-standardized method, included weighing A4 size sheets in a scale and calculating the grammage of the sheet. The coat weight was measured by subtracting the dry sheet weight from the corresponding weight of a coated sheet.

Thickness measurement

Thickness (μm) was measured according to the standard ISO 534. Nine points of measurement per sheet were measured by using the L&W Micrometer thickness tester. The points of measurement were marked in advance into an extra A4 sized sheet. In this paperboard, nine holes were poked to facilitate the accurate locating of the nine thickness measurements per sample, by using the dimensions marked primarily with a pen as illustrated in **Figure 33** in **Section 8.3.7**. As with the calculation of coat weight, the coating thickness was measured by subtracting the thickness of the uncoated sheet from the thickness of the corresponding coated sheet.

8.3. Results and discussion

As stated earlier in **Section 2**, like dissolves like: as a rule of thumb, polar molecules dissolve into polar materials and non-polar molecules to non-polar materials. However, the connections between the variables that determine the barrier properties are more

complicated as they include the interaction between the coating and the base sheet as well as the impact of device parameters, here meaning rod coater parameters. In the **Results and discussion** part, the impact of rod coater parameters will be covered in the primary sections until **Section 8.3.6** while in the secondary sections from **Section 8.3.7** onwards the focus will continue more on the behavior of the coated film composite as a whole. There will be shown mainly results about barrier properties, although also some mechanical properties, wetting behavior and flow behavior insights regarding the interaction of the coating and the base sheet.

8.3.1. Rod coater parameter connection to shear rate

In order to quantify the speed settings, which were provided in the rod coater as unspecified units from 1 to 10, a measurement was conducted by recording the time using each setting from 2 to 10 for the rod to pass from start to finish. Thereafter, the rod speeds were calculated for the speed settings 2-10 of the rod coater (1-10 settings altogether) as indicated in **Table 9**. Moreover, setting 1 was declared too slow for testing since the rod barely moved.

Rod metering speed conversion					Speed setting				
	2,0	3,0	4,0	5,0	6,0	7,0	8,0	9,0	10,0
t/[s]	16,1	6,2	3,7	2,8	2,2	1,7	1,4	1,3	1,3
	15,5	6,3	3,8	2,8	2,2	1,7	1,5	1,3	1,3
t(ka)/[s]	15,8	6,3	3,8	2,8	2,2	1,7	1,4	1,3	1,3
v/[cm/s]	1,5	3,9	6,4	8,7	11,2	14,3	17,0	18,8	19,2
Δv		2,3	2,6	2,3	2,5	3,1	2,7	1,8	0,4

Table 9. The measured rod metering speed v in cm/s for different settings of rod metering speed (2-10).

The respective shear rates of the rod speeds were calculated corresponding to the speed settings of Test series 1 (2, 5 and 8) and Test series 2 (2, 4,7, 7,3 and 10). The shear rate was calculated according to the "rod-specific shear rate" as defined by **Equation 4**. In **Table 10**, a short calculation was done to estimate the corresponding shear rates for the rods with varying gap size and speeds. The height h indicated in **Figure 27 a** was selected to be the height h of **Equation 4**. The height h corresponds to a quarter of the wire diameter, as thereafter it was perceived to resemble the most the flow behavior of the CNF coating running through the gaps between the wires.
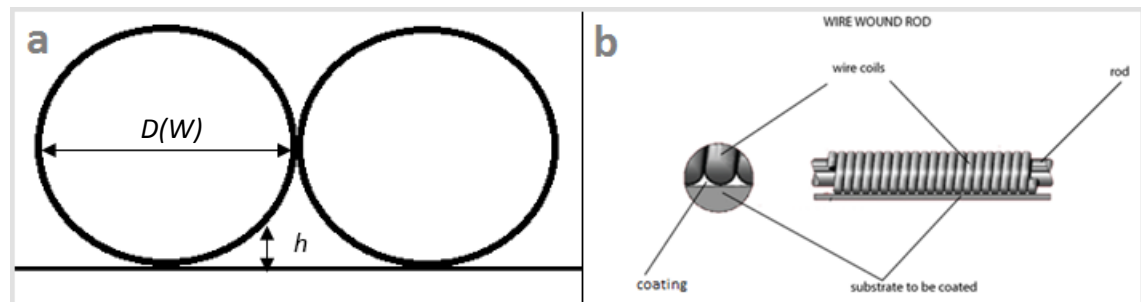

Figure 27. a) The wire diameter $D(W)$ of a wire-wound rod (long arrow) and the agreed height h of the basic shear rate equation (small arrow). A gap is left between two cross-sectional spheres, namely, the adjacent parts of the wire. **b)** Nomenclature of a wire wound rod (Holoeast).

The rod-specific shear rate

$$\gamma_{Rod} = \frac{V(R)}{\frac{1}{4}*D(W)} = \frac{v}{h} \; [s^{-1}]$$

(4)

where,

$D(W) = $ *Rod wire diameter* [mm]
$V(R) = $ *Rod metering speed* [cm/s]
$h = $ *Gap height* [mm] $= \frac{1}{4}*D(W)$

Shear rate γ [1/s]		$D(W)$ [mm]:	Small rod	Medium	Large
Setting	V(w) [m/min]	V(R) [cm/s]	0,15	0,64	1,27
2	0,9	1,5	410	96	48
4,7	4,8	8,0	2 134	500	252
7,3	9,1	15,1	4 035	946	477
10	11,5	19,2	5 122	1 201	605

Table 10. Shear rate calculated based on the operation of the laboratory rod coater. The two inspected parameters include the rod speed *V(R)* and rod wire diameter *D(W)* a.k.a. rod gap size. For comparison with industrial scale units, the rod speed was converted to web speed *V(w)*. In addition, all speeds corresponded to a continuously adjustable speed setting from 1 to 10. For detailed specifications, see **Table 5.** Test series 2.

Flocculation behavior and rod metering

As indicated earlier in **Figure 15** in **Section 4.4**, the flocculation of MNFC fibrils typically occurs somewhat between shear rates of 5 and 100 s^{-1}. Further, while calculating the rod-specific shear rate of the small wire diameter rod at the smallest speed, the result is the following:

$$\gamma_{Rod} = \frac{1,54 \; cm/s}{\frac{1}{4}*0,015 \; cm} = 410 \; s^{-1}$$

This result, which is also observable from **Table 10**, indicates that the flocculation effect of nanofibrils should in theory have no impact on barrier properties or coat weight behavior at low rod metering speeds. As indicated later on, the barrier and coat weight behavior at lower rod speeds was found somewhat unexplained.

Shear rate and viscosity

At different sub-processes and unit operations of a coating process, the viscosity of the coating suspension varies as a consequence of varying shear rate to which the different sub-processes and unit operations are exposed to. Therefore, to provide optimum runnability for a coating suspension in question, it is important to maintain a viscosity level that is a compromise between the different sections of the coating process. In the following, unit operations typical for each three different shear rate ranges are being described:

1) Low to moderate shear (0,1 to 1000 s^{-1}) – Pumping, mixing and other type of handling of the coating. Long duration processes, lasting from a few seconds to minutes.

53

2) High-shear (1000 to 100 000 s^{-1}) – Short duration processes of a few milliseconds which take place during filtering and application of the coating via rod, air-knife, etc.

3) Ultra-high shear (100 000 to 2 000 000 s^{-1}) – Very short duration processes of only a few microseconds, which take place during final metering of the coating, for example under the blade. (Roper 2009)

In summary, when looking at **Table 10**, it appears that with the laboratory rod coater the higher rod speeds can reach the high-shear range with small gaps a.k.a. small wire diameters while metering with enough speed. In contrast to low-shear range, the high-shear range is the typical shear range in industrial scale coating. Therefore, it can be summarized that the barrier results of the laboratory rod coater parameters with the wire diameters and speeds providing a shear of over 1000 s^{-1}, should be taken less lightly and more seriously in terms of industrial scale coating. This would be explained by the similarity to the exposed shear in industrial metering, where it is around the ultra-high shear range. As indicated in **Table 10**, this means especially the small rod gap size but also the medium rod gap size.

8.3.2. Impact of rod parameters on coat weight and coating thickness

Summary

As displayed in **Figure 28**, both coat weight and coating thickness were found to be directly proportional to the gap size a.k.a. wire diameter of the rods. This explains why air permeability and oil absorption decrease as a function of rod gap size. Moreover, no clear relation was found between rod metering speed and coating thickness. On the contrary, coat weight appeared to decrease mildly as a function of rod metering speed. This can be explained completely by less water penetrating to the base paper while increasing rod speed, which results into less expansion in the fiber network and thus less apparent increase in coat weight as a consequence of increased base paper grammage. Therefore, it should be noted that the displayed coat weight is only apparent, while the actual nanocellulose coat weight does not necessarily show a decrease as a function of rod speed. In general, the behavior of coat weight in response to grooved rods was in line with literature. For instance, the small-diameter rod showed a dependency on rod metering speed due to its negligible hydrodynamic forces when compared to the larger diameter rods. This dependency can be seen as lower coat weight at the smallest rod speed of 1,5 cm/s.
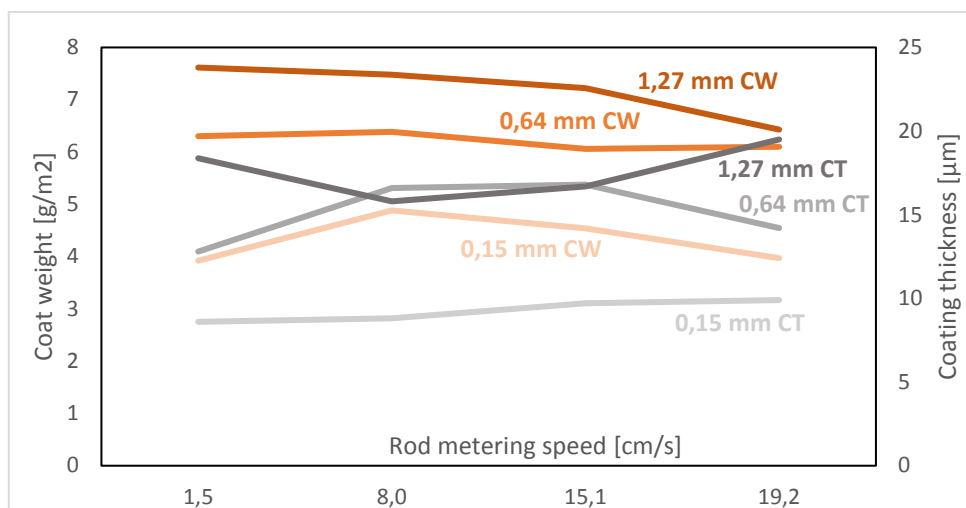
Figure 28. Coat weight and coating thickness for different rod wire diameters as a function of rod speed. CW = Coat weight, CT = Coating thickness. For detailed specifications, see **Table 4.** Test series 1. and **Table 5.** Test series 2.

