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# **Layer-by-layer assembly of nanoclays for improved barrier properties of biobased polymers**

**Camilla Fulian Werring Werner**

Food Science and Nutrition: Production and Product Development

## Preface

This master's thesis was written during the spring 2021 and is the final achievement of five years of food science studies at The Norwegian University of Life Sciences (NMBU). This thesis is connected to the following projects: PackTech (Project no 12596), internal strategic project funded by Nofima and FutureFoodControl (Project no 314743), a strategic programme funded by Norwegian Levy on Agricultural Products.

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## Abstract

Today, 26 % of the total plastic volume in the world is used for packaging, and over 90 % of this plastic is fossil-based (MacArthur et al., 2016). A growing consumer awareness has led to a demand for alternatives to fossil-based plastic. Polymers made of biobased resources, called biobased polymers, are therefore of interest. Biopolymers are a promising replacement to fossil-based packaging. The industrial application of biopolymers for packaging has been limited because most biopolymers have poor mechanical- and barrier properties compared to fossil-based plastic. To improve these properties nanoclay can be used.

The purpose of this thesis was to find the best combination of liquids and substrates which was able to create an even coating and improve the barrier properties of the substrates. The study was performed step by step, and only one nanoclay-suspension was combined with PEI at the time. Changes and adjustments of the experimental design were done to improve the method. The biobased polymers PLA and three carton qualities were used as substrates. The substrates were coated with a polyethyleneimine (PEI)-solution and three different nanoclays by using the layer-by-layer (LBL) method through dip-coating. The three nanoclays were montmorillonite K10, halloysite and hydrophilic bentonite. Dip-coating includes using liquids to coat a solid substrate by immersing it and then withdraw and dry it. After drying the substrate were immersed in liquid again. The dip-cycle was repeated for as many times as necessary based on the experimental design.

The gas barrier properties were measured to examine the effect of the coatings. This was tested by measuring the oxygen transmission rate (OTR) and carbon dioxide transmission rate (CO<sub>2</sub>TR) for PLA. Two different methods were used for these measurements for comparison. All the carton qualities had relatively poor gas barrier properties. Of the three, Invercote Duo was most promising. Thus, this was chosen for further work after initial testing. To measure the gas barrier, OTR and air permeance were used. The OTR for PLA, measured with Dualperm 8001, increased from 106,75 ml O<sub>2</sub>/m<sup>2</sup>\*day to 109,8 ml O<sub>2</sub>/m<sup>2</sup>\*day after coating. The OTR for PLA, measured with AOIR, decreased from 115,8 ml O<sub>2</sub>/m<sup>2</sup>\*day to 114,8 ml O<sub>2</sub>/m<sup>2</sup>\*day after coating. The barrier property of Invercote Duo was improved with the use of PEI and nanoclay-coating, and the air permeance was reduced from 1,341 ml O<sub>2</sub>/min to 0,431 ml O<sub>2</sub>/min. The gas barrier-results for PLA were not significant. The gas barrier-results for

Invercote Duo were significant, but this substrate still showed poor barrier properties. More research should be done to obtain better barrier properties.

# Table of content

Preface .....	i
Abstract .....	iii
Abbreviations and symbols .....	vii
Table of figures .....	viii
Table overview .....	ix
1 Introduction.....	1
2 Theory .....	4
2.1 Plastic polymers .....	4
2.2 The importance of good gas barrier properties.....	5
2.3 Coating of solid materials.....	6
2.3.1 Wettability .....	6
2.4 Nanoclay used for coating of polymers.....	9
3 Materials and method.....	11
3.1 Substrate thickness .....	11
3.2 The contact angle measurements.....	12
3.3 Surface Free Energy .....	14
3.4 Gas barrier measurements .....	14
3.4.1 OTR and CO <sub>2</sub> TR measured with Dualperm 8001 .....	15
3.4.2 OTR and CO <sub>2</sub> TR measured with AOIR.....	15
3.4.3 Air permeance of carton .....	16
3.5 The UVC-treatment.....	17
3.6 The dip-coating experiment.....	18
3.6.1 Combination 1 with MMT-K10 and PEI.....	21
3.6.2 Combination 2 with halloysite and PEI.....	22
3.6.3 Combination 3 with bentonite and PEI.....	25
4 Results and discussion .....	28
4.1 Thickness.....	28
4.2 Dip-coating cycles .....	29
4.3 Contact angle measurements of uncoated substrates.....	31
4.4 UV-treatment of substrates.....	33
4.5 Combinations of PEI-solution and nanoclay-suspensions.....	34
4.5.1 Combination 1: PEI and MMT-K10.....	35
4.5.2 Combination 2: PEI and halloysite.....	36
4.5.3 Combination 3: PEI and hydrophilic bentonite .....	37
4.6 Gas barrier measurements .....	40

4.6.1	OTR and CO <sub>2</sub> TR for PLA .....	40
4.6.2	Air permeance for carton.....	41
5	Conclusion .....	42
6	Future work.....	43
7	References.....	44
8	Appendix.....	46

## Abbreviations and symbols

### **Abbreviation Definition**

AOIR	Ambient Oxygen Ingress Rate
CO <sub>2</sub>	Carbon dioxide
CO <sub>2</sub> TR	Carbon dioxide transmission rate
EVOH	Ethylene vinyl alcohol
LBL	Layer- by-layer
MMT	Montmorillonite
MMT-K10	Montmorillonite K10
N <sub>2</sub>	Nitrogen
O <sub>2</sub>	Oxygen
O <sub>3</sub>	Ozone
OTR	Oxygen transmission rate
PAA	Polyacrylic acid
PE	Polyethylene
PEI	Polyethyleneimine
PET	Polyethylene terephthalate
PGA	Polyglycolic acid
PLA	Polylactic acid
SEM	Scanning electron microscopy
SFE	Surface free energy
ST	Surface tension
$\theta$	Theta, contact angle

## Table of figures

<b>Figure 1: Contact angle of a liquid on a wetting(left) and non-wetting(right) surface.....</b>	<b>7</b>
<b>Figure 2: Thickness measurements of the substrates (photograph) .....</b>	<b>12</b>
<b>Figure 3: The surface of the substrate-samples (photographs).....</b>	<b>13</b>
<b>Figure 4: The measurement equipment, Theta Light (Biolin Scientific, Sweden) (photographs).....</b>	<b>13</b>
<b>Figure 5: Benzyl alcohol drops on substrate samples (photographs).....</b>	<b>14</b>
<b>Figure 6: OTR and CO<sub>2</sub>TR of PLA measured with Dualperm 8001 (photograph).....</b>	<b>15</b>
<b>Figure 7: The cells used for OTR and CO<sub>2</sub>TR-determination of PLA by using a method based on AOIR (photographs). .....</b>	<b>16</b>
<b>Figure 8: Measurement of O<sub>2</sub>- and CO<sub>2</sub>- % in the gas cells with a headspace gas analyser (photograph). .....</b>	<b>17</b>
<b>Figure 9: Illustration of the of the UV-treatment.....</b>	<b>17</b>
<b>Figure 10: A sample of Invercote Duo in UVC-light (photograph).....</b>	<b>18</b>
<b>Figure 11: Schematic illustration of the dipping process. ....</b>	<b>20</b>
<b>Figure 12: A schematic illustration of the last dip-coating process. ....</b>	<b>21</b>
<b>Figure 13: Dip-coating of PLA and Invercote Duo in MMT-K10 and PEI (photograph). .....</b>	<b>22</b>
<b>Figure 14: Overview of the five Falcon tubes with halloysite (photograph).....</b>	<b>23</b>
<b>Figure 15: Dip-coating of carton and PLA in halloysite (photograph). .....</b>	<b>24</b>
<b>Figure 16: Sonication of bentonite suspension (photograph).....</b>	<b>26</b>
<b>Figure 17: Dip-coating of PLA in PEI and bentonite (photograph).....</b>	<b>27</b>
<b>Figure 18: The Invercote Duo(upper) and PLA (lower)-samples in the oven (photograph). .....</b>	<b>27</b>
<b>Figure 19: Contact angle measured on PLA with benzyl alcohol (left) and water (right) (digital image). .....</b>	<b>32</b>
<b>Figure 20: Contact angle measured on uncoated CrownBoard Craft with water(left) and benzyl alcohol(right) (digital image).....</b>	<b>32</b>
<b>Figure 21: The contact angle of water on PLA without UV-treatment(left) and after 10min of UV-treatment(right) (digital images). ....</b>	<b>34</b>
<b>Figure 22: PLA coated with PEI and MMT-K10 (photographs).....</b>	<b>35</b>
<b>Figure 23: PLA coated with halloysite and PEI. ....</b>	<b>36</b>
<b>Figure 24: PLA coated with 10 bilayers of bentonite and PEI (photograph). .....</b>	<b>38</b>
<b>Figure 25: Coated sample of Invercote Duo with bentonite and PEI (photograph).....</b>	<b>39</b>
<b>Figure 26: PLA coated with halloysite, MMT-K10 and bentonite (photograph).....</b>	<b>39</b>
<b>Figure 27: Overview of the OTR-measurements for PLA. ....</b>	<b>40</b>

## Table overview

<b>Table 1: Experimental design.....</b>	<b>19</b>
<b>Table 2: Overview of the five halloysite mixtures. ....</b>	<b>23</b>
<b>Table 3: Overview of the halloysite suspension and PEI-solution with benzyl alcohol added. ....</b>	<b>24</b>
<b>Table 5: Overview of the solutions with MMT and PEI mixed with 10 % ethanol. ....</b>	<b>25</b>
<b>Table 6: Overview of the mean thickness of PLA and Invercote Duo before and after dip- coating.....</b>	<b>28</b>
<b>Table 8: Contact angle of benzyl alcohol and water on the substrates. ....</b>	<b>31</b>
<b>Table 9: Mean contact angle of water on PLA and CrownBoard Craft after UV-treatment. ....</b>	<b>33</b>
<b>Table 12: Air permeance (ml O<sub>2</sub>/min) for Invercote Duo uncoated and coated with PEI and bentonite. ....</b>	<b>41</b>

# 1 Introduction

Packaging plays a crucial role in protecting food from the ambient conditions and maintain optimal conditions inside the packaging. By using proper packaging, the food quality and shelf-life can be prolonged. Some examples are fruit and vegetables wrapped in plastic which protect them from dehydration and mechanical damage during transport and storage, or meat wrapped in plastic which protect against microbial and chemical changes which can occur when meat is exposed to air and light. The food quality is affected by light, moisture, temperature, physical treatment, gas composition and the presence of microorganisms among other factors. To maintain optimal conditions, a packaging with optimal barrier properties is necessary. Today, most packaging is made of fossil-based plastic. But a growing consumer awareness and demand for environment friendly packaging solutions is gaining strength. This means that new packaging materials, which is not derived from the petroleum industry, is an interesting field to research.

Plastic is a polymer. Polymers can be natural, half-synthetic or synthetic depending on which raw material it is based on. Polymers are often long and thread-like chains. They can be branched and form a network through chemical cross-linking. Examples of polymers are wool, cotton, proteins, cellulose and polyethylene (Van der Vegt, 2006). Plastic can have very different properties depending on which polymers it is made of. Petroleum-based plastic is versatile, easy to mould, lightweight, affordable and have superior barrier properties compared to carton, which many consumers think of as an eco-friendly and good alternative. According to MacArthur et al. (2016), food waste can be reduced when the food is wrapped in plastic because the packaging extends the shelf life. Plastic is also lightweight, compared to for example glass, which can reduce the fuel consumption needed for transport. A lot of plastic is made from organic compounds which are derived from the petroleum industry. This is a problem as this resource is limited and has long degradation time. The latter is a problem because millions of tons ends up in the ocean every year (MacArthur et al., 2016). These are some of the reasons why many consumers want to replace packaging based on plastic with alternatives which are more environment friendly. A promising replacement to fossil-based plastic is polylactic acid (PLA) and carton. In this thesis, PLA and three carton qualities are used as solid substrates dip-coated in polyethyleneimine and different nanoclays.