Coat weight

A typical coat weight of industrial-scale dispersion coatings is between 4 and 15 g/m² (Kimpimäki et al. 2008). Each sample had all the values inside this interval. A common cause for large coat weight variations is the roughness of the substrate (Kimpimäki et al. 2008). However, in this case the coat weight indicated a steady decrease for all three rods as a function of rod metering speed. This trend is explainable by fiber network expansion in the base sheet causing apparent increase in coat weight. The fiber network deformation or expansion behavior was reported by Manninen et al. (2011), and demonstrated more thoroughly by Gustafsson (2011). On the contrary, Richmond et al. (2014) reported an increase in coat weight as a function of metering speed while using the CLC-coater. In addition, an increase in wet film amount [g/m²] a.k.a. coat weight as a function of rod metering speed was documented by Linnonmaa and Trefz (2009) while rod coating high-viscosity starch. In contrast to the apparent coat weight caused by the increase in paper grammage due to fiber network expansion, the actual coat weight most likely did not vary as a function of rod speed. This would be in line with what is documented of the interaction between large-diameter grooved rods and coat weight (Linnonmaa and Trefz, 2009). Moreover, according to tests by Lavoine et al. (2014), with MFC concentrations of about 1,0 wt%, the coat weights on paper are typically around 5,0 and 8,0 g/m². As such, the coat weights obtained appear rather expected. Furthermore, the slight increase in coat weight at low rod speeds regarding the smallest rod wire diameter of 0,15 mm was hypothesized to be an indication of flocculation, as displayed earlier in **Section 4.4**. However, as according to **Equation 4** in **Section 8.3.1**, the shear rate obtained by the smallest wire diameter at the lowest rod speed would be 410 s⁻¹, which easily exceeds the higher limit of flocculation of about 100 s⁻¹. Furthermore, the small-diameter rod showed a dependency on rod metering speed due to its negligible hydrodynamic forces when compared to the larger diameter rods (Linnonmaa and Trefz, 2009). This dependency can be seen as lower coat weight at the smallest rod speed of 1,5 cm/s.

Coating thickness

The rod speed did not appear to have a clear impact on coating thickness. In dispersion coating industry, coating thicknesses typically range between 5 and 15 µm. In the thickness measurements presented in **Table 11**, the upper limit of 15 µm was exceeded in half of the samples of the medium wire diameter rod, and in each sample of the large wire diameter rod. Nevertheless, pinholes might have a substantial impact on the barrier properties, because the coating thicknesses herein as well as in dispersion coating industry are relatively low. Conclusively, the thicknesses of especially the small wire diameter rod might be vulnerable to pinholes, as is the case in dispersion coating industry with similar coating thicknesses. (Kimpimäki et al. 2008)

8.3.3. Impact of rod speed on air permeability and coating thickness

Summary

Three sheets were coated, each with a rod of different wire diameter. There appeared to be no significant variance in coating thickness a.k.a. coating coverage as a function of rod speed, although the nuisance of some unsuccessful points of thickness measurement might slightly distort the observable trends. However, the variance in air permeability decreased both externally between each three sheets as well as internally within one sheet as a function of rod speed. The variance was large with the small wire diameter rod and small with the medium wire diameter rod, whereas with the large wire diameter rod both internal and external variance was negligible. The overall results are displayed in **Figure 29**.
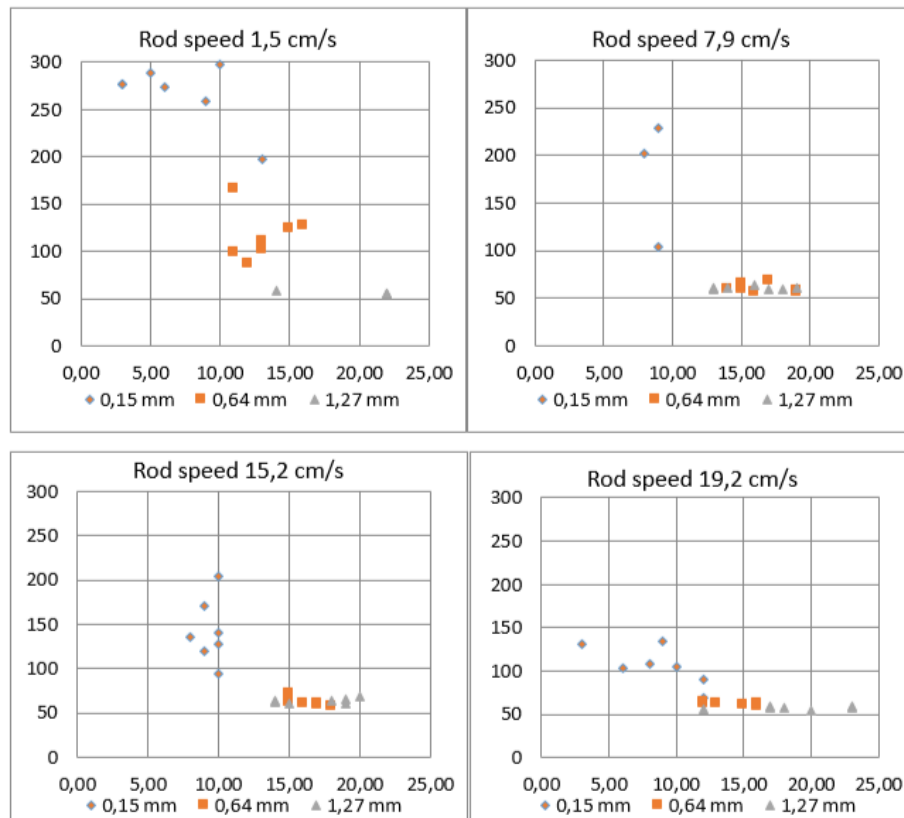
Figure 29. Air permeability [ml/min] of different points of coating thickness measurement as a function of rod speed [cm/s]. Each sheet was measured as according to the thickness measurement described in **Section 8.2.2**. For detailed specifications of this test, see **Table 5.** Test series 2.

Air permeability and rod speed

From the diagrams, it is noticeable that the dots form a shape which slightly reforms after an increase in rod speed. However, the variations in coating thickness appear to stay relatively similar irrespective of rod metering speed. Moreover, as calculated in **Section 8.3.1,** the shear rates of the lower rod speeds are way higher than the shear rate area of flocculation presented by Saarikoski et al. (2012), which is displayed in **Figure 15** in **Section 4.4.** This most likely excludes the possibility of flocculation being the cause of decreasing air permeability as a function of rod speed.

8.3.4. Impact of rod parameters on water absorption

Summary

As displayed in **Figure 30**, the type of base paper a.k.a. substrate typically has a considerable impact on water absorption. The largest difference in results was found while comparing between the paperboard substrates of Polyethylene Raw Cupboard (PEr) and Uncoated Duplex (UD). The former substrate as a cupboard is dedicated more on keeping liquid, while the latter is not. Regarding the substrates, the high moisture resistance is most likely due to surface sizing or internal sizing, and/or higher refining amount. Regarding the coating suspension, nanocellulose is hydrophilic and thereafter a higher coat weight of nanocellulose absorbs more water. According to **Section 8.3.2**, the nanocellulose coat weight should decrease as a function of rod speed. However, as evidenced by the increase in water absorption as a function of rod speed regarding the Uncoated Duplex (UD) substrate, the coat weight decrease presented therein was most likely only apparent.
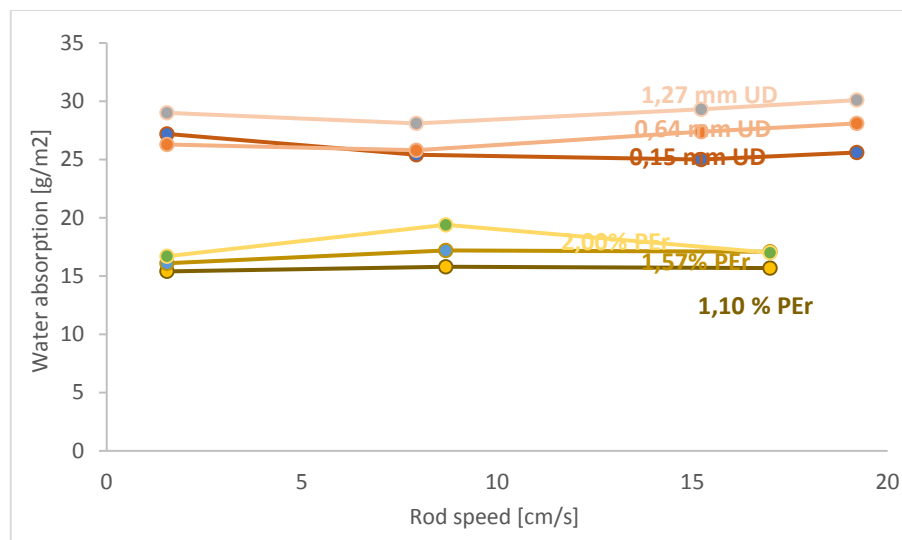

Figure 30. The impact of nanocellulose concentration (curves below) and rod wire diameter (curves above) on water absorption as a function of rod speed. The type of base sheet affected notably on water penetration into the coated sheet. The base sheet is Polyethylene

Raw Cupboard (PEr) on the curves below, and Uncoated Duplex (UD) on the curves above. For detailed specifications of this test, see **Table 4.** Test series 1. and **Table 5.** Test series 2.

Nanocellulose absorption capacity was increased by both rod gap size and solids content

It is noticeable, that the COBB water absorption increased along with increase in both rod wire diameter a.k.a. rod gap size as well as in solids content. In terms of solids content, a similar behavior was reported by Sjöholm (2010) and Kimpimäki et al. (2008) regarding coat weight. Sjöholm tested in his test the effect on nanocellulose coating, while Kimpimäki et al. reported the same behavior for polymer dispersion coatings. Likewise, both of the effects measured in this test, the effect of rod gap size and the effect of solids content, are explainable by the increase in the coat weight of the nanocellulose suspension. In addition, the substrate clearly had an impact on the extent of water penetration. This is displayed as Polyethylene Raw Cupboard having a COBB value a half that of Uncoated Duplex. Moreover, Richmond et al. (2014) presented that nanocellulose has a peculiar tendency to exhibit a higher dewatering rate the higher its solids content a.k.a. concentration. Herein, this type of behavior should indicate as lesser or at least a compensation of water absorption increase while increasing solids content.

8.3.5. Impact of rod parameters on air permeability

Summary

There was suspected to occur a common effect of low coat weight and high water penetration, which caused an exponentially high air permeability at low rod metering speeds (1,5 – 8,0 cm/s) while coating with a small gap size rod (0,15 mm), as displayed in **Figure 31**. With the medium gap size rod (0,64 mm), the effect was not so pronounced at this rod speed interval, because the coat weight resulted higher. Finally, with the large gap size rod (1,27 mm) the coat weight was so high that it appeared to diminish the effect of water penetration on air permeability at low rod speeds completely. The effect of water penetration on air permeability was due to fiber network expansion inside the base sheet, causing non-uniformity in z-directional structure. As with low coat weights the base sheet also has an impact on the total air permeability of the coated film composite in question, the air permeability showed a considerable decrease. Nevertheless, although flocculation was decided not to have an impact, there might be other rheological properties taking place during the rod movement that might be worth further investigation. Furthermore, also the dependency between air permeability and coat weight was inspected. As a result, it remains unexplained why in some cases the dependency between air permeability is linear and in others non-linear as a function of the amount of MNFC coating applied. One reason could be, that it makes a difference whether the coating is applied at once or in several times as layers. Finally, this might be one relevant topic for further investigation.
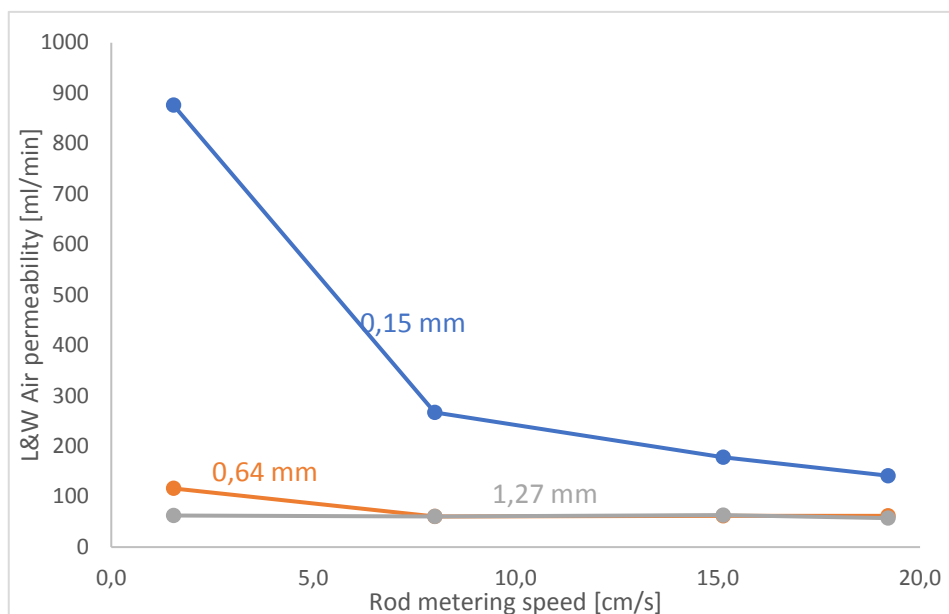
Figure 31. The influence of rod wire diameter on air permeability as a function of rod speed. For detailed specifications, see **Table 5.** Test series 2.

Air permeability and rod parameters

While coating with a small wire diameter rod (0,15 mm), air permeability is considerably higher within lower rod metering speeds, especially between the interval of $v = 0 - 8$ cm/s. With a rod of moderate wire diameter (0,64 mm) the air permeability is somewhat higher within this rod metering speed interval, whereas with the high wire diameter rod there appears not to occur any increase in air permeability as a function of rod speed. Thereafter, it appears that the reason for high air permeability at low rod metering speeds cannot be fully explained by coat weight. Likewise, the reason for this most likely cannot be explained by nanofibril flocculation, as supported by the theorem presented in **Section 8.3.1** about the lowest rod speed being too high to allow flocculation to occur herein. However, the water penetration from the coating to the base paper is higher with lower rod speeds. Consequently, the higher water amount expands the fiber network to a large extent, causing significant non-uniformity in the z-directional structure of the base paper. Finally, this would indicate as high air permeability. In addition, this effect is emphasized when the coating coverage is thinner, as a consequence of smaller gap sizes. Thence, the small wire diameter rod provides a common effect of low rod speed and small gap size, leading to high water penetration and low coat weight, which eventually shows as an exponentially high air permeability. Furthermore, it is documented that in contrast to large-diameter (LD) rod metering, in small-diameter rod metering the hydrodynamic forces are virtually non-existent (Linnonmaa and Trefz, 2009).

Air permeability and coat weight

Gustafsson (2011) reported a non-linear correlation between air permeability and the amount of applied coating layers, while using a spray coater and a CLC-coater. The results showed therein that air permeability was non-linearly proportional as a function of added coating layers. More exactly, air permeability decreased by a decelerating rate as a function of the number of added coating layers. This kind of non-linear dependency of air permeability on the amount of coating applied can also be evidenced in this test when comparing the non-

linear differences in air permeability of **Figure 31** with the linear differences of **Figure 28**, between the three rods: Instead of non-linear difference, the difference is actually linear regarding coat weight, between the three rods. Furthermore, Richmond et al. (2014) reported air permeability to be inversely proportional with coat weight, while using a rod coater to coat CNF on paper. However, in contrast to what was reported by Gustafsson (2011), the dependency was linear. Furthermore, with small-diameter rods the rod metering speed is documented to have an impact on coat weight, whereas with large diameter rods it does not. This is also supported by **Figure 28** where there can be observed a slight decrease in coat weight of the small-diameter rod at the lowest rod metering speed of 1,5 cm/s. This decrease in coat weight is most likely due to the lack of hydrodynamic forces while comparing to the other two rods with a larger wire diameter.

8.3.6. Impact of rod parameters on oil absorption

Summary

Although the amount of tested samples was very limited for an oil absorption test since no replicates existed, the trends obtained are prominent: The results displayed in **Figure 32** conform the trend of the air permeability test displayed in **Figure 31**, and thereafter support the theorem by Aulin et al. (2010). More exactly, this suggests that the reason behind the results is the same as with the air permeability test, which is most likely the common effect of water drainage amount and coat weight. On the contrary, there was not found such dependency between air permeability and oil absorption regarding the heat treatment test, the pretreatment and substrate test and the crosslinking test. However, this might be for instance due to the rod parameters remaining constant in these test, which is contradictory to the one displayed in **Figure 32**. Nevertheless, more testing should be done to confirm the relation between oil absorption and air permeability, and whether the rod parameters are the common divisor between the two barrier properties.
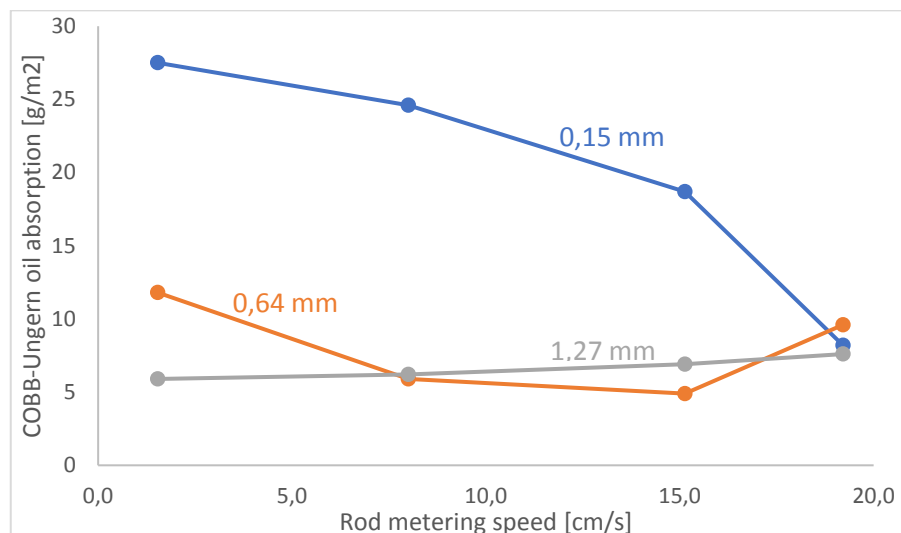

Figure 32. Oil absorption as a function of rod metering speed. For detailed specifications, see **Table 5.** Test series 2.

Discussion

As was the case of air permeability, the oil absorption appears to be clearly the highest with the smallest wire diameter, although the difference greatly decreases as a function of rod metering speed. Similarly, this is likely caused by the decreasing water amount penetrating to the base sheet as a function of rod speed. Moreover, Gustafsson (2011) inspected the behavior of oil absorption and air permeability. As originally reported by Aulin et al. (2010), oil absorption was found out to be directly proportional to air permeability, and thus predictable from air permeability. This correlation between oil absorption and air permeability is also demonstrated by the appearance that both **Figure 32** and **Figure 31** exhibit a rather similar graph profile considering the smallest wire diameter rod. Finally, it can be concluded that both oil absorption and air permeability are non-linearly correlative with coat weight.

8.3.7. Test of composition thickening

Description

As indicated in **Table 11**, there were two tests conducted: The *first one* (based on test series 1) inspected the coating coverage as a function of nanocellulose coating solids, the *second one* (based on test series 2) inspected the coating coverage as a function of rod wire diameter. In addition, the first test used PE Raw Cupboard as base paper, as indicated in **Table 4.** Test series 1., whereas the second test used Uncoated Duplex as base paper, as indicated in **Table 5.** Test series 2. The coating coverage was measured by ten different points of thickness measurement, as indicated in **Figure 33 a**. The target of these measurements was to detect variations of enough significance to evidence the presence of the hypothesized decreasing trend in the amount of water drainage, as indicated by the light-colored arrows in **Figure 33 b**. In case no significant variation was found in coating thickness, the alternative hypothesis is a constant water drainage amount, resembled by the dark-colored arrows in **Figure 33 b**.

Hypothesis

The resulting coating thickness was hypothesized to demonstrate a slight increase towards the end of the rod travel path with both base papers being tested. This hypothesis based on an assumption of an effect which ought to be called "composition thickening", in which the solids content of the CNF suspension would increase towards the end of the rod travel path as a consequence of reduced water drainage. In case this effect was to exist, the coating thickness would gradually increase along the rod travel path due to an increased solids content of the remaining coating in front of the metering rod towards the end of the rod travel path. Consequently, this would lead to a decreasing amount of water penetrating along the rod travel path, as displayed by the lighter arrows in **Figure 33 b**.
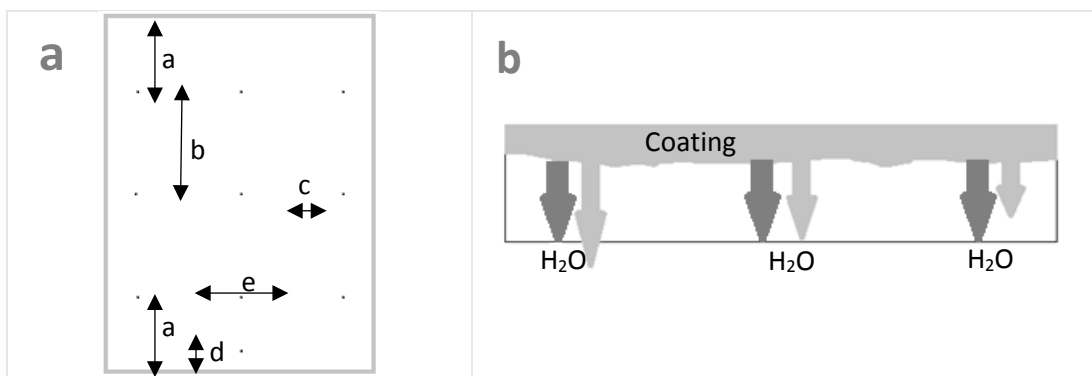
Figure 33. a) Altogether there were ten points of thickness measurement in order to recognize possible variations in coating thickness, a.k.a. coating coverage. The distances between the points of thickness measurement being marked onto an A4-sized paperboard acting as a substrate were a=7,00 cm; b = 7,85 cm; c = 3,00 cm; d = 2,00 cm; e = 7,50 cm. In the figure, the rod travel path goes from top to bottom. **b)** Two alternative hypotheses of water drainage are displayed. The darker arrows suggest a constant water drainage, while the lighter arrows suggest an increase in water retention during rod metering leading to decreasing water drainage.