According to Giannikas and Leontiou (2018), PLA is a biobased, renewable and biodegradable material. It can be made from fermentation of carbohydrates, which yield lactic acid. Lactic acid exists as two mesoforms, L-PLA and D-PLA. The property of the PLA depends on the ration between the two mesoforms. PLA is a promising alternative to fossil-based plastic because of its low cost and high availability. The disadvantage is that it has poor barrier properties, and especially for gas. Other factors that limit the use is that PLA is brittle and has poor heat resistance. Despite these disadvantages, PLA is already used for film and containers, but the large- scale is use is limited. To improve the properties of PLA, nanoclay can be used.

Carton and paper are made primarily by cellulose, which is a “homopolysaccharide composed of ( $\beta$ -1,4)-linked glucopyranose units” (Giannakas and Leontiou, 2018). According to Coles et.al (2003) paper-based packaging is used for multiple products, from tea bags to large boxes. Paper is a versatile packaging material, which is printable, flexible, easy to shape and fold. It is also sustainable since it is made from plants. The biggest disadvantage is that paper has poor barrier properties against water, moisture, fat, organic solvents, gas and volatile flavors. To overcome these challenges, paper is usually coated or laminated with materials that improves the barrier properties. Common laminates are plastic polymers, aluminum and wax. The amount of fiber determines the properties of the paper and this is expressed as weight per unit area, also called gram weight, which is written as  $\text{g/m}^2$ . A weight per unit area which is more than  $200 \text{ g/m}^2$  is called paperboard/board.

The liquid solution combined with the different nanoclays in this thesis is polyethyleneimine (PEI). This is a cationic polymer which can be used for several purposes, especially within biotechnology. PEI is a cationic polymer, which means it has positive charges. It can be branched or linear. The linear PEI(LPEI) is a white powder, while the branched PEI(BPEI) is a viscous colorless liquid (Chen et al., 2020).

According to Guo et al. (2018), nanoclay are layered silicates in nanosize, 1-100nm, which are stacked together. This stacked structure can form complex units. The layers consist of tetrahedral and/or octahedral sheets, which can be arranged in different ways which affect their functions. Their arrangement also divides them into different groups, for example smectite, kaolinite, illite and chlorite. The most common structures are 1:1, 2:1 and 2:1:1. 1:1 means that one octahedral and one tetrahedral layer are connected. 2:1 means that one

octahedral sheet is between two tetrahedral sheets. 2:1:1 means that two octahedral sheets are next to each other and connected to two tetrahedral sheets. In this thesis, montmorillonite and halloysite have been used. Montmorillonite is plated and can be used for gas barrier modification. Hydrophilic bentonite, which is also used in this thesis consists mainly of montmorillonite. Halloysite is a hollow nanotube, which is often used for medical application, but it can also be used for food packaging.

In this work, polylactic acid (PLA), Ecovio F2224 (BASF, Germany) and three carton qualities, CrownBoard Craft 285g/m<sup>2</sup> (Billerudkorsnäs, Sweden), Invercote G 380g/m<sup>2</sup> (Holmen Iggesund, Sweden) and Invercote Duo 450 g/m<sup>2</sup> (Holmen Iggesund, Sweden) have been used as substrates. They have been coated with alternating layers of polyethyleneimine (PEI) and nanoclay. In previous research, (Hagen et al., 2014, Jang et al., 2008, Priolo et al., 2010), polyethylene terephthalate (PET) has been coated with MMT and/or polyacrylic acid (PAA) and PEI. Hagen et al. (2014) reported that when PET was coated with 20 trilayers of PEI, MMT and PAA, the OTR was reduced so it was close to the detection limit of the measuring equipment. Jang et al.(2008) also reported that after depositing 70 PEI/clay layers, the OTR was below the detection limit of the measuring equipment. These studies showed improved barrier properties for the coated samples. The gas barrier improvement of carton has been researched by coating it with a quadlayer of carrageenan, chitosan, montmorillonite and chitosan. This combination lead to a reduced air permeability when the amount of quadlayers were increased (Li et al., 2019). To our knowledge, the experiments performed associated with this thesis is the first research where the effect of layer-by-layer (LBL)-assembly of PEI and either MMT K10, hydrophilic bentonite or halloysite on PLA and carton has been studied.

## 2 Theory

### 2.1 Plastic polymers

Plastic has been a gamechanger in the packaging industry. It is lightweight, waterproof, versatile, easy to shape and cheap to produce. Replacing glass and metal with plastic can reduce the costs during transport as it weighs less than glass and metal and takes up less space. According to MacArthur et al. (2016), 6 % of the global oil consumption is used for plastic materials. Plastic packaging makes up 26 % of this. Through distillation, crude oil is turned into gas and other oil components. A small part of these components is called naphtha. Naphtha is turned into several monomers through a process called cracking. Plastic materials are made from monomers into polymers, through a process called polymerization. Coles et al. (2003) write that “the rate of polymerization is dependent on temperature, pressure, reaction time, concentration, the nature of the monomer and the presence of catalyst(s)”.

Plastic consists of one, or more, polymers. According to Young and Lovell (2011), polymers can be separated into homopolymers and copolymers. A homopolymer consist of only one type of monomer. A copolymer consists of two, or more, different monomers. Copolymers consist of repeated units, which can be one, or several monomers. The structure of the monomers characterises the copolymer. The order of the repeated units can be statistical, random, alternating or block. Statistical copolymers have a sequential distribution of repeated units that follow statistical rules. Random copolymers have a random distribution of repeated units. In alternating polymers, the repeated units are alternating, while block polymers are branched. The simplest version of block polymers consists of two different monomers. One monomer is linear while the other is connected as branches at branch points on the linear structure.

According to Young and Lovell (2011) polymers can be linear or non-linear. Examples of non-linear structures are cyclic, branched and network-polymers. The skeletal structure of the polymers determines some of their properties like melting point and flexibility, which in turn determines the area of use. Polymers are classified into three groups based on molecular structure: thermoplastics, elastomers and thermosets. Thermoplastics are linear or branched, and when heat is applied, they become liquid. But because of their amorph structure, they do

not melt but gain very low viscosity. A characteristic feature of thermoplastics is that they can be remoulded if reheated. Thermoplastics make up the largest part of commercial production today. Elastomers are crosslinked rubbery polymers which are stretchable and when stress is applied and released, they bounce back to their original shape. Thermosets are rigid, have a high degree of crosslinking and cannot be remoulded. They are hard to shape, and when the heat is applied, they degrade, rather than become fluid.

Polymers can be used for several packaging types, depending on their structural composition which gives them different properties. For example, polyethylene (PE) can be used for trays, bottles and film. Often, the polymers are added different compounds, or other polymers, to improve their properties and processability. By combining polymers with different properties, packaging with desired functionality can be created. For example, ethylene vinyl alcohol (EVOH) has a good oxygen barrier, but a poor moisture barrier. Polyethylene (PE) has a good moisture barrier. Polyamide (PA) has a good oxygen barrier, but this is dependent on the moisture level. A laminate of PE/PA/PE is therefore widely used, as it gives a good oxygen- and moisture barrier because of the combination (Eie, 2007).

## 2.2 The importance of good gas barrier properties

To maintain the food quality, the use of different gases is used to modify the environment inside a packaging. A packaging material should therefore have good gas barrier properties to retain the altered gas composition. The gas barrier property of a material depends on several factors, among them the type of material, the thickness, surface area, method of processing, concentration and storage temperature (Coles et al., 2003). A lot of food is sensitive to air, and especially to oxygen. According to Eie (2007) the exposure to oxygen can cause a lot of undesirable reactions, such as oxidation and change of color because of chemical reactions. Limiting the oxygen supply is also important to prevent microbial growth. A good gas barrier is therefore important to maintain the food quality and shelf-life for as long as possible.

The air inside the packaging is often replaced by a combination of nitrogen (N<sub>2</sub>) and (carbon dioxide) CO<sub>2</sub> to prevent microbial growth and undesirable chemical changes. These gasses have different properties, and the ratio depends on which food it is used for. A lot of spoilage bacteria and fungi needs oxygen to grow, and by limiting the oxygen supply the growth of these organisms can be prevented (Coles et al., 2003). CO<sub>2</sub> is used to inhibit microbial

growth, but has high solubility in water, which can make the packaging collapse. N<sub>2</sub> is therefore used to replace the oxygen and to prevent collapse of the packaging when CO<sub>2</sub> dissolves into the food (Warriss, 2010). A good gas barrier is therefore necessary to keep the replacement-gasses inside the packaging to prevent spoilage.

## 2.3 Coating of solid materials

According to Kausar (2018), coating techniques can be used for many applications, for example within printing, painting and for combining two, or more, materials. The latter can be done in several ways, for example through roll-, spray-, and dip-coating, or printing. A coating is often used to improve the properties of the coated material by modifying technical, physical or chemical properties. The chosen method depends on the material which is coated, financial cost, processability and area of use. Examples where a coating technique has been used during manufacturing are solar cells, batteries and packaging. The wettability of the solid material is of great importance in a coating process. The wettability describes how well a liquid can spread on a solid surface. The contact angle between a liquid and a solid is a measurement of the solid's wettability by a particular liquid. The wettability of a material depends on the surface free energy of the solid and the surface tension of the liquid. A surface treatment can alter the surface energy and improve the wettability. By measuring the contact angle, information about the wettability of a material can be achieved.

### 2.3.1 Wettability

The contact angle is the angle between the tangent of the liquid-vapor phase and the liquid-solid interface. When a droplet is deposited on a solid surface it can spread or remain in a spherical shape on the surface. The contact angle describes how well the droplet is spreading. If the contact angle is less than 90°, the surface is wetted, and if the contact angle is more than 90°, the surface is not wetted (Järn, 2010).

The Young equation describes the relationship between the contact angle ( $\theta$ ) and the surface free energy, and is given below:

$$\gamma_{SV} = \gamma_{LV} \cos\theta + \gamma_{SL}$$

$\gamma_{SV}$  = solid surface free energy

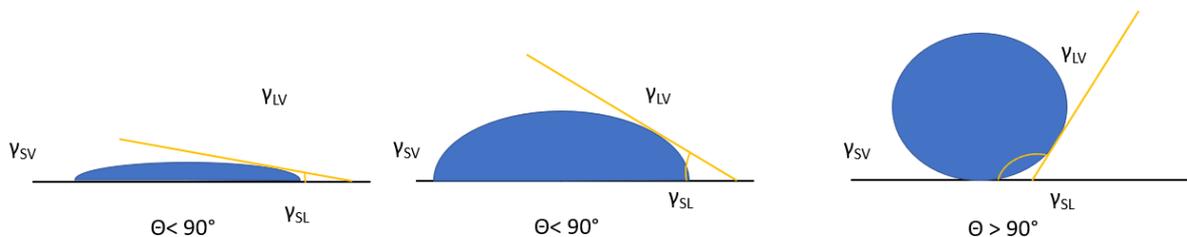
$\gamma_{LV}$  = liquid surface free energy

$\gamma_{SL}$  = solid/liquid interfacial free energy

$\Theta$  = contact angle

The Young equation provides information about the contact angle, but only does at the measured point. A surface is often heterogenous, so the contact angle may vary depending on where the measurement is done. This means that the measured contact angle is an estimate of the true contact angle for a given material (Järn, 2010).

**Figure 1** is an illustration of how a drop of liquid can act on a surface. To the left, a small contact angle is obtained because the liquid spreads on the surface. To the right, the droplet remains in a spherical shape and a high contact angle is obtained.



*Figure 1: Contact angle of a liquid on a wetting(left) and non-wetting(right) surface. The illustration shows how a drop acts on a surface. The contact angle,  $\theta$ , obtained through the Young's equation, is shown in the interphase between the liquid, solid and vapor-phase (the angle between the yellow and black line).*

By measuring the contact angle of a solid with two different probe liquids with known properties, the surface energy can be estimated. The two probe liquids must have known polar and dispersive components, which is used to determine the surface energy of the solid. This can be used to predict the wettability of other liquids on that solid material (Määttänen, 2014). As a rule of thumb, the surface tension of the liquid should be lower than the surface energy of the solid for good wetting (Järn, 2010).

According to Rulison (1999), a surface energy measurement of a solid is dependent on several measurements with different probe liquids. The surface energy can be calculated based on these measurements by using a theoretical model. There are several theories, which have different ways of calculating the surface energy. Examples of different theories are the Zisman Theory, Owens/Wendt Theory, Fowke's Theory and van Oss Theory. These models calculate the surface energy based on one, two or three components, respectively. The choice theory determines how the surface energy is calculated.

The Owens/Wendt Theory is used to calculate the surface energy by using two components. In this theory the surface energy is viewed as consisting of two components, polar and dispersive. Polar components are dominated by forces which occur between atoms and molecules in a specific arrangement and combination, for example dipole-dipole forces or hydrogen bonding (Rulison, 1999). Dispersive components include van der Waals forces and electrostatic forces, among others (Adibnia et al., 2020). By dividing surface energy into two phases, polar and dispersive, Owens/Wendt uses a two parameters model to calculate the surface energy. The theory combines Good's and Young's equation, to create a new equation, which has a linear form. This equation can be used to calculate the polar and dispersive components of the surface energy (Rulison, 1999).

The Fowke's Theory is the most used method to calculate the surface energy of a solid. Like Owens/Wendt, it is based on a two component-model. The solid is viewed as consisting of two components, the polar and the dispersive. The Fowkes Surface Theory equation is based on Young's equation, Dupre's Definition of Adhesion Energy and the Fowkes theory. Fowkes theory states that the adhesive forces between a solid and a liquid can be divided into interaction between the dispersive components and interaction between the polar components of each of the two phases. The three equations combined make up the primary equation of Fowke's surface energy theory. By measuring the contact angle of the solid with a liquid with only polar components, and then with a liquid with both polar and dispersive components, the surface energy can be calculated (Rulison, 1999).

The wettability of a surface depends on its surface energy. This can be modified to improve the wettability. For painting and printing a good wettability is desirable, but for materials which should be protected from moisture, a reduced wettability is desirable. The surface energy can be modified by using different surface treatment methods. For plastic, common surface treatment methods are corona- and plasma-treatment. During a corona treatment the surface of the material is oxidized because ozone( $O_3$ ) is created due to high voltage above the

material. This leads to better adhesion between the materials (Eie, 2007). Other surface treatments used for polymers include mechanical or chemicals treatments, where the surface is exposed to flame, photon or ion beams (Subedi et al., 2009).

The parameters mentioned above are important to consider when a solid material is coated. An example of a coating method where the adhesion-ability of a liquid solution is important is dip-coating. Through dip-coating several layers are applied on a solid surface by immersing a solid into liquid solutions. This is called layer-by-layer (LBL)-assembly. According to Richardson et al. (2015), the layer-by-layer method has been of interest for the past few decades, and during the last two decades it has been used in a wide area of science fields. The LBL-method is a method used to create thin films on a surface which can be done in many ways. Normally, it is done by immersing a solid material alternately in two, or more, water-based solutions which contains polyelectrolytes. One dip-cycle in each liquid solution produces a bilayer, which is 1-100nm thick (Jang et al., 2008). If three or four solutions are used, one round of dipping creates a tri- or quad-layer. The layer-by-layer method utilizes the difference in the electric charge of materials. Because of different charge the materials stick together when they are layered alternately. A substrate, for example PET, is dipped in a solution of a polymer with a positive charge, then withdrawn and dried. After drying, the substrate is dipped in a material with a negative charge, then withdrawn and dried. This cycle represents one bilayer, consisting of two layers of liquids on a solid. The dipping process is repeated until the desired number of layers is achieved.

## 2.4 Nanoclay used for coating of polymers

The use of biopolymers is promising for food packaging. But because of poor barrier properties, the usage of biopolymers has been limited. To overcome this, research on biopolymers and the use of nanoclay for barrier improvements has been performed and have shown promising results. Nanoclay can be implemented in packaging through various methods, for example through coating or by mixing nanoclay into a polymer matrix.

The use of nanotechnology gives new possibilities and functions to materials because the scale of the nano compounds is between 1-100nm. The small size makes it possible to create structures with improved properties because of large surface area-to-volume ratio and the ability to carry small molecules such as drugs or DNA (Roco, 2003). This can be utilized in

several fields, for example medicine, electrical devices and food industry. Nanotechnology enables new functions and structures because the atoms can be manipulated into a specific position. There are several nanoparticle types, with different properties, among them nanoshells, nanowires, carbon nanotubes and nanobiosensors (Singh, 2016).

Relevant fields for nanotechnology within the food industry are agriculture, food processing, packaging and supplements. Within packaging, nanotechnology can be used for sensors which monitors the presence of different compounds or as barrier materials (Singh, 2016).

According to Idumah et al. (2019), the use of nanocomposites in food packaging has led to enhanced mechanical and chemical properties such as increased strength and modulus of the packaging, reduced gas permeability and increased resistance to water. Nanocomposites, and especially films made of silver, has shown antimicrobial properties. The antimicrobial mechanisms are probably due to the silver nanoparticle's ability to damage DNA and permeate the cell wall by degrading lipopolysaccharides (De Azeredo, 2009).

According to Giannakas and Leontiou (2018), a common nanoclay used for food packaging in recent years is montmorillonite (MMT) which is a natural phyllosilicate mineral. It has been shown that the use of MMT enhances the thermal and barrier properties of biopolymers and polymers used for food packaging both when MMT is used for dip-coating and mixed into the polymer matrix mechanically. According to Jang et al. (2008), the ability of montmorillonite to reduce the permeability of a material is due to its structure. Montmorillonite has a platelet structure, which creates a brick wall structure together with the polymer it is combined with. This brick wall structure forced the gas molecules to move sideways when they try to penetrate the substrate. This takes longer time and therefore the barrier properties are enhanced. By combining MMT with PEI and PAA, Hagen et al. (2014) have shown that the PAA function as filler in the gaps between the MMT and PEI, which enhance the barrier properties further. In the study they also showed that a trilayer increased the barrier properties by at least one order of magnitude.

### 3 Materials and method

In this work, solid materials were dip-coated alternately with two different liquids. In the beginning, four solid materials were used as substrates. One PLA-film, Ecovio F2224 (BASF, Germany) and three carton qualities which were laminated on one side. Some measurements were therefore performed on both sides, when relevant. The carton qualities were CrownBoard Craft 285g/m<sup>2</sup> (Billerudkorsnäs, Sweden), Invercote G 380g/m<sup>2</sup> (Holmen Iggesund, Sweden) and Invercote Duo 450 g/m<sup>2</sup> (Holmen Iggesund, Sweden). In this thesis, the carton qualities are hereby referred to as CrownBoard Craft, Invercote G and Invercote Duo. The liquid solutions used in this thesis were a PEI-solution and three nanoclay suspensions, which were montmorillonite K10, hydrophilic bentonite and halloysite. The PEI-solution is referred to as PEI-solution or just PEI. The liquid nanoclay suspensions are referred to as MMT-K10, bentonite and halloysite.

#### 3.1 Substrate thickness

The thickness of the substrates was measured before and after the dip-coating for comparison. The thickness was measured using a Model 543 Film Thickness Gauge (Qualitest, Japan). The machine has a “resolution to 50 millionths of an inch with accuracy to 120 microinches.” (Qualitest, n.d.). For the measurements of uncoated samples, three small square pieces of each substrate were measured. The thickness was measured on all the uncoated substrates. The thickness of coated substrates was only measured on PLA and Invercote Duo coated with ten bilayers of bentonite and PEI. The measurements were performed in ambient conditions. The thickness measurement is shown in **Figure 2**.



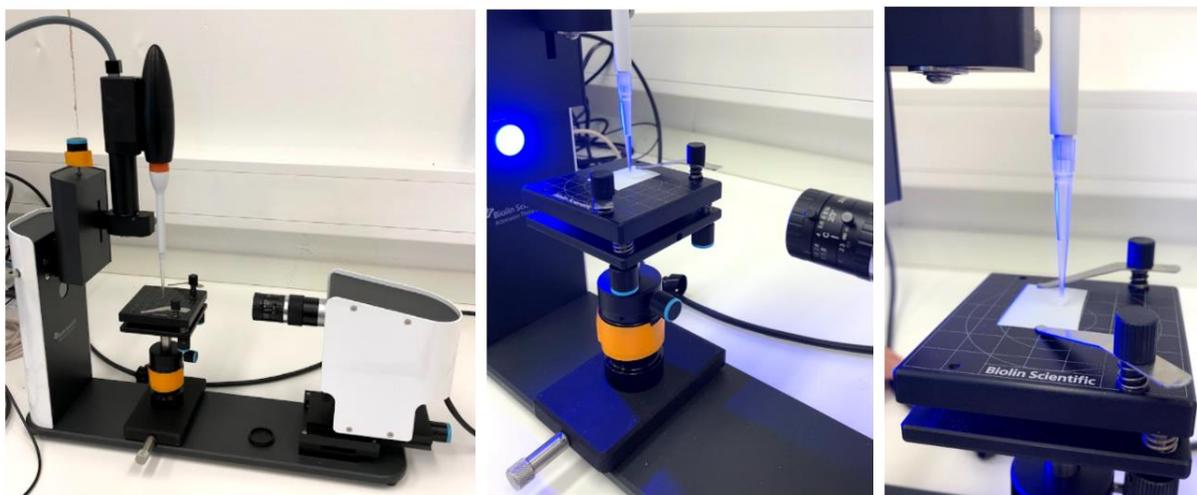
*Figure 2: Thickness measurements of the substrates (photograph) The thickness was measured using a Model 543 Film Thickness Gauge (Qualitest, Japan). The pictures show thickness measurements of uncoated Invercote Duo (left) and PLA coated with bentonite and PEI (right).*

### 3.2 The contact angle measurements

To quantify the wettability of the materials, a Theta Lite (Biolin Scientific, Finland) with 0,5-200 $\mu$ l optifit tips (Sartorius, Germany) was used. The data was treated in the OneAttention (Biolin Scientific, Finland). The equipment is shown in **Figure 4**. Four small, square pieces, were cut from different parts of the four substrates. To remove dust on the surface, an AIR DUSTER PRF 4-44 (Taerosol, Finland) was used. Four drops of water were deposited on each piece at four points. The procedure was repeated with benzyl alcohol (Sigma Aldrich, Germany) for comparison and to calculate the surface free energy. The contact angle measurements were done on both sides of the carton qualities to compare possible differences because one side was coated. The PLA was only measured on one side because both sides were similar. Both sides of the substrates are shown in **Figure 3**.