Rod travel	Test series 1			Test series 2		
	1,10 %	1,57 %	2,00 %	0,15 mm	0,64 mm	1,27 mm
Start	19,1	21,4	23,5	8,8	15,9	15,1
Middle 1	20,7	22,8	23,4	9,8	15,3	18,6
Middle 2	21,0	21,7	23,7	8,7	14,4	17,2
Finish	19,7	21,2	23,2	10,8	14,0	19,0

Table 11. The coating thickness was measured from various parts of the coated base sheet to indicate variance in coating coverage along the rod travel path. The thickness measurement was conducted as a function of nanocellulose concentration by using PE Raw Cupboard as substrate (left) and as a function of rod wire diameter by using Uncoated Duplex as substrate (right). For detailed specifications, see **Table 4.** Test series 1. and **Table 5.** Test series 2.

Discussion of the first test

In the first test (left side of **Table 11**), the base paper was PE Raw Cupboard. As a typical cupboard it most likely contained surface size, which consecutively inhibited water penetration into the cupboard. However, it is worth a thought whether the type of base paper had any influence on the drainage trend of water, the two alternatives of water drainage being illustrated in **Figure 33 b**. Nevertheless, the CNF coating, with a relatively low solids content between 1 and 2 wt% in respect to e.g. industrial dispersion coatings, appeared to drain relatively well into the apparently more fibrous side of the cupboard. Finally, it appears that the concentration of nanocellulose had no impact on water penetration into the Polyethylene Raw Cupboard. Therefore, the water drainage amount was declared constant, as indicated by the dark-colored arrows of **Figure 33 b**.

In the second test (right side of **Table 11**), the base paper was Uncoated Duplex. As a typical linerboard it most likely did not contain any surface size, thus allowing water to penetrate freely. The CNF coating appeared to drain very well into the apparently more fibrous (more brown) side of the paperboard. Finally, it appears that the gap size a.k.a. wire diameter, and subsequently the deposited coat weight, had no impact on water penetration into the Uncoated Duplex board. Therefore, the water drainage amount was declared constant, as indicated by the dark-colored arrows of **Figure 33 b**.

8.3.8. Test of mechanical properties

Summary

In this test, the nanocellulose coating suspension was suspected according to the results of **Table 12** to exhibit behavior which has been reported to occur for MNFC coating suspensions at concentrations above the point of percolation, a.k.a. percolation threshold. Although normally indicated as volumetric percent, the point of percolation occurs typically for MNFC suspensions well below the concentration of 1,0 wt% (Dufresne 2013). In terms of mechanical properties, Sjöholm (2010) inspected the behavior of internal bond strength and bending stiffness while coating MFC by using rod coater, both of which appeared to show a decreasing trend as a function of MFC coat weight. This is contradictory to what was reported by Richmond et al. (2014) considering coat weight, while rod coating CNF on top of paper. However, this difference in results might be explained by the difference between coat weight and concentration as a unit of measurement: In contrast to coat weight, many rheological features likely have an impact on concentration, e.g. viscosity. Further, according to Hubbe et al. (2017), the slight weakening of nanocellulose fibrillar network as a function of concentration above its percolation threshold is most likely a consequence of fibril entanglement, due to fibrils being forced closer to one another. Therefore, it might occur that a pretreatment, such as carboxymethylation or TEMPO-mediated oxidation, would inhibit or even prevent this decreasing trend in fracture toughness. Moreover, as also reported by Sjöholm (2010), MFC coat weight did not have a notable impact on tensile strength.

Test series 1	Tensile strength [kN/m]			Fracture toughness [J/m]		
Rod speed	1,10 %	1,57 %	2,00 %	1,10 %	1,57 %	2,00 %
1,5 cm/s	13,5	13,1	13,6	2,3	1,9	1,7
8,7 cm/s	14,3	13,4	-	2,1	1,9	-
17,0 cm/s	13,8	13,8	13,7	2,1	2,1	2,0

Table 12. Tensile strength and fracture toughness in three different nanocellulose concentrations as a function of rod metering speed. The tests were performed in machine direction (MD). For detailed specifications, see **Table 4.** Test series 1*.

8.3.9. Heat treatment test

Summary

As displayed in **Figure 34**, heat treatment was observed to improve the water resistance of coated film composites. This most likely also means, that heat treatment reduces WVTR. This

result is suspected to be a consequence of aggregation between adjacent cellulosic surfaces, as presented by Österberg et al. (2013). In addition, the decreasing trend of both coat weight and coating thickness might support the aggregation phenomenon, as displayed in **Figure 35**. However, the pigment coating on the board caused most likely a nuisance factor while measuring air permeability, and possibly also while measuring oil absorption. This is predicted even though the pigment coated side was the opposite of the measured side. Finally, the pigment coated side might somewhat explain the unpredicted behavior of air permeability and oil absorption, which does not obey a similar trend as water absorption: According to Nair et al. (2014), oxygen permeability should also decrease as a consequence of heat treatment.

Future development

The behavior of air and oil barrier in response to heat treatment would require more testing, with a substrate that is not pigment coated. In addition, the effect of drying time would be interesting to investigate: Kimpimäki et al. (2008) reported a considerable decrease in WVTR of polymer dispersion coatings exposed to 80-120°C for only 15 and 30 seconds. Although the consolidation mechanism between dispersion coatings and nanocellulose might differ remarkably, this suggests that the same could apply for nanocellulose coatings. In addition, the increase in wet strength and other mechanical properties after heat treatment could also be investigated.
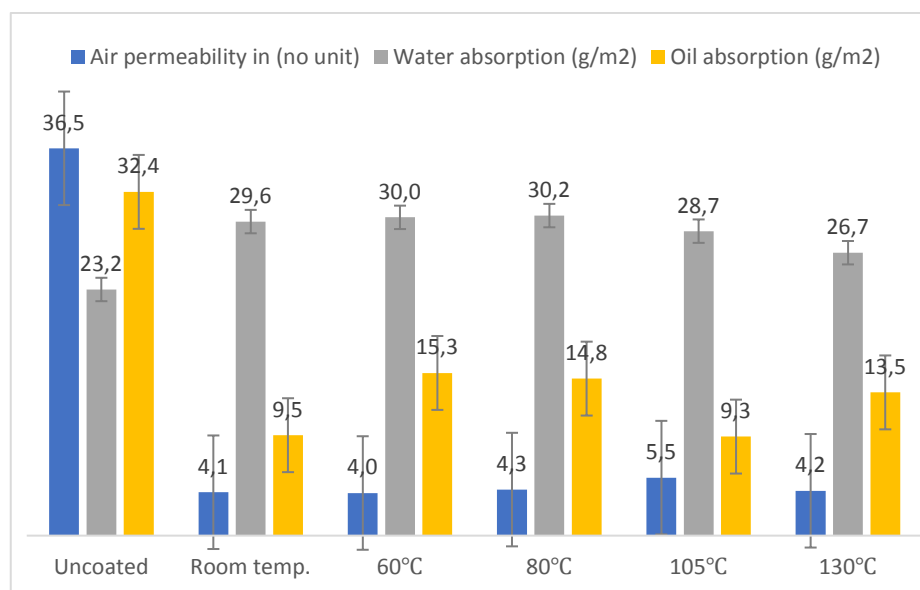

Figure 34. The effect of heat treatment a.k.a. drying in elevated temperature on barrier properties. The treatment was conducted inside an oven for 1,5 hours in the reported temperatures. For detailed specifications, see **Table 7.** Heat treatment test.

Effect on water absorption

The only clear effect the heat treatment had on the measured barrier properties of water, air and oil was the one on COBB water absorption. As reported by Kimpimäki et al. (2008), water vapor transmission decreases by the increase in drying temperature. As illustrated in **Figure 34**, the decrease in COBB water absorption occurs only when drying above 80 °C, which is in line with the documented behavior by Kimpimäki et al. (2008). Likewise, Österberg

et al. (2013) reported an increase in water-resistance of films prepared from nanofibrillar cellulose: By heating up CNF films, wet strength was imparted to the film. This effect was suspected to originate from coalescence of adjacent nanocellulose fibril surfaces, an effect also referred to as aggregation. In addition to water-resistance, it is likely that the aggregation of adjacent cellulosic surfaces is also the microstructural cause of reduced COBB water absorption, which should basically be synonymous. Moreover, the pigment coating on the non-fibrous side of the substrate appeared not to have an impact on the COBB water absorption results.

Effect on air permeability

According to Nair et al. (2014), heat treatment should have a reducing effect on oxygen permeability. This suggests, air and oxygen permeability being rather alike, that the air permeability should indicate a notable decrease by the increase in drying temperature. However, the substrate was pigment coated from the non-fibrous side, which blocked most of the outbound air flow. This most likely had a disturbing effect also on the air flow inbound, which somewhat explains its twisted curve profile.

Effect on oil absorption

Aulin et al. (2010) reported that oil absorption is somewhat predictable from air and gas permeability (Sjöholm 2010). However, regarding the oil and air barrier results of the coated samples displayed in **Figure 34**, the correlation between oil and air barrier appears inversely proportional.

Heat treatment test by coat weight and coating thickness
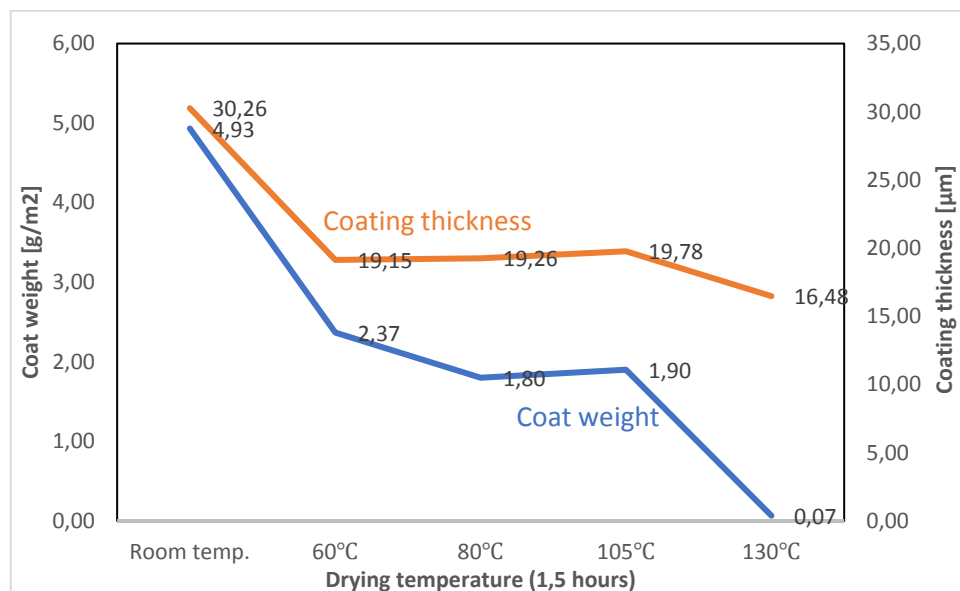
Figure 35. The influence of drying temperature on coat weight and coating thickness. For detailed specifications, see **Table 7.** Heat treatment test.