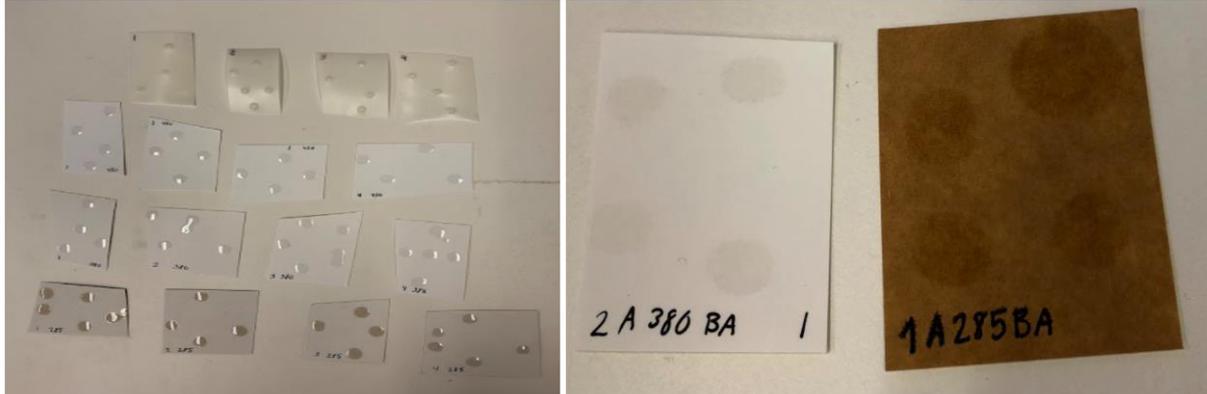
**Figure 3: The surface of the substrate-samples (photographs).** The pictures shows both sides of each substrate.  
 A) The white and brown side of CrownBoard Craft. B) Both sides of Invercote G. C) Both sides of Invercote Duo.



**Figure 4: The measurement equipment, Theta Light (Biolin Scientific, Sweden) (photographs).** The instrument was used to measure the contact angle of water and benzyl alcohol on the PLA and the carton samples. The samples were held in place using the metal clips, and the liquid was deposited from the pipette.

The settings for water and benzyl alcohol used for contact angle measurements were set to drop size of 5 $\mu$ l and 20 $^{\circ}$ C in the software. The contact angle was measured by using the “Sessile drop”-function. The deposition of the drop was recorded for 10 seconds by using the

“record”-function. The mean contact angle for each drop, given by the statistics in the software, was used as contact angle value. The mean contact angle of each water and benzyl alcohol drop was calculated based on all the mean values given by the software.



*Figure 5: Benzyl alcohol drops on substrate samples (photographs). The pictures show benzyl alcohol drops on all the substrates (left) and on Invercote G and CrownBoard Craft (right).*

### 3.3 Surface Free Energy

The surface free energy was calculated in OneAttension. Each contact angle for water was compared with the equivalent drop of benzyl alcohol. For example, water drop 1 on piece 1 of PLA was compared with the benzyl alcohol drop 1 on piece 1 of PLA. The surface free energy was also calculated between the highest and lowest contact angle between water and benzyl alcohol for each material.

### 3.4 Gas barrier measurements

The gas barrier properties were measured for all the substrates. For PLA, the oxygen transmission rate (OTR) was measured with two different methods for comparison. One with a Dualperm oxygen permeation analyser model 8001 (Systech Illinois, USA), abbreviated to Dualperm 8001, and one based on the Ambient Oxygen Ingress Rate Method (AOIR) (Larsen et al., 2000). The AOIR-based method was also used to measure carbon dioxide transmission rate (CO<sub>2</sub>TR). The air permeance of carton was measured with the method based on AOIR, and the air permeance was calculated as ml O<sub>2</sub>/min. The gas barrier properties were measured

for all the uncoated substrates and for coated PLA and Invercote Duo. The cell volume for the cells measured with the method based on AOIR was 276ml.

### 3.4.1 OTR and CO<sub>2</sub>TR measured with Dualperm 8001

Two circular pieces of PLA were cut to fit the analyser and adhered with grease (Apiezon) (M&I Materials, United Kingdom) in the machine. The tests were stopped when the measured values were stable and the graph had flattened.



*Figure 6: OTR and CO<sub>2</sub>TR of PLA measured with Dualperm 8001 (photograph). Two samples of PLA were put in the analyser and adhered with grease (M&I, United Kingdom). From left to right: The Dualperm 8001 and two samples of coated PLA in the machine and the lids which covered the samples.*

### 3.4.2 OTR and CO<sub>2</sub>TR measured with AOIR

Four circular pieces of PLA were placed in four cells. High vacuum grease (DOW CORNING, USA) was used to adhere the PLA-film to the edge of the cells and to keep the substrates straight. The cells were flushed with a gas mixture (Linde, Germany) of 20 % CO<sub>2</sub>, 0,3 % O<sub>2</sub> and 79,7 % N<sub>2</sub>. Each cell was flushed for 45 seconds. The cells were stored at 23°C in a room with relative humidity (RH) of 50 % outside the cell and 0 % inside the cell. The oxygen and carbon dioxide levels were measured in percentage of the cell volume after 19 hours (Day 1), four days (Day 2) and seven days (Day 3) with a headspace gas analyser (Checkmate II (Dansensor, Denmark)). The AOIR was used to determine the OTR and CO<sub>2</sub>TR.



*Figure 7: The cells used for OTR and CO<sub>2</sub>TR-determination of PLA by using a method based on AOIR (photographs). The pictures show cells used to measure the OTR and CO<sub>2</sub>TR for PLA. Similar cells were used to measure air permeance of carton. The cells on the picture contains a sample of PLA.*

### 3.4.3 Air permeance of carton

Carton has a porous structure, and the gas permeability is higher than for PLA. The air permeance was therefore determined by measuring the O<sub>2</sub>- and CO<sub>2</sub>-level in percentage of the cell volume every third minute for 30 minutes. These measurements were converted to ml O<sub>2</sub> and CO<sub>2</sub> of the total volume, and the permeance in ml gas per minute was calculated. This value equals the increasing rate of the linear measurements over time.

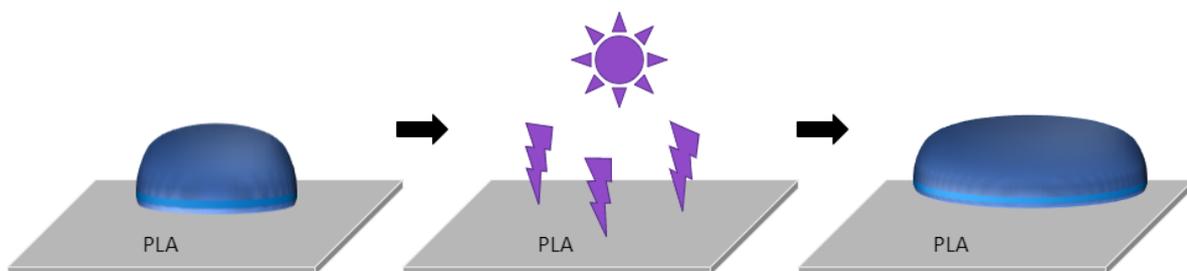
Four circular pieces were cut and placed in four cells. The same high vacuum grease (DOW CORNING) was used to adhere the carton to the edge of the cells and to coat the edges of the carton-samples to prevent air from entering the cell through the sides of the carton. The cells were flushed with the same mixture as the PLA-samples, for 45 seconds. After 45 seconds the oxygen and carbon dioxide levels were measured immediately and then every third minute for 30 minutes using a headspace gas analyser, Checkmate 9900 (Dansensor, Danmark). The O<sub>2</sub>- and CO<sub>2</sub>-levels were measured until the gas composition in the cell were almost the same as in the ambient air. The ambient mean temperature was 15,81°C (std 0,69°C) and the ambient mean relative humidity was 37 % (std 5,22 %).



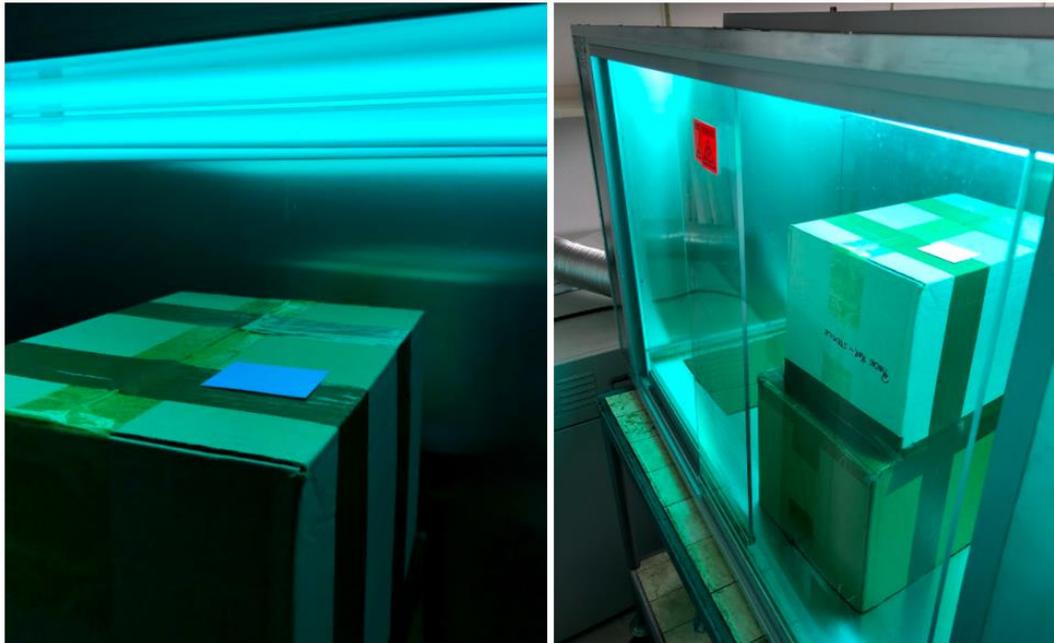
*Figure 8: Measurement of O<sub>2</sub>- and CO<sub>2</sub>- % in the gas cells with a headspace gas analyser (photograph). The O<sub>2</sub>- and CO<sub>2</sub>- % in the cells were measured using a Checkmate II (Dansensor, Denmark ).*

### 3.5 The UVC-treatment

A UVC-treatment of the PLA and CrownBoard Craft was performed to improve their wettability. A UVC-lamp was used to treat the samples for 1,5,10 and 30 minutes to see if the wettability was affected by treatment-time. The UVC-treatment was only done on one side of the substrate.



*Figure 9: Illustration of the UVC-treatment. . The illustration shows the UVC-light as a purple sun and beams on PLA. The blue waterdrop is wetting the PLA better after the UVC-treatment because the drop spreads out more than before the treatment.*



*Figure 10: A sample of Invercote Duo in UVC-light (photograph). The samples were UVC-treated with a UVC-lamp in a box, made at Nofima.*

### 3.6 The dip-coating experiment

The substrates were dip-coated alternately in a PEI-solution and a nanoclay suspension. The suitability of the chosen nanoclay suspensions for dip-coating of PLA and carton were unknown. Therefore, three different nanoclay suspensions were tested to examine how uniform layers of PEI and nanoclay could be achieved on the different substrates. In this chapter, the three different suspensions and time-combinations are presented. PEI and the nanoclay suspensions were also added benzyl alcohol and ethanol (Antibac, Finland) to improve their coating-abilities. The suspensions were tested in the following order:

1. MMT-K10 and PEI (subchapter 3.6.1)
2. Halloysite and PEI, added 10 % benzyl alcohol (subchapter 3.6.2)
3. Bentonite and PEI, added 10 % ethanol (subchapter 3.6.3)

The same branched PEI was used to make all the PEI-solutions. All the nanoclays and the PEI was produced by Sigma Aldrich, Germany.

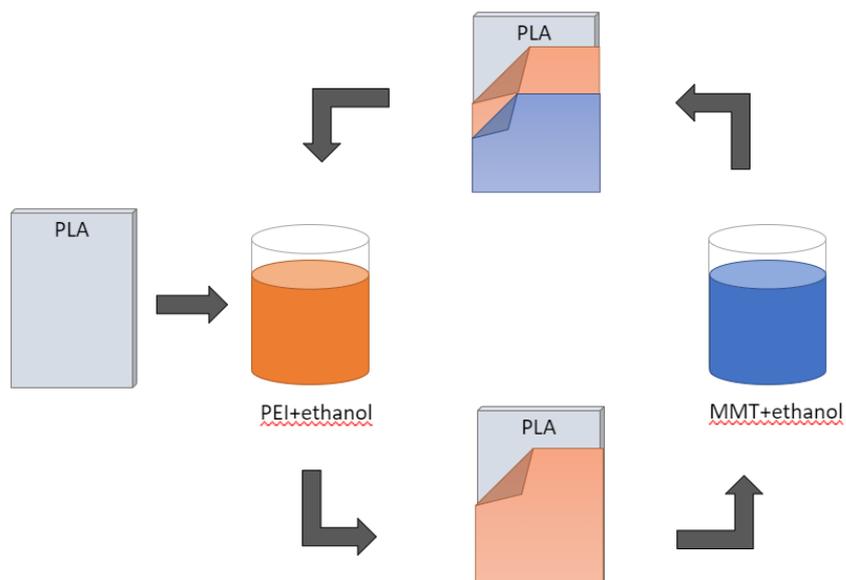
The dip-coating was performed by using a dip-coater, KSV NIMA (Biolin Scientific, Sweden), to immerse the substrates in the PEI-solution and the nanoclay suspension

alternatingly. The experimental design was changed during the process as the coated substrates were analyzed visually and considered unsatisfying. Detailed information about the experimental design is found in **Table 1**. The first two immersions in each liquid were longer than the subsequent immersions. After the immersion, the substrates were withdrawn and dried. The drying time was longer after the first two immersions in each solution, than after the subsequent ones.

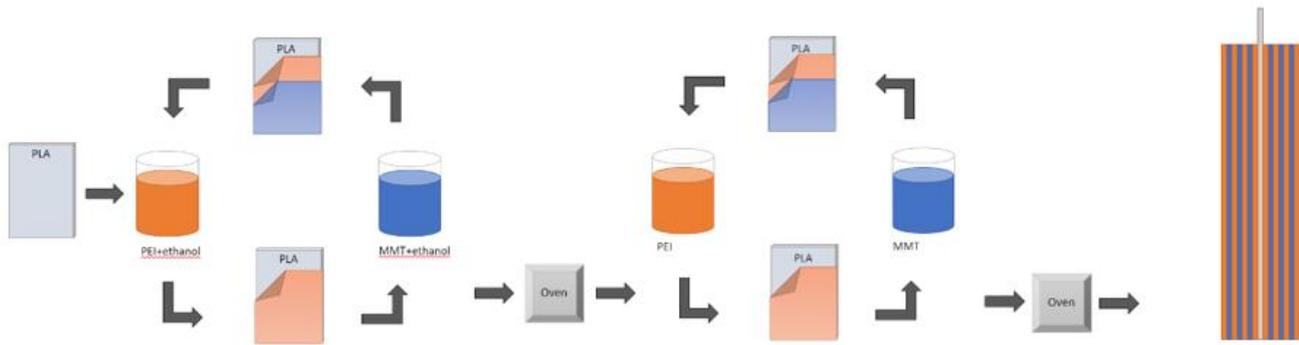
*Table 1: Experimental design. The table shows an overview of the dip-cycles, drying time, the substrates and number of bilayers used in the different coating-attempts.*

<b>Combination</b>	<b>1</b>	<b>2</b>	<b>3</b>
<b>Coating*</b>	MMT-K10	Halloysite	Bentonite
<b>UV-treatment</b>	10 min	10 min	None
<b>Dip cycles</b>	First dip: 5min in each solution  Subsequent dip: 1min in each solution	First dip: 2min in each solution  Subsequent dip: 1min in each solution	First dip: 2min in each solution  Subsequent dip: 1min in each solution
<b>Drying time in ambient temp</b>	The first two dryings: 3min  Subsequent dryings: 2min	The first two dryings: 2min  Subsequent dryings: 2min	2min after being immersed in PEI and 3min after being immersed in bentonite
<b>Drying in oven</b>	No	No	60 min at 40°C x2
<b>Total time pr replicate</b>	116min	72min	192min
<b>Substrates</b>	PLA and CrownBoard Craft	PLA, CrownBoard Craft and Invercote Duo	PLA and Invercote Duo
<b>Number of bilayers</b>	16	10	10
* All the coatings consisted of one PEI-solution and the mentioned nanoclay suspension			

The dip-coating process consisted of numerous dip-cycles, which is illustrated in **Figure 11** and **Figure 12**.



*Figure 11: Schematic illustration of the dipping process. The illustration shows the dip-cycle of PLA in PEI, and MMT. The PLA is first immersed in PEI, then dried and immersed in MMT. One round in the cycle creates one bilayer consisting of PEI and MMT.*



**Figure 12:** A schematic illustration of the last dip-coating process. The last dip-coating process, with bentonite and PEI mixed with 10 % ethanol, and drying in the oven (Termaks, Sweden) (grey square). The substrate was first coated with five bilayers of PEI and MMT. Then the samples were dried in an oven for 60 minutes at 40°C before a similar dip cycle of five bilayers was repeated. The cycle ended with a drying in the oven again, at the same conditions as earlier. The figure to the right shows an oversized cross section of the final substrate coated with PEI (orange) and MMT (blue) alternately.

The three combinations of PEI and nanoclay suspensions are presented below in subchapters. All the solutions were stirred with a magnetic stirrer, RCT Basic (IKA WERKE, Germany) between each dip.

### 3.6.1 Combination 1 with MMT-K10 and PEI

- 0,92g PEI mixed with 920ml distilled water, pH adjusted from 10,51 to 9,03 with 1M HCl made by 8,3ml HCl (Merck KGaA, Germany) and 91,7ml distilled water
- 1,02g MMT-K10 mixed with 1000ml distilled water, sonicated for 30 minutes with Q55 sonicator (QSonica, USA)
- Two samples of PLA and CrownBoard Craft was used as substrates. They were UV-treated for 10 minutes each before the dip-coating.

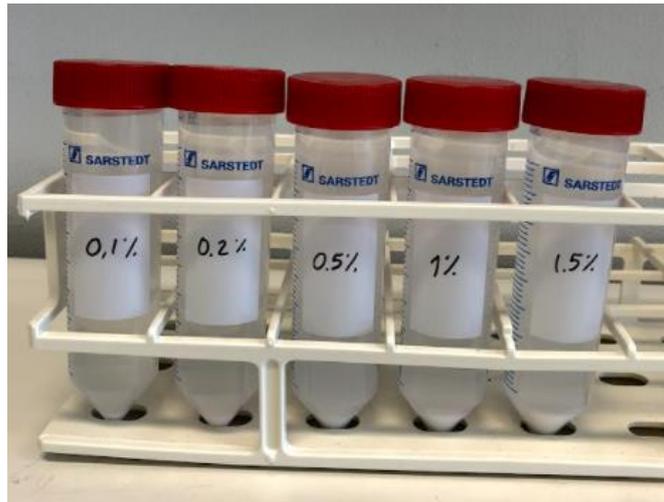
The dip-coating of PLA in MMT-K10 and PEI is shown in **Figure 13** below:



*Figure 13: Dip-coating of PLA and Invercote Duo in MMT-K10 and PEI (photograph). The substrates were immersed in PEI and MMT-K10 alternately. The MMT-K10 sank to the bottom quickly after stirring, which is seen as a white layer on the bottom (right picture).*

### 3.6.2 Combination 2 with halloysite and PEI

A suspension of halloysite was prepared to replace the MMT-K10 in the dip-coating process. Five Falcon tubes were filled with halloysite and distilled water, so the concentrations were 0,1 %, 0,2 %, 0,5 %, 1 % and 1,5 %. The mixing ratio is shown in **Table 2** and the Falcon tubes are shown in **Figure 14**. The halloysite did not disperse very well, but a mix with 0,5g halloysite in 1000ml distilled water was prepared and used for dip coating to test the coating abilities. The pH was adjusted to 12 with 3M NaOH.



*Figure 14: Overview of the five Falcon tubes with halloysite (photograph). The photo shows the falcon tubes with different concentrations of halloysite, and the sedimentation of the halloysite in the bottom of each tube.*

*Table 2: Overview of the five halloysite mixtures. The table shows the mixing ratios of the halloysite samples in the Falcon tubes. All the tubes contained 50ml distilled water.*

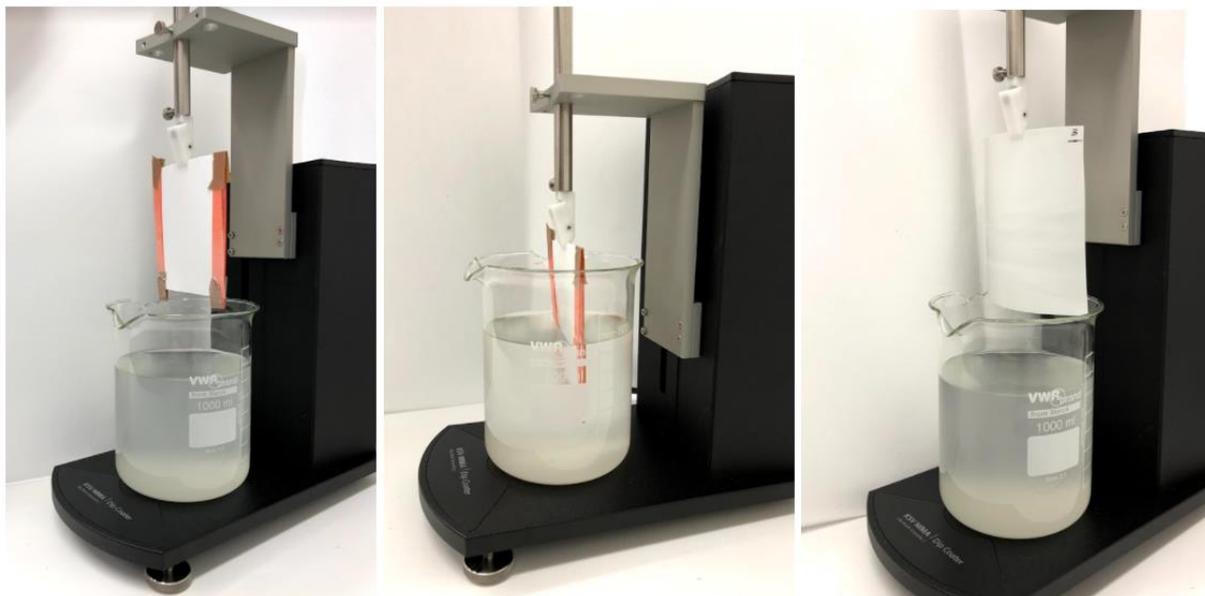
<b>Halloysite (g)</b>	<b>Concentration (%)</b>
0,05	0,1
0,1	0,2
0,25	0,5
0,5	1
0,75	1,5

10 % benzyl alcohol was added to the halloysite-suspension and the PEI-solution to improve the wettability of the substrates. The new mixtures are presented in **Table 3**.