Analogy of coat weight and coating thickness behavior with water transmission behavior

Kimpimäki et al. (2008) reported that the WVTR of polymer dispersion coatings decreases in drying temperatures of about 90 ℃ and above. Similarly, the COBB water absorption of nanocellulose coat weight and coating thickness appears to decrease in the drying

65

temperature of 105°C and above. In addition to Kimpimäki et al., according to **Figure 34** the behavior of coat weight and coating thickness is somewhat in line with the behavior of COBB water absorption, where water absorption experiences a decrease at temperatures above 80°C.

The effect of fiber network deformation

Water penetration into the base sheet was reported by Manninen et al. (2011) to cause an increase in base sheet grammage and base sheet thickness (Gustafsson 2011). Due to the measurement method of both coat weight and coating thickness (subtraction of coated paper from dry paper), this would exaggerate the results which are displayed in **Figure 35**. Moreover, due to heat treatment, the penetrated water should evaporate at an increasing extent as a function of drying temperature. However, the abrupt decrease of both coat weight and coating thickness at temperatures of 105°C and above seems unexplainable by the explanation of Manninen et al. (2011). As fiber network deformation and drying shrinkage of the base sheet caused by water evaporation from the base sheet would suggest a steadier decrease of both coat weight and coating thickness as a function of drying temperature, it could be that the abrupt decrease of coat weight and coating thickness at temperatures above 105°C was caused by the aggregation of adjacent cellulosic surfaces, meaning nanofibrillar surfaces. This kind of behavior which showed as increased wet strength was reported by Österberg et al. (2013) with nanocellulose films.

8.3.10. Pretreatment and substrate test

Summary

In summary, when interpreting the data in **Table 14**, it can be declared that *the coating-substrate combination of Polyethylene Raw Cupboard and non-pretreated nanofibrillar cellulose (PE/NFC) performs the best as a coated film composite*. However, the result was not predicted by the theoretical result in **Table 14**, which considered only the theoretical interfacial adhesion and theoretical barrier properties based on the rule of polarity, "like dissolves like". As the theoretical result did not predict the actual result, it ought to conclude that the interaction between the coating and the base sheet is relatively complicated, and involves phenomena covered by the wetting and adhesion theories which are typical for paper, which were not taken into account herein. Out of the ones relevant within paper products, these phenomena include mechanical interactions, the diffusion theory, thermodynamic adsorption theory, weak boundary layer theory and the penetration of liquid into porous material (Kuusipalo and Avellan, 2008). Moreover, also the sizing of the Polyethylene Raw Cupboard might explain its superiority, as also the second highest total barrier was achieved by this paperboard in terms of the actual results. In addition, the actual cause of the results is even more encouraged to be left in the state of speculation, because the tracking of base sheet compositions is often difficult for instance due to their commercial interest.

9. Combination	IF	OB (-)	MB (+)	AB (-)	Total barrier	Theory
PEr(-)/TEMPO(-)	Low	Low	High	Low	Low	-
UD(+)/TEMPO(-)	High	Low	High	Low	Medium	-
PEr(-)/NFC(+)	High	High	Low	High	High	-
UD(+)/NFC(+)	Low	High	Low	High	Medium	-
PEr(-)/TEMPO(-)	-	5,5(+1)	25 (+1)	2,1 (-1)	Med.(+1)	N/A
UD(+)/TEMPO(-)	-	17,3(-2)	31 (-2)	1,3 (+2)	Low(-2)	N/A
PE(-)/NFC(+)	-	6,6(-1)	24 (+2)	1,7 (+1)	High(+2)	OK
UD(+)/NFC(+)	-	4,6(+2)	27 (-1)	2,8 (-2)	Med.(-1)	OK

Table 13. In the table, the higher rows indicate a theoretical approach, while the lower rows indicate an approach based on the test results indicated in **Figure 36**. Theoretical barrier results are based on the theory that both interfacial adhesion as well as polarity/ionic charge affect the final barrier of the coated sheet. In the table, OB = Oxygen barrier, MB = Moisture barrier, AB = Air barrier, IF = Interfacial adhesion. The plus and minus signs of PE, UD, TEMPO, OB, MB and AB indicate charge, whereas the plus and minus numbers in the lower part of the table indicate a rating between samples based on barrier results from **Figure 36**. Finally, the total barrier results and their alignment with theory is indicated.

Theories that were predicted to show in the results

1. *Oil absorption* - Aulin et al. (2010) stated that oil absorption is predictable from air permeability (Gustafsson 2011). However, as indicated **Figure 36**, instead of direct proportionality the only way would be as inversely proportional considering all the coated samples.
2. *All barrier properties* - Like dissolves like: Polar gases and liquids dissolve into polar materials, while non-polar gases (such as oxygen and nitrogen) and liquids (such as oil) dissolve into non-polar materials. As such, the theory applies also vice versa. As indicated in **Figure 36**, this theory appears to apply rather well.
3. *Aggregation of TEMPO-oxidized CNF* - Permanent aggregation could explain worse air barrier with TEMPO-oxidized nanocellulose. In principle, while increasing ionic strength, the shear rate level which leads to permanent aggregation should decrease, as explained in **Section 4.4**. However, the rod metering speed and the rod type, and thereafter also the shear rate, were equal for each sample throughout the test. Therefore, both TEMPO samples should have shown an increase in e.g. air permeability as a consequence of permanent aggregation, which was not the case.
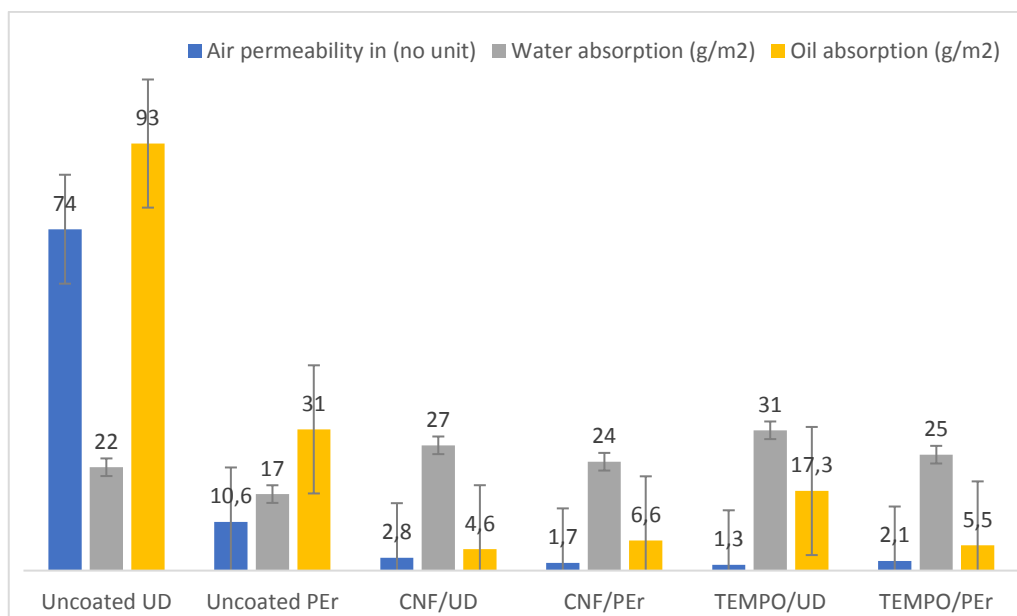
Figure 36. The fundamental impact of the type of pretreatment and the type of substrate on barrier properties. For detailed specifications, see **Table 8.** Pretreatment and substrate test.

Oil absorption

Gustafsson (2011) measured both air permeability and oil absorption of a greaseproof paper, and concluded them to be directly proportional: When oil absorption increases linearly, air permeability increases exponentially. However, in the tests illustrated in **Figure 36**, the oil absorption appears to be inversely proportional to air permeability, which remains unresolved. Nevertheless, it can be explained by random variation regardless of three replicates of each sample, since the nature of the COBB oil absorption test is relatively inaccurate.

Water absorption

The Cobb-value of both samples, the TEMPO-pretreated and the non-pretreated NFC, increased when compared to the uncoated sheet. As already presented in **Figure 30**, the water holding capacity of nanofibrillar cellulose is very high, as evidenced by Sjöholm (2010). Nevertheless, there are still notable differences between the four coated samples, two of which are explained by the selection of base substrate: PEr substrate as a cupboard absorbs less water than UD substrate. Furthermore, the TEMPO-pretreated coating absorbed more water than the non-pretreated coating. As these coatings had the same concentration of 1,70 %, the explanation lies elsewhere, most likely in the polar carboxylated groups which attract more water molecules. Subsequently, these water molecules will interfere with interfibrillar hydrogen bonds while increasing the water content of the suspension.

Air permeability behavior of TEMPO-oxidized CNF

Visanko et al. (2015) as well as Chinga-Carrasco and Syverud (2012) reported a decrease in the oxygen permeability of CNF as a consequence of TEMPO-mediated oxidation (Hubbe et al. 2017). The reduction was considered to occur due to the polar nature of carboxylic acid groups, which were suspected to introduce a higher cohesive energy density to the film

material. In addition, this would also be explained by "like dissolves like", since the carboxylic groups render TEMPO-oxidized CNF more hydrophilic. Further, as illustrated in **Figure 36**, the impact of the TEMPO-oxidation on air permeability of CNF resulted somewhat ambiguous: When compared to the non-pretreated CNF, it had a reducing impact on air permeability with Uncoated Duplex (UD) as a base substrate, although the result was contradictory with Polyethylene Raw Cupboard (PEr) as substrate. This variation might be explained by the worse interfacial adhesion between TEMPO-pretreated CNF and PEr substrate when compared to the adhesion with the UD substrate, consequently leading to a reduced coating coverage of TEMPO-pretreated CNF. Indeed, the requirement of interfacial adhesion might be higher with TEMPO-pretreated CNF due to its higher viscosity when compared to non-pretreated CNF. Moreover, the consequent difference in interfacial adhesion between the two nanocellulose suspensions might have critically increased the air permeability of TEMPO-oxidized CNF on top of PEr substrate.