*Table 3: Overview of the halloysite suspension and PEI-solution with benzyl alcohol added.*

	Solution	
	Halloysite	PEI
<b>Distilled water (ml)</b>	900	800
<b>Solute (g)</b>	0,5	0,1
<b>Benzyl alcohol (ml)</b>	100	89

Samples of PLA, CrownBoard Craft and Invercote Duo was dip-coated in halloysite and PEI. A dip-coating of PLA in halloysite is shown in **Figure 15**.



*Figure 15: Dip-coating of carton and PLA in halloysite (photograph). The halloysite-solution was opaque for a longer time than the MMT-K10 after stirring. Plastic frames, the red pieces on the edges, were made to keep the samples straight during the dip-coating.*

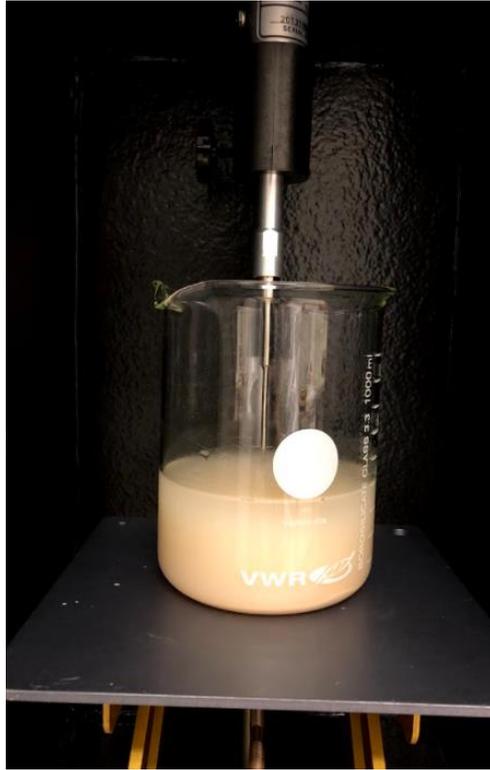
### 3.6.3 Combination 3 with bentonite and PEI

The last combination of PEI and nanoclay was PEI and bentonite, both mixed with 10 % ethanol. The mixing ratio is shown in **Table 4**.

*Table 4: Overview of the solutions with MMT and PEI mixed with 10 % ethanol.*

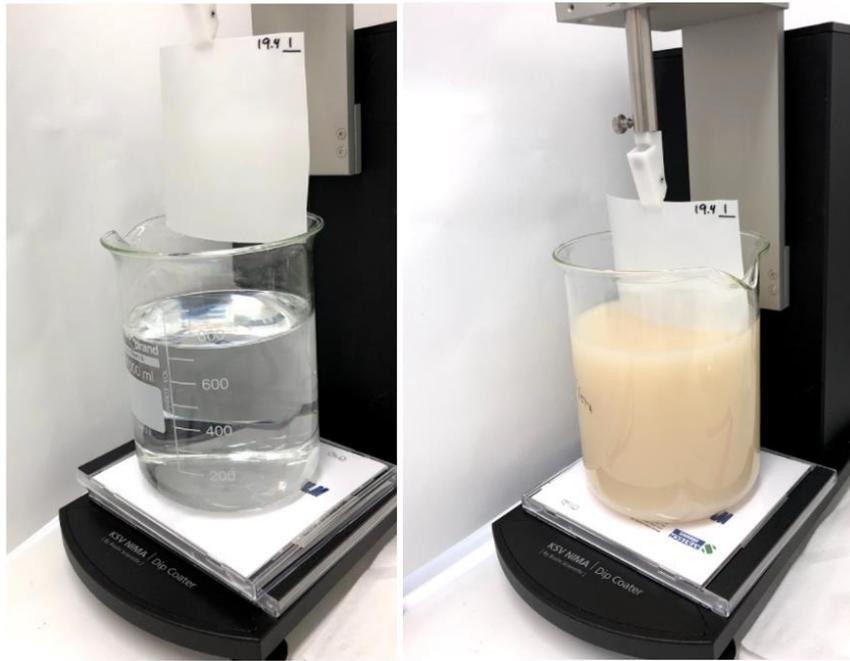
	Solution	
	MMT	PEI
<b>Distilled water (ml)</b>	800	720
<b>Solute (g)</b>	8,04	0,8
<b>Ethanol (ml)</b>	80	80

The bentonite suspension was made by mixing 8,014 g bentonite in 400 ml distilled water which was sonicated, shown in **Figure 16**, for 15 minutes. Then 200 ml distilled water and 80 ml ethanol was added. The suspension was sonicated again for 15 minutes and then stirred while 120 ml water was added. The PEI-solution was made by mixing 720 ml distilled water with 0,8 g PEI which was stirred for 20 minutes with a magnetic stirrer. Then 80 ml ethanol was added.

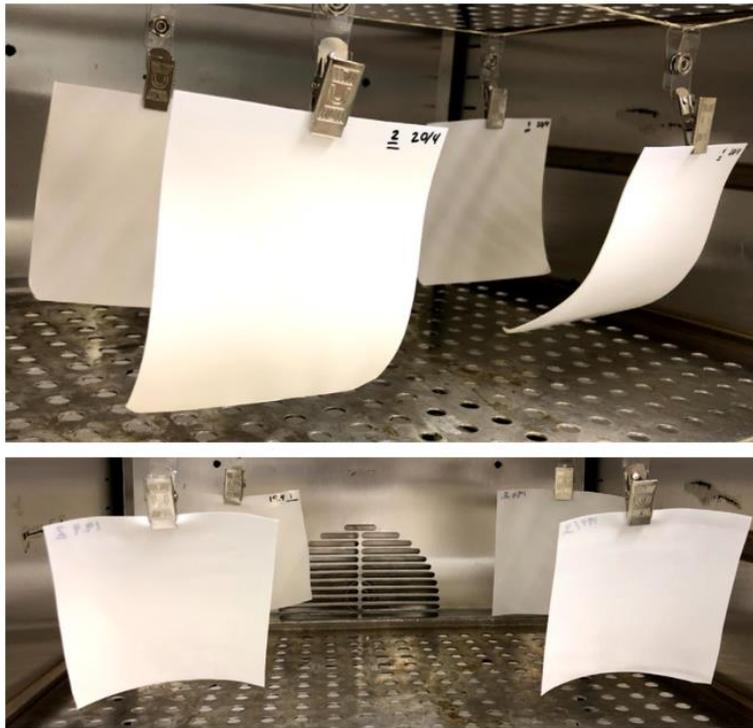


*Figure 16: Sonication of bentonite suspension (photograph). The bentonite suspension was sonicated for 15 minutes two times.*

Four samples of PLA and four samples of Invercote Duo was coated with the bentonite and PEI-solution, both mixed with 10% ethanol. The dip-coating of PLA is shown in **Figure 17** and the drying is shown in **Figure 18**. The dip-coating of Invercote Duo was performed the same way. The dip-cycle and drying process is presented in **Table 1**. The dried samples were placed in cells so the OTR and CO<sub>2</sub>TR could be measured for PLA. The air permeance was measured for the Invercote Duo.



*Figure 17: Dip-coating of PLA in PEI and bentonite (photograph). PLA was coated with ten bilayers of bentonite (left) and PEI (right), both mixed with 10% ethanol.*



*Figure 18: The Invercote Duo(upper) and PLA (lower)-samples in the oven (photograph). The samples were dried at 40°C for 60 minutes two times. Once after the first five bilayers were applied, and then again after the last five bilayers were applied.*

## 4 Results and discussion

The results from the experiments are presented below, and raw data is available in the Appendix. PLA and Invercote Duo showed the best results, so the results of these substrates are emphasized.

### 4.1 Thickness

The thickness of PLA and the three carton qualities was measured before and after the dip-coating. Of the uncoated substrates, PLA showed the most promising barrier properties. All the carton qualities had poor barrier properties, but Invercote Duo was the most promising, relatively. PLA and Invercote Duo were therefore coated with combination 3 of PEI-solution and bentonite-suspension and ethanol to see if the barrier properties could be improved. The thickness of the coated substrates was therefore only measured for PLA and Invercote Duo. These values are shown in **Table 5**.

*Table 5: Overview of the mean thickness of PLA and Invercote Duo before and after dip-coating. The table shows the mean thickness and standard deviation (std) of uncoated and coated PLA and Invercote Duo. The coated substrates were coated with ten bilayers of bentonite and PEI, both mixed with 10% ethanol. The mean thickness values for uncoated substrates are based on 9 measurements, while the thickness values for coated substrates are based on 18 measurements each.*

Substrate	Mean thickness ( $\mu\text{m}$ )		Std ( $\mu\text{m}$ )	
	Uncoated	Coated	Uncoated	Coated
PLA	305,1	343	14,66	20,70
Invercote Duo	515,89	649	1,34	15,8

Based on these measurements, it looks like the thickness of coated Invercote Duo increased a lot more than the thickness of the coated PLA. It was difficult to measure the thickness of coated Invercote Duo correctly because the carton was stiff and warp after drying because of the moisture it was exposed to during the dip-coating. This is seen on the picture in the middle in **Figure 25**. The thickness of the coated Invercote Duo may be less than the results show in this thesis. Based on these measurements, the coating on PLA is 37,9  $\mu\text{m}$  thick, and the coating on Invercote Duo is 143,11  $\mu\text{m}$  thick. According to Hagen et al.(2014) a 10-bilayer coating of PEI and MMT was about 45 nm thick. The 10-bilayer coating obtained in these

experiments were much thicker. This can be due to different factors. The substrate samples were difficult to measure accurately, and the combination of method and liquids may not have been ideal.

## 4.2 Dip-coating cycles

The immersion- and drying time which was used for the dip-coating of PEI and MMT-K10 was based on the time-intervals which was used in three different dip-coating studies (Hagen et al., 2014, Jang et al., 2008, Priolo et al., 2010). The time-intervals from these studies were immersion for 5 minutes in each coating and then 1 minute for all the subsequent dips. This time-interval was used for combination 1, with PEI and MMT-K10. The studies did not mention drying time, so a drying time of 3 minutes after the first two dips and 2 minutes after the subsequent dips was used for combination 1. The first dip and drying was longer than the others, probably to let the PEI and MMT adhere properly to the material to make a good foundation before the rest of the layers were applied. Despite being immersed for 5 minutes the MMT-K10 did not adhere as an even layer. Instead, it coated the surface with many small clay-aggregates, which created a rough surface. According to the producer's webpage (Sigma Aldrich, n.d.), the MMT-K10 is used as catalyst for different chemical reactions, and several research articles have used MMT-K10 as a catalyst (Bahulayan et al., 2003, Kumar et al., 2014, Safari and Sadeghi, 2016). The MMT-K10 inability to be used for dip-coating is probably because this type of MMT is not made for that purpose. According to Uddin (2018), montmorillonite is modified to disperse better in polymers. This is achieved by making it organophilic, which means it disperses better in organic compounds. In this work, the MMT-K10 was dispersed in water, which means it would aggregate with itself instead because water is polar. The producer of the MMT-K10 does not state if any modification has been done, but there is reason to believe so, because of the poor dispersing abilities in water. The MMT-K10 was therefore replaced by halloysite, and the time-intervals were reduced to see how these adjustments affected the dip-coating.