8.3.11. Crosslinking test of soy protein

Summary

It appears that soy protein increases the COBB water absorption value, which is logical since soy protein, as does nanocellulose, possesses a high water holding capacity due to its abundant free hydroxyls. However, as soy protein contains also hydrophobic amino groups, soy protein likely interacts more readily with the crosslinking agent glutaraldehyde than nanocellulose. The crosslinking agent, in turn, reduces the water holding capacity of soy protein, making it more water-resistant. This suggests, that with even higher amounts of crosslinking agent, the water absorption of the nanocellulose soy protein suspension could be decreased to a lower level than that of pure nanocellulose. Finally, the result encourages to try adding more crosslinking agent, and also soy protein, in continuation. The overall barrier results are displayed in **Figure 37**, although it is noteworthy that there were no replicates in this test to confirm the trends.
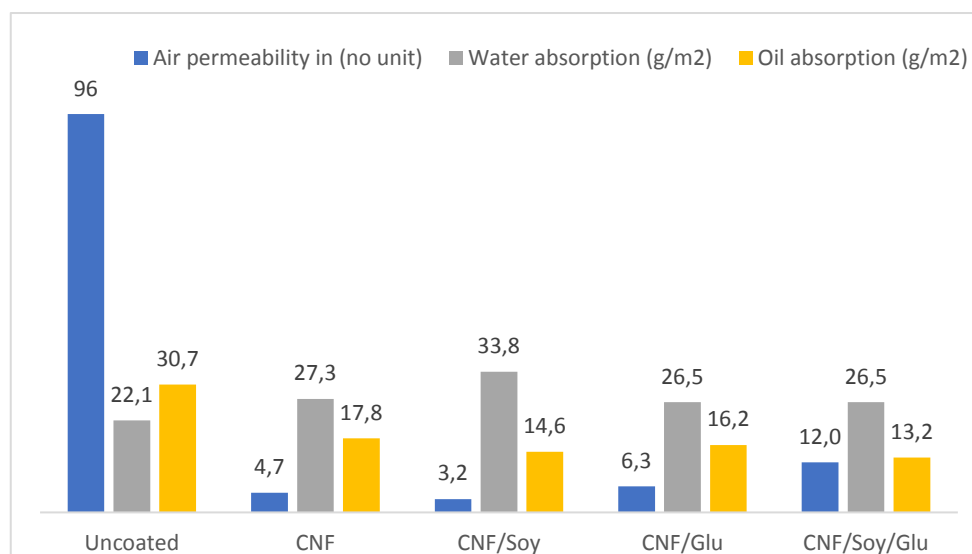
Figure 37. The measured barrier properties were water absorption, oil absorption, and air permeability of the coated sheet. The substrate used was Uncoated Duplex. For detailed specifications, see **Table 6.** Crosslinking test.

69

Oil absorption

The soy protein appeared to lower the oil absorption. In terms of the rule of thumb "like dissolves like", this is explained by the hydrophilicity of soy protein, although after denaturation the hydrophobic groups were also activated. When comparing samples with and without glutaraldehyde (Glu), it appears that crosslinking improved oil resistance even more. Finally, the common effect of soy protein and glutaraldehyde indicated the highest oil barrier. Nevertheless, the COBB-Ungern oil absorption test has a high error margin, and more tests should be done to confirm the trends.

Water absorption

The high water-holding capacity of soy protein was evidenced by the high water absorption of the sheet coated with soy protein (Soy) and nanocellulose (CNF). Furthermore, the drop of water absorption as a consequence of glutaraldehyde addition to the CNF/Soy coating clarifies the effect of crosslinking on water absorption. Likewise, the effect of crosslinking was also notable after adding glutaraldehyde to pure nanocellulose, although the effect was much lesser most likely due to the absence of the readily crosslinking hydrophobic side groups.

Air permeability

It is quite ambiguous why the permeability was the least with the coating of nanocellulose and soy protein. However, both contain large amounts of free hydroxyls, so this could also be explained by "like dissolves like". Moreover, based on the results it is likely that crosslinking increases air permeability, yet the reason for this remains unclear.

The effect of crosslinking

By using a *crosslinker*, Gustafsson (2011) reported that the influence of fibrillar structure opening being caused by water in a MFC suspension was fully eliminated. However, in the same experiment the predicted decreasing effect of the crosslinker on air and gas permeability did not show with the applied MFC suspension coat weight of 0,2-0,5 g/m2, and only some decrease until reaching a 20 wt% content of crosslinker. In addition, no notable effect was obtained between coat weight and oil absorption while adding crosslinker in MFC suspension. However, in the test some samples were deteriorated by excessive oil permeation.

8.3.12. Scanned electron microscope analysis

Description

The primary target of the following Scanned Electron Microscopy (SEM) inspections, as displayed in **Figure 38** and **Figure 39**, was to find any visual indication of nanofibril alignment which was presumed to increase mainly by the increase in rod metering speed, and possibly also due to other rheological phenomena such as extensional viscosity between the wires of the rods. The presumptions were based on fibril alignment reported by Karppinen et al. (2012) and Saarikoski et al. (2012) regarding flocculation, on the increasing fibrillar orientation as a function of shear rate as reported by Gustafsson (2011), and on the extensional viscosity behavior, as described in **Section 4.4**. Furthermore, the applied

accuracies of 10 µm and 2 µm enabled to monitor the nanofibrils and their orientations to a satisfactory extent.
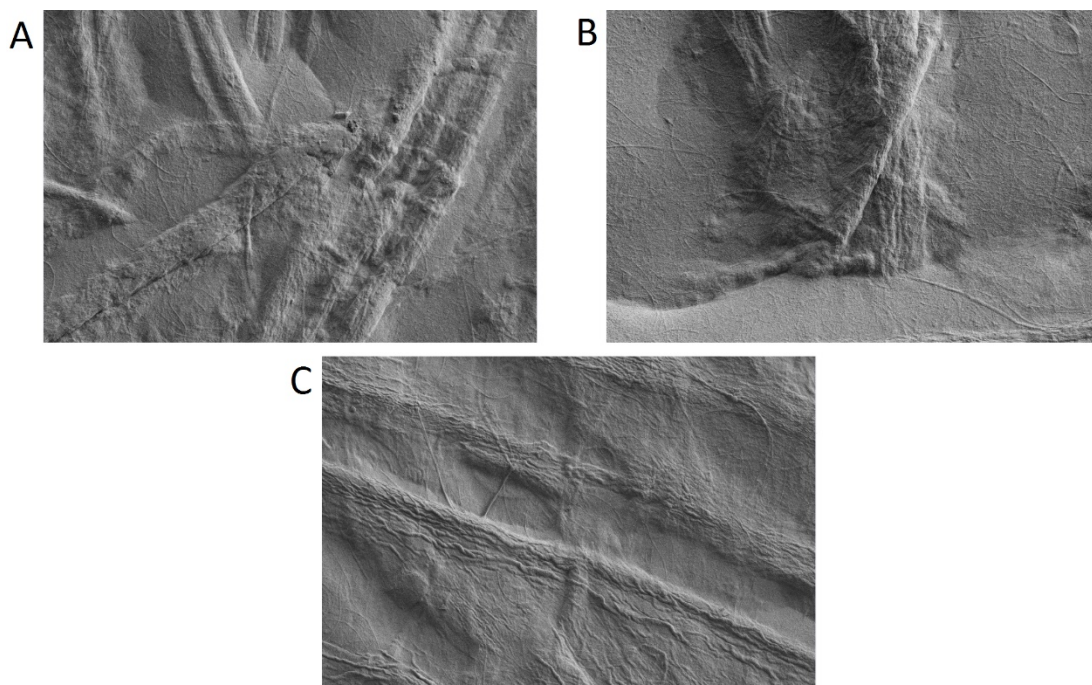

Figure 38. SEM images from samples of test series 2 at an accuracy of 10 µm: **a)** Rod speed 19,2 cm/s and rod wire diameter 1,27 mm. **b)** Rod speed 1,5 cm/s and rod wire diameter 1,27 mm. **c)** Rod speed 19,2 cm/s and rod wire diameter 0,64 mm.
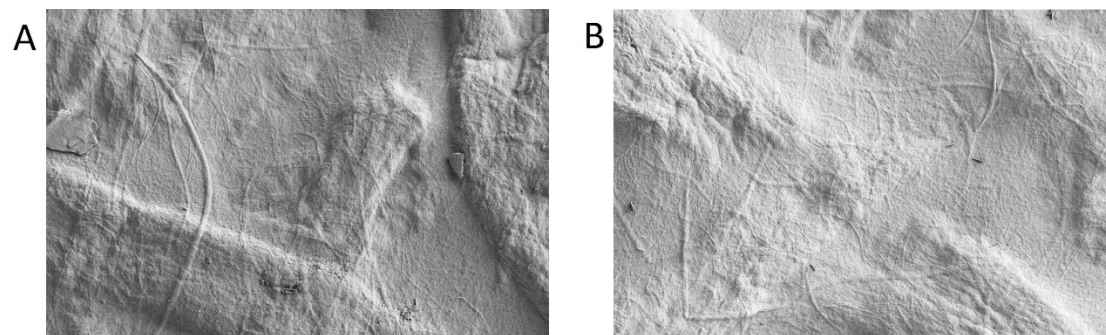
Figure 39. SEM images from heat treated samples at an accuracy of 2 µm: **a)** Drying at room temperature. **b)** 1,5 hour heat treatment at 130°C.

Summary

Both the increase in rod speed as well as to some extent the decrease in rod wire diameter was mainly expected to increase fibril alignment, or fibrillar anisotropy. However, whilst the nanofibrils demonstrated an apparently isotropic behavior regarding each sample, no collective fibril alignment was found between images. Therefore, it is difficult to believe that fibril alignment would have a considerable impact on barrier properties while increasing rod speed. Instead, based on the report by Gustafsson (2011), the decreasing content of water penetrating to the base sheet by the increase of rod speed appears a more likely cause of

reduced air and gas permeability. Based on the report by Aulin et al. (2010), this should predict oil absorption as well.

8.4. Optimum barrier coating with optimum parameters

As presented by Kimpimäki and Savolainen (2015), the coated film composite is practical to approach as separate factors. These include the coating, the substrate, and the coating process. In the coating process, viscosity is especially important when the coating travels in the pipes and goes through unit operations which experience high shear. Moreover, during coating consolidation the drying method is relevant.

8.4.1. Coating and substrate

Before the actual coating operation, the variables involving the composition of the coating and the substrate are determined. In principle these variables are numerous, although in this thesis they cover the pretreatment method of both the coating and the substrate, the crosslinking amount added to the coating, and the composition of the coating and also the substrate. However, the substrate composition is usually predetermined in the industrial facility from where it has been delivered.

Sizing

As a rule of thumb, stated earlier in **Section 4.2** already: The less the base sheet absorbs water from the coating, the better the properties of the coated film composite. However, it is beneficial for the water to penetrate in limited amounts to the base sheet. In terms of sizing, there are two alternatives. One is to coat with a surface size, another is to mix hydrophobic size, or internal size, into the paper slurry prior to coating. Regarding surface sizing, issues such as surface charge of the base sheet, particle size, electrostatic stability, solids content and viscosity of the surface size should be considered while selecting a proper surface size. (Paltakari and Lehtinen, 2009) The investigation on a proper sizing method requires knowing adhesion theories which are relevant to paper and board, as indicated in **Section 4.2.2.** However, in this thesis a proper sizing method was not investigated more exactly.

Composition

Affecting the composition by adding other substances into the coating is undoubtedly a considerable method to improve the properties of the final coating. Since nanocellulose suspensions typically exhibit a low moisture barrier, it should be increased somehow. One method which appeared promising on behalf of the Crosslinking test (**Table 6**), which would take place prior to the coating operation, is the addition of crosslinked soy protein. Based on results of **Section 8.3.11**, a composition of nanocellulose and crosslinked soy protein could improve the moisture barrier considerably. In addition, montmorillonite nanoparticles (Nair et al. 2014) decrease WVTR and vermiculite nanoparticles (Sjöholm 2010) increase oxygen barrier at high RH.