The time-intervals were reduced to 2 minutes for each dip, and 2 minutes of drying time, when halloysite and PEI was used. Even though an immersion for 5 minutes in nanoclay gave unsatisfying results, a longer immersion- time would not necessarily have been better. The halloysite-coating were uneven, like the MMT-K10-coating. But the halloysite deposited as a smaller aggregates on the surface compared to the MMT-K10. But the halloysite did not coat

the surface sufficiently. According to Huang et al. (2016), halloysite is hydrophilic, but because it has low density of hydroxyl groups on the surface it disperses easily in other polymers, and not necessarily water.

The halloysite also dissolved from the substrate when it was immersed in PEI again after drying. According to Lvov et al.(1999), washing of the substrate between each immersion can be done to avoid the dissolution of absorbed compounds. But in this experiment the nanoclay adhered very poorly so a washing would probably remove all the nanoclay. The dissolution of nanoclay in PEI during the immersion can be caused by too short drying time because the halloysite did not have time to dry and stick to the substrate. The halloysite was therefore replaced with bentonite.

The bentonite was the last nanoclay suspension which was used. The immersion time was the same as for halloysite, but the drying time was changed to 3 minutes after being immersed in bentonite and 2 minutes after being immersed in PEI. This was done to let the bentonite get longer time to dry to prevent it from dissolving like the halloysite did. These samples were dried in an oven at 40°C for 60 minutes two times. This was the most time-intensive dip-cycle, but it gave the best result because the coating was even. After drying it was not possible to brush off the coating as easily as with the other nanoclays. The time-intervals did probably not play a crucial role to create a satisfying coating of the PEI and bentonite because the bentonite was hydrophilic and dispersed better in water compared to the other materials. But it shows that a good coating can be obtained with reduced immersion-time in the first two immersions of each solution.

### 4.3 Contact angle measurements of uncoated substrates

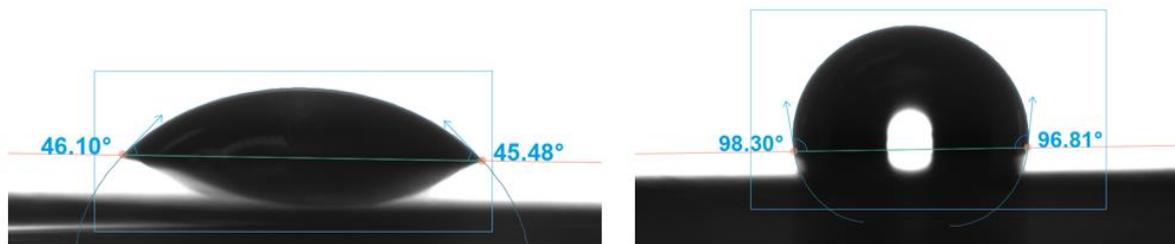
The contact angles of each substrate were measured with two probe liquids, distilled water and benzyl alcohol. These measurements are shown in **Table 6**.

*Table 6: Contact angle of benzyl alcohol and water on the substrates. The table shows the mean contact angle of water and benzyl alcohol (BA) on PLA and both sides of all the carton substrates. The mean value of each liquid on each substrate is based on 16 contact angle measurements.*

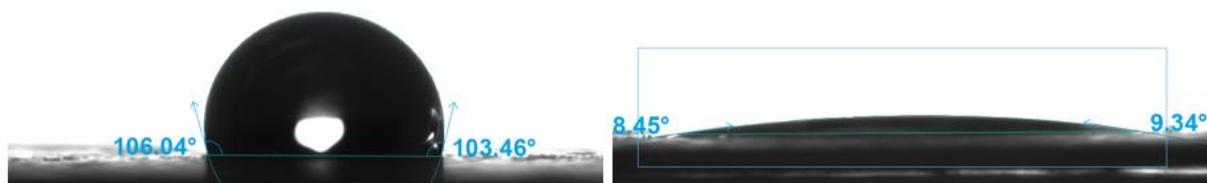
Substrate	Mean contact angle of liquid	
	BA (°)	Water (°)
<b>PLA</b>	49,23	99,68
<b>CrownBoard Craft side 1</b>	21,25	103,87
<b>CrownBoard Craft side 2</b>	14,7	106,45
<b>Invercote G side 1</b>	24,11	75,45
<b>Invercote G side 2</b>	16,7	99,72
<b>Invercote Duo side 1</b>	23,81	75,46
<b>Invercote Duo side 2</b>	24,58	79,91
<b>Side 1</b>		
CrownBoard Craft: White, smooth side		
Invercote G: Smooth side		
Invercote Duo: Rough side		
<b>Side2</b>		
CrownBoard Craft: Brown, rough side		
Invercote G: Rough side		
Invercote Duo: Smooth side		

Benzyl alcohol had lower contact angle than water, on all the substrates. This is expected because benzyl alcohol has lower surface tension than water, 39mN/m and 72,8mN/m, respectively (Rulison, 1999). This means that the forces that holds the droplet together are weaker for benzyl alcohol than water. The contact angle of a liquid on a material is also dependent on the surface energy of the solid. Water had higher contact angle on all the materials and remained in a spherical shape on most of the substrates, which is probably due to higher surface tension. The benzyl alcohol had lower contact angle on the rough sides of the substrates. This can be explained by observations done by Wenzel, which states that a

rough surface will amplify the behavior of a fluid. A hydrophobic fluid will act more hydrophobic on a rough surface, while a hydrophilic fluid will act more hydrophilic (Hay et al., 2008). Benzyl alcohol already had lower contact angle in general compared to water. On the rough surface this was amplified. These tendencies can also be seen on the digital images in **Figure 19** and **Figure 20**.



*Figure 19: Contact angle measured on PLA with benzyl alcohol (left) and water (right) (digital image). The images show that benzyl alcohol has lower contact angle than water on PLA, which means that it is more wetting than water on PLA.*



*Figure 20: Contact angle measured on uncoated CrownBoard Craft with water (left) and benzyl alcohol (right) (digital image). The images show that the contact angle of benzyl alcohol is much lower than the contact angle of water on the rough side of CrownBoard Craft.*

## 4.4 UV-treatment of substrates

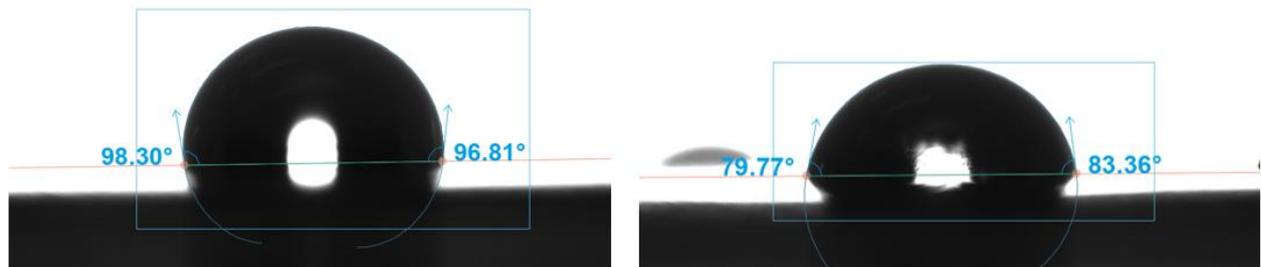
Benzyl alcohol had the highest contact angle on PLA. Water had the highest contact angle on CrownBoard Craft. Dip-coating is based on the ability to create an even layer of coating on the substrates. A high contact angle can result in poor adhesion of the layers during dip-coating. The PLA and the CrownBoard Craft were therefore UV-treated to improve the wettability by modifying the surface energy of the samples. Several surface treatments can be applied to modify the surface energy, for example corona and flame treatment. Equipment for those treatments were not available, so a UV-treatment was tried instead. According to Koo and Jang (2008), UV-treatment of PLA can be used to reduce the water contact angle and increase the surface energy. In their research the water contact angle was reduced from 61° to 39° and the surface energy increased a little, after being treated with UV/O<sub>3</sub> irradiation. In this work, a UVC-lamp was used to treat the substrate samples. After the UV-treatment, drops of water were deposited on the substrates to see if the wettability was improved. The mean contact angles after the UV-treatment are presented in **Table 7: Mean contact angle of water on PLA and CrownBoard Craft after UV-treatment.**

*Table 7: Mean contact angle of water on PLA and CrownBoard Craft after UV-treatment. The table shows the mean contact angle of water on PLA and CrownBoard Craft after 1,5,10 and 30 minutes of UV-treatment and without UV-treatment.*

UV-treatment time (min)	Mean contact angle (°)	
	PLA	CrownBoard Craft(side 1)
<b>1</b>	87,72	98,59
<b>5</b>	79,92	95,63
<b>10</b>	79,31	91,52
<b>30</b>	83,97	95,66
<b>Without UV-treatment</b>	99,68	103,87

The contact angle of water was reduced after the UV-treatment regardless of treatment-time. The mean contact angle for water on PLA and CrownBoard Craft before UV-treatment was 99,68° and 103,87°, respectively. After the UV-treatment, the contact angles were below 90°

for PLA and below 99° for CrownBoard Craft. According to Asha et al. (2017) a UV-treatment of produces a large number of free radicals on the surface it is applied. These are reactive, and when they react with air they oxidate and this can change the surface of the treated material physically, chemically and mechanically. A study on UV-treatment of polyamide (Tsuda, 2016) showed that the UV-treatment made the amount of hydrophobic groups decrease, while the amount of hydrophilic groups increased. This can be an explanation for the increased wettability of PLA. The measurements show that a UV-treatment of 10 minutes was most effective. Thus, it was decided to apply this treatment-time for further UVC-treatments of the substrates. A digital image of the reduced water contact angle on PLA is shown in **Figure 21**.



*Figure 21: The contact angle of water on PLA without UV-treatment(left) and after 10min of UV-treatment(right) (digital images).The pictures show that the contact angle of water was reduced after the UVC-treatment.*

## 4.5 Combinations of PEI-solution and nanoclay-suspensions

To find the combination of PEI-solution and nanoclay suspension which would be most suitable for the layer-by-layer assembly, three combinations were examined. The work was performed step by step as the combinations were tested for dip-coating, with adjustments during the process. The dip-coating cycles and concentrations were based on the dip-coating experiments of Hagen et al.(2014), Prioli et al. (2010) and Jang et al. (2008). In this chapter, the three combinations of PEI-solution and nanoclay suspensions are reviewed with regards to the appearance of the coated substrates. The combinations of PEI-solution and nanoclay suspension are mentioned is **Table 1**.