72

Pretreatment of nanocellulose coating

Since the substrate is often sized and Sjöholm (2010) reported a decrease in barrier properties due to cationic starch being added as surface size into the nanocellulose suspension, it is likely that cationic starch as blended into the nanocellulose dispersion would turn out as a good option to reduce moisture absorption of nanocellulose coating suspension. According to Sjöholm, the starch should be cationic to provide a low surface charge. Consequently, this prevents aggregation with nanocellulose fibrils, which otherwise deteriorate the barrier properties. In this case, the mixture of cationic starch and nanocellulose resulted into a rough surface where the starch containing areas were smoother and nanocellulose containing areas were rougher. (Sjöholm 2010)

8.4.2. Coating process

Coating viscosity

In dispersion coating, polymer dispersions typically exhibit a viscosity in the range between 500 and 1000 mPa*s (Kimpimäki et al. 2008). With nanocellulose coating dispersions, an issue is its high viscosity (Richmond et al. 2014). Due to the pseudoplastic a.k.a. shear thinning nature of nanocellulose suspensions, the high viscosity might turn out a problem especially in sub processes that experience shear rates within the low-shear range area. In the coating process, this range typically involves pumping and mixing (Roper 2009), whereby a high viscosity might result into clogging. On the contrary, the viscosity of nanocellulose suspensions might also turn out too low especially in the ultra-high shear range. In the coating process, the ultra-high shear range typically involves the metering of the coating, and the exposition to ultra-high shear is very momentary (Roper 2009), as described in **Section 8.3.1**.

Regulation of viscosity

A proper viscosity is essential for a good coating runnability, and as such there exist many ways of regulating viscosity in coating industry, such as the addition of latex. The regulation of viscosity involves either reducing or increasing viscosity. The reduction of viscosity might be useful within sub processes that experience low shear rates, typically lasting from seconds to minutes. One way of reducing coating viscosity is the addition of minerals. Nygårds (2011) reported a decrease in coating viscosity by adding BarriSurf® LX minerals, which represent a type of kaolin. Apart from decreasing viscosity the target was also to enhance barrier properties, although the minerals finally proved ineffective in this respect. On the contrary, the augmentation of viscosity might be useful within unit operations that experience ultra-high shear rates, typically lasting for a few microseconds. Among various possibilities, one way of increasing coating viscosity would be to increase its solids content.

Coating parameters for different end-uses

Table 15 is a brief qualitative recapitulation based on earlier results in this thesis. It summarizes the permeability and absorption properties obtainable by using different combinations of parameter settings of the rod coater. In general, the lower the permeability or absorption properties, the better, although different food products naturally have different barrier requirements, as presented earlier in **Figure 4** in **Section 3**.

73

Rod coater parameters		Rod Gap Size / Wire diameter					
		High			Low		
Rod Speed	High	AP	WA	OA	AP	WA	OA
		Low	High	Low	Medium	Medium	Medium
	Low	AP	WA	OA	AP	WA	OA
		Medium	High	Medium	High	Medium	High

Table 14. The qualitative results are based on the results in this thesis, obtained by using different rod parameter settings. In the table, AP = Air permeability, WA = Water absorption, and OA = Oil absorption.

Heat treatment

Based on the results of **Figure 34** as well as earlier tests by e.g. Österberg et al. (2013), drying for 1-2 hours at elevated temperature increases moisture resistance. As the polymer dispersion coatings appear to follow the same conformity to law (Kimpimäki et al. 2008), it ought to be that the effect of heat treatment will be maintained to a fair extent even though additional materials, such as crosslinked soy protein, would be added to the nanocellulose suspension. Nevertheless, also a very short heat treatment of only 15 or 30 seconds could already impart drastic improvement in moisture resistance, as according to Kimpimäki et al. (2008) regarding polymer dispersion coatings. If this applies also for nanocellulose coatings, the heat treatment would be even more suitable for a continuous process.

Wire and hot press

A wire and a hot press could form the final process line after the coating operation, and could possibly also be combined with the heat treatment stage. As presented in Hubbe et al. (2017), a hot press or some radiation treatment could prove as a useful method to finalize the nanocellulose film preparation. For instance, hot pressing appears to enhance wet strength of nanocellulose films (Österberg et al. 2013), which is significant in liquid packaging and thereafter a strong attribute of the liquid packaging board. In addition, filtration by a wire could improve interfacial adhesion. By the aid of pressure difference, this could integrate the cellulose nanofibrils more rigorously into the base sheet shortly after the coating operation. This behavior appears to be covered by some adhesion theories, such as the penetration into a porous material, as mentioned in **Section 4.2.2**.

8.5. Future development

Investments on dispersion coating are promising in regard of environmental awareness, although the use of biopolymers in dispersion coatings appears not to have been implemented to date. The problem with biopolymers is typically their relatively low moisture barrier properties compared to the already existing polymers, such as LDPE. In addition, biopolymers usually have a high price. However, possible applications for dispersion coated biopolymers could include liquid and aseptic packages, where the dispersion coatings would function as a primary layer. (Sjöholm 2010) Moreover, rod coating has been practiced for decades in the pigment coating industry, and as such this technology provides useful

information in respect of the adjustment of the coating operation. For instance, the impact of hydrodynamic forces on the dependency of coat weight on rod metering speed appears worth further research. (Linnonmaa and Trefz, 2009).

Experiments

Although the laboratory rod coater was selected in this thesis as the device for performing the coating operation, there undoubtedly exist various competitive device alternatives. For instance, Gustafsson (2011) reported the spray coater / CLC-coater to suit the coating of MFC suspension on paperboard rather well. Other examples of implementable coating device alternatives could be drawn from today's industrial coating. Moreover, examples of topics worth research by e.g. testing with various coating device alternatives include testing of the effect of fibril alignment on barrier properties by comparing the barrier properties of coatings coated in MD and coatings coated in CD in respect to the base paper, testing of the dependency of oil absorption and air permeability and whether the rod parameters play a crucial role, testing of the common effect of water drainage and coat weight to air permeability and whether there is additional influence of rheological phenomena that takes place during metering, testing of metering speeds which induce a shear that reaches the shear rate range of flocculation, testing of how the coating method has an impact on the properties required from a base paper, among others. In addition, the air permeability results conducted by the Lorentz & Wettre measuring device could be reconducted by using the Ambertec device for more precise results. Likewise, the mutual dependency between the different barrier properties of air permeability, water absorption or water vapor transmission, as well as oil absorption, are worth more research. Especially considering the fact that the measurements were conducted by using the quantities air permeability and water absorption instead of the more applied and cited quantities of OTR and WVTR. Finally, some analysis tool such as SIMCA could be useful in determining linkages between various properties and parameters, such as between rod parameters, coat weight and barrier properties.

General research

In terms of general research, both the interaction between the coating and the base paper as well as the coalescence of nanocellulose a.k.a. curing behavior appear relevant topics. In practice, there are diverse grade options existing for cartonboard and generally paperboard grades. It would be interesting to investigate more closely the connection between the base paper structure and the final coating distribution, and the adhesion theories relating to it: How much coating is being deposited on the base paper surface depending on which type of coating composition and which type of base paper structure. Moreover, the coalescence of nanocellulose is defined as curing, and should be investigated more in terms of e.g. the adhesion theories existing for papermaking. The base paper structure is partially responsible of the amount of particles which deposit on the surface of the base paper during coating drainage. The extent of coating drainage could be connected to e.g. the surface charge of the base paper, which could be tested by contact angle measurement.

9. Conclusion

The thesis target was to understand the flow behavior of nanocellulose as a coating layer deposited on paper by using a laboratory rod coater. The experimental efforts covered tests related to the rod coating parameters and the properties of the deposited nanocellulose, while the main target was to investigate the response of the end-use properties on both the device parameters and the properties of the coated material.

In general, the behavior of the coating layer was approached from various perspectives. In the pretreatment and substrate test, the extent of interfacial adhesion and ionic charge or polarity were hypothesized to predict the total barrier capability of a coated sheet. According to results, these predictions were close to reality. This suggests that the hypotheses were somewhat correct. Furthermore, the water drainage to the coating was hypothesized to vary along the rod travel path as a function of nanocellulose concentration, which was hypothesized to increase towards the end of the rod travel path. However, no significant variance was found regarding the coating coverage of the coated sheets, which led to conclude that the concentration is constant and the water drainage is even during the coating operation.

Both air permeability and oil absorption were observed to respond to rod metering speed while using rods with small wire diameter. In contrast, these properties barely varied with large-diameter rods as a function of rod metering speed. This is to a large extent explained by hydrodynamic forces, which are negligible with small-diameter rods and prevailing with large-diameter rods. In addition, there was presumed to occur a common effect of water penetration and low coat weight. In practice, water penetration is suspected to cause z-directional non-uniformity to the base sheet and the low coat weight is non-linearly proportional to air permeability, leading to an exponential increase of air permeability at low coat weights. Nevertheless, apart from water penetration into the base sheet and hydrodynamic forces, also other rheological properties could have had an impact on air permeability and oil absorption. However, the presence and impact of fibril agglomeration on the results was determined to be negligible due to shear rate differences. In terms of mechanical properties, fracture toughness was found to exhibit a slight decrease as a function of concentration, which could be a cause of nanocellulose percolation. However, there was found earlier results only as a function of coat weight, which likely is not fully compatible to compare with concentration. In addition, tensile strength was not found to have any correlation with concentration, although the result might be different with coat weight.

Both heat treatment and the addition of cross-linked soy protein were found as practical methods to increase the water-resistance of nanocellulose. The soy protein, while containing hydrophobic groups, was able to crosslink with glutaraldehyde, thus reducing water absorption. Moreover, the heat treatment was suspected to induce the aggregation of adjacent cellulosic surfaces, which apparently implies the aggregation of nanofibrils. However, no notable difference considering the nanofibrils between a non-treated and a heat-treated sheet was found from SEM images. Furthermore, as predicted, the base paper had a considerable impact on the extent of water penetration into the coated sheet while measuring water absorption with the Cobb-test. However, a slight increase in water absorption was found as a function of rod gap size, which evidenced the hydrophilicity of

nanocellulose. Moreover, the fiber network expansion due to water penetration caused an increase in both paper grammage and paper thickness, which added a nuisance factor to the coat weight and coating thickness results. The exaggeration was higher with lower rod metering speeds, which allowed more time for water to penetrate into the base paper. Nevertheless, a water vapor transmission test could have provided more exact results than a water absorption test in terms of the individual coating layer.

The flow behavior of nanocellulose in terms of rod coating was identified. The main forces acting during the coating operation include rheological forces such as hydrodynamic forces, which together with water drainage to the base sheet define the effect of rod metering speed on air permeability and oil absorption of the coated film composite. However, regarding water absorption the effect was not obvious, although water vapor transmission tests might have proven differently. In addition, nanocellulose properties were affected by decreasing water absorption by cross-linked soy protein and heat treatment.

References

ANDERSSON, C., ERNSTSSON, M., JÄRNSTRÖM, L., 2002. Barrier Properties and Heat Sealability/failure Mechanisms of Dispersion-coated Paperboard. Karlstad University, Department of Chemical Engineering. *Packaging Technology and Science 2002*; **15**: 209-224.

AULIN, C., GÄLLSTEDT, M., LINDSTRÖM, T., 2010. Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. *Cellulose*, **17**(3), pp. 559-574.

AUVINEN, S. and LAHTINEN, K., 2008. Chapter 9: "Converted paper and paperboard as packaging materials", in Book 12: Paper and Paperboard Converting, 2nd Edition, J. Kuusipalo (ed.). *Finnish Paper Engineers' Association.* ISBN 978-952-5216-28-8. pp. 286-332.

BORCH, J., 1991. *Journal of Adhesion Science and Technology.* **5**(7):523. Paper and Paperboard Converting. Chapter 2: Wetting and adhesion. *Finnish Paper Engineers' Association.* ISBN 978-952-5216-28-8. pp. 14-49. 346 p.

CAPRON, I., ROJAS, O. J., BORDES, R., 2017. Behavior of nanocelluloses at interfaces.

DOROUDGARIAN, N., 2011. Nanocomposite Films of Hemicellulose and Nanocelluloses with Improved Barrier Properties for Packaging Applications. Master's thesis, Luleå University of Technology (LUT).

DUFRESNE, A., 2013. Nanocellulose – From Nature to High Performance Tailored Materials. *De Gryuter.* ISBN 978-3-11-025456-3, 476 p.

FORSSTRÖM, U., 2009. Chapter 3: *Base paper*, in Book 12: Pigment Coating and Surface Sizing of Paper, 2nd Edition, J. Paltakari (ed.). *Gummerus Oy.* ISBN 978-952-5216-27-1, pp. 42-55.

GRÖN, J., SALMINEN, P., TOIVAKKA, M., PALTAKARI, J., 2009. Chapter 11: *Coating layer consolidation and formation of the coating layer structure*, in Book 11: Pigment coating

and surface sizing of paper, 2nd Edition, pp. 356-389. Jyväskylä, 2008. ISBN 978-952-5216-27-1. 615 p.

GUSTAFSSON, E., 2011. The use of bio-based coatings as a barrier material applied with spray-coating technology. Master's thesis. Aalto University, School of Chemical Technology. Espoo, 2011. 89 p.

HANCIOGULLARI, H., 2009. Chapter 7: *Co-binders and thickeners*, in Book 11: Pigment coating and surface sizing of paper, 2nd Edition, J. Paltakari (ed.). Jyväskylä, 2008. ISBN 978-952-5216-27-1, pp. 228-274.

Holoeast, Wire wound rod, http://www.holoeast.com/machines/coating/WIRE-WOUND-ROD.png. 6.4.2017.

HUBBE, M. A., FERRER, A., TYAGI, P., YUANYUAN, Y., SALAS, C., PAL, L., ROJAS, O. J., 2017. Nanocellulose in Thin Films, Coatings, and Plies for Packaging Applications: A Review. "Nanocellulose in Packaging", *BioResources* **12**(1), pp. 2143-2233.

Anonymous, The rod coater user manual: "K Control Coater User Manual" http://www.testingmachines.com/pdf/30-01-k-control-coater.pdf, 6.4.2017.

KARPPINEN, A., SAARINEN, T., SALMELA, J., LAUKKANEN, A., NUOPPONEN, M., SEPPÄLÄ, J., 2012. Flocculation of microfibrillated cellulose in shear flow. *Cellulose (2012)* **19**: 1807.

KARVO, A., KANALA-SALMINEN, H., KOPONEN, H., 2009. Nanomateriaalien hyödyntämismahdollisuudet pakkausteollisuudessa. *Teknologiakeskus Ketek Oy*, pp.14-15.

KAILA, MERILÄINEN, OJALA, PIHKO, 2008. Reaktio 4: Lukion kemia. Metallit ja materiaalit, v. **1-2**. *Tammi.* ISBN 978-951-26-5467-3.

KIMPIMÄKI, T., LAHTINEN, K., AVELLAN, J., 2008. Chapter 3: *Dispersion coating,* pp. 60-103, in Book 12: Paper and Paperboard Converting, 2nd Edition. *Finnish Paper Engineers' Association/Paper ja Puu Oy.* Jyväskylä, 2008. ISBN 978-952-5216-28-8.

KIMPIMÄKI, T., SAVOLAINEN, A. V., 2015. Barrier dispersion coating of paper and board. *Surface Application of Paper Chemicals,* pp. 208-209.

KUUSIPALO, J., 2008. Book 12: Paper and Paperboard Converting, 2nd Edition. *Finnish Paper Engineers' Association.* ISBN 978-952-5216-28-8. 346 p.

KUUSIPALO, J., AVELLAN, J., TAIPALE, J., PIETARI, I., 2008. Chapter 6: *Lamination*, pp. 188-207, in Book 12: Paper and Paperboard Converting, 2nd Edition. *Finnish Paper Engineers' Association/Paper ja Puu Oy.* Jyväskylä, 2008. ISBN 978-952-5216-28-8.

LAVOINE, N., DESLOGES, I., KHELIFI, B., BRAS, J., 2014. Impact of different coating processes of microfibrillated cellulose on the mechanical and barrier properties of paper. *Journal of Material Science* **49**, pp. 2879-2893.

LEHTINEN, E., IMPPOLA, O., PALTAKARI, J., 2009. Chapter 1: *Introduction to pigment coating and surface sizing of paper and board.* Pigment Coating and Surface Sizing of Paper. *Gummerus Oy.* ISBN 978-952-5216-27-1, 615 p.

LILJESTRÖM, A., 2016. Cellulose adhesion by nanocellulose hydrogels. Master's thesis, Aalto university School of Chemical Technology.

LINDSTRÖM, T. and AULIN, C., 2014. Market and technical challenges and opportunities in the area of innovative new materials and composites based on nanocellulosics. *Scan. J. Forest Res.* **29**(4), 345-351. DOI: 10.1080/02827581.2014.928365.

LINNONMAA, J., TREFZ, M., 2009. Chapter 14: *Coating and surface sizing technologies,* pp. 462-546. Pigment Coating and Surface Sizing of Paper. *Gummerus Oy.* ISBN 978-952-5216-27-1, 615 pp.

MANNINEN, M., KAJANTO, I., HAPPONEN, J., PALTAKARI, J., 2011. The effect of microfibrillated cellulose addition on drying shrinkage and dimensional stability of wood-free paper. *Nord. Pulp Pap. Res. J.* **26**(2011):4.

MCKEEN, L. W., 2012. Permeability Properties of Plastics and Elastomers, 3rd Edition. *Elsevier*, 2012. ISBN 978-1-4377-3469-0.

NAIR, S. S., ZHU, J. Y., DENG, Y., RAGAUSKAS, A. J., 2014. High performance green barriers based on nanocellulose. *Sustainable Chemical Processes*, **2**:23, pp. 1-7.

NYGÅRDS, S., 2011. Nanocellulose in pigment coatings – Aspects of barrier properties and printability in offset. Master's thesis. Linköping University Department of Physics, Chemistry and Biology. LITH-IFM-A-EX--11/2533—SE.

PAJARI, H., RAUTKOSKI, H., MOILANEN, P., 2012. Replacement of synthetic binders with nanofibrillated cellulose in board coating: pilot scale studies. *TAPPI International Conference on Nanotechnology for renewable material*. June 5.7.2012.

PALTAKARI, J., 2009. Pigment Coating and Surface Sizing of Paper. *Gummerus Oy.* ISBN 978-952-5216-27-1, 615 pp.

PALTAKARI, J., LEHTINEN, E., 2009. Chapter 9: *Surface sizing chemicals*, pp. 310-315. Pigment Coating and Surface Sizing of Paper. *Gummerus Oy.* ISBN 978-952-5216-27-1, 615 pp.

RICHMOND, F., HAUGHWOUT, C., BOUSFIELD, D., 2014. The Use of Cellulose Nanofibers in Paper Coating Formulation. University of Maine. *Paper Conference and Trade Show, PaperCon*, pp. 828-841.

ROPER, J., 2009. Chapter 10: *Rheology of pigment slurries and coating formulations*, in Pigment Coating and Surface Sizing of Paper, J. Paltakari (ed.). *Gummerus Oy.* ISBN 978-952-5216-27-1, pp. 318-351.

SAXENA, A., ELDER, T. J., RAGAUSKAS, A. J., 2011. Moisture barrier properties of xylan composite films. *Carbohydrate Polymers* **84** (2011), pp. 1371-1377.

SIRÓ, I. and PLACKETT, D., 2010. Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose,* **17**(3), pp. 459-494.

SJÖHOLM, K. 2010. Use of bio-based materials in fiber-based packaging. Master's thesis. Aalto University, School of Chemical Technology. Espoo, 2010. 99 p.

SPENCE, K. L., VENDITTI, R. A., ROJAS, O. J., HABIBI, Y., PAWLAK, J. J., 2010. The effect of chemical composition on microfibrillar cellulose films from wood pulps: water interactions and physical properties for packaging applications. *Cellulose*, **17**:835-848.

TOLBERT, L., KIM, Y., LEE, E., SHARMA, S., 2016. Fabrication and characterization of nanocellulose hydrogels for facile coating applications. *AATCC 2016 – (2016) AATCC International Conference Proceedings*, pp. 151-157.

TUOMINEN, M., VÄHÄ-NISSI, M., KUUSIPALO, J., 2008. Paper and Paperboard Converting. Chapter 2: Wetting and adhesion. *Finnish Paper Engineers' Association.* ISBN 978-952-5216-28-8. pp. 14-49. 346 pp.

VASILE, C., PASCU, M., 2005. Practical Guide to Polyethylene. *Rapra Technology Limited.* ISBN 1-85957-493-9.

VIRTANEN, S., 2015. Mikro- ja nanofibrilloidun selluloosan reologia. Bachelor's thesis, Aalto University School of Chemical Technology.

WANG, Z., SUN, X., LIAN, Z., WANG, X., ZHOU, J., MA, Z., 2013. The effects of ultrasonic/microwave assisted treatment on the properties of soy protein isolate/microcrystalline wheat bran cellulose film. *Journal of Food Engineering* 114(2013) 183-191.

YAICH, A. I., EDLUND, U., ALBERTSSON, A. C., 2011. Wood Hydrolysate Barriers: Performance Controlled via Selective Recovery. KTH, 2011. *Biomacromolecules 2012*, **13**, pp. 466-473.

ZHANG, W., XIAO, H., QIAN, L., 2014. Enhanced water vapour barrier and grease resistance of paper bilayer-coated with chitosan and beeswax. *Carbohydrate Polymers,* **101**, pp. 401-406.

ÖSTERBERG, M., VARTIAINEN, J., LUCENIUS, J., HIPPI, U., SEPPÄLÄ, J., SERIMAA, R., LAINE, J., 2013. A Fast Method to Produce Strong NFC Films as a Platform for Barrier and Functional Materials. American Chemical Society, *Appl. Mater. Interfaces*, **5**, 4640-4647.