#### 4.5.1 Combination 1: PEI and MMT-K10

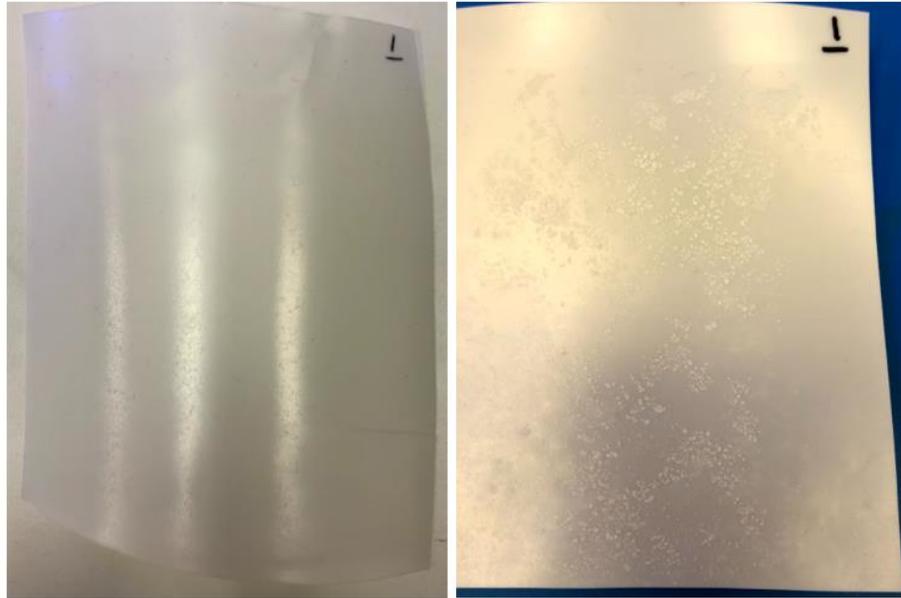
The first combination of PEI-solution and nanoclay suspension was 0,1 % PEI-solution and 0,1 % MMT-K10. A piece of CrownBoard Craft and PLA was dip-coated, but the coatings did not adhere satisfyingly to substrates. The purpose of the experiments was to obtain an even coating which could improve the gas barrier property. To do this, an even coating was desirable. A UV-treatment of these substrates was performed because earlier studies used surface treatments to modify the surface of plastic to increase wettability. After a visual evaluation it was considered that the coatings adhered a little better after the UV-treatment, but the clay still aggregated on the surface, as seen in **Figure 22**. After drying, the aggregates could easily be scratched off. The PEI-layer was transparent, and therefore not visible on the finished samples. But during the dip-coating it was observed as droplets on the surface when the substrates were withdrawn. After the UV-treatment it looked like more droplets of PEI adhered to the substrate. Because of poor dispersion, the MMT-K10 sank to the bottom of the beaker quickly after the stirring ceased. This made it difficult to coat the substrates, when all the clay sedimented at the bottom of the beaker. To summarize, this combination of PEI and nanoclay did not give satisfying results as the coating was uneven with visible clay-aggregates on the surface. The MMT-K10 was therefore replaced with halloysite.



*Figure 22: PLA coated with PEI and MMT-K10 (photographs). The pictures show PLA coated with combination 1, 16 bilayers of MMT-K10 and PEI.*

#### 4.5.2 Combination 2: PEI and halloysite

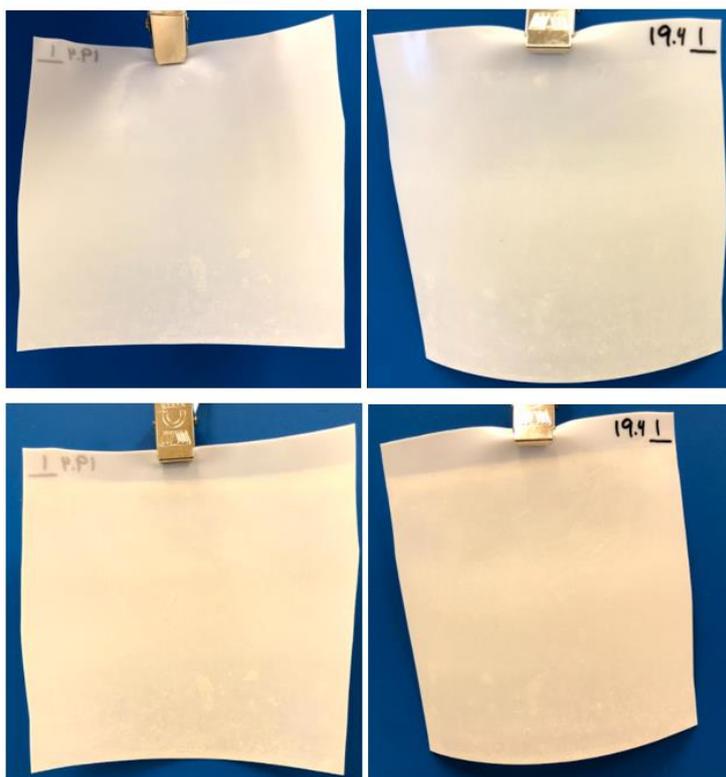
A 0,05 % halloysite suspension and a 0,1 % PEI-solution were used for dip-coating after the PEI and MMT-K10. A smaller clay-concentration was used because the halloysite dispersed poorly in water, as seen in **Figure 14**. According to Othman et al. (2019) the gas barrier property of PLA was improved when a 3,7 and 9 % MMT suspensions were used for coating. Similar concentrations were not tested in these experiments because of the poor dispersion in water which was assumed to be even worse if the concentration was increased. The nanoclay concentration was instead reduced to obtain better dispersion in water than the MMT-K10. The halloysite dispersed a little better in water than MMT-K10, but it sedimented in the bottom of the beaker quickly after the stirring ceased. The halloysite-coating was better than the MMT-K10-coating because smaller clay-aggregates deposited on the surface. But visible aggregates are still undesirable. 10 % benzyl alcohol was added to PEI and halloysite to see if this could improve the coating-abilities. This led to a more uneven coating, and a rough surface with larger aggregates. This is seen on the right picture in **Figure 23**. This can be due to changes on the surface because of the addition of benzyl alcohol.



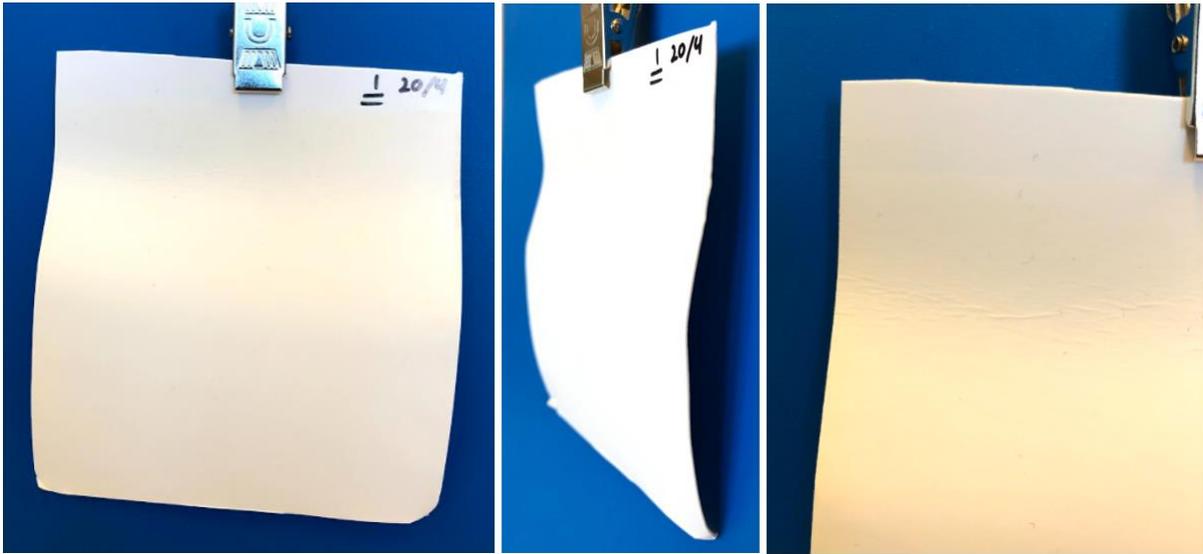
*Figure 23: PLA coated with halloysite and PEI. The pictures show PLA coated with 10 bilayers of halloysite and PEI (left) and coated with 10 bilayers of halloysite and PEI, both mixed with 10% benzyl alcohol.*

#### 4.5.3 Combination 3: PEI and hydrophilic bentonite

After experimenting with MMT-K10 and halloysite, with and without benzyl alcohol, the bentonite was tested. The bentonite was mixed with 10 % ethanol to improve the wettability. According to Sefiane et al. (2003), increased concentration of ethanol in a water/ethanol mixture gave a reduced contact angle on polytetrafluoroethylene (PTFE). The bentonite suspension was therefore added ethanol to improve the wettability of the substrate. After sonication, the bentonite was dispersed in water and did not sediment as fast as the other nanoclays when the stirring ceased. Sonication is used to break down aggregates into the smallest units possible to obtain a better dispersion (Marín et al., 2017). PLA and Invercote Duo was dip-coated, and the coatings deposited as an even layer on the surface of the substrates. This can be seen on pictures in **Figure 24** and **Figure 25** and **Figure 26**. It is uncertain if it was the bentonite itself, or the sonication which improved the coating-ability. Probably a mix, as the bentonite itself dispersed better in water, and the sonication may have amplified the dispersibility. The combination of PEI and bentonite showed the best coating ability, since the layers were even on the substrates. Despite the improved wettability after the UV-treatment of PLA and CrownBoard Craft, the PLA and Invercote Duo was not UV-treated because the wettability of the samples were satisfying without a UV-treatment. That being said, a UV-treatment would probably have improved the coating further. After drying the coating solidified as a hard layer which was resistant to physical removal like scratching, unlike the other coated substrates. The substrates coated with this PEI and bentonite were therefore used for gas barrier measurements. A visual comparison of the coatings with different nanoclays is shown in **Figure 26**.



**Figure 24: PLA coated with 10 bilayers of bentonite and PEI (photograph).** *The pictures show both sides of a PLA-sample coated with 10 bilayers of bentonite and PEI. The two pictures at the top shows the sample after five bilayers and the two at the bottom shows the sample after 10 bilayers. The coating looked the same on all the four samples and was slightly uneven on all of them. This can be seen as spots on the coating, especially at the bottom of the sample.*



*Figure 25: Coated sample of Invercote Duo with bentonite and PEI (photograph). The pictures show Invercote Duo coated with 10 even bilayers of bentonite and PEI.*

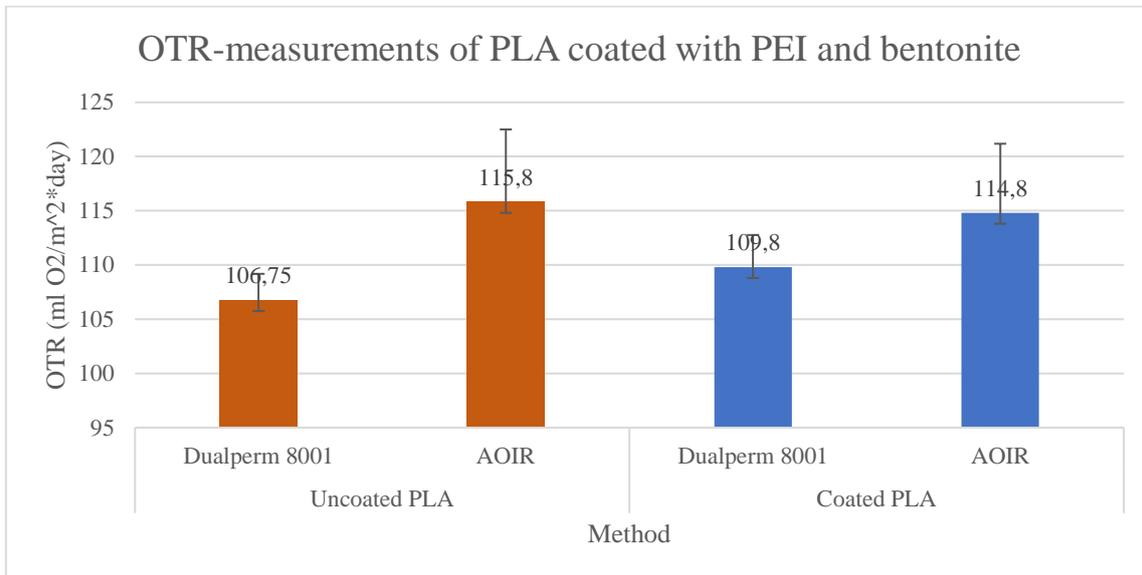


*Figure 26: PLA coated with halloysite, MMT-K10 and bentonite (photograph). The three pictures show PLA coated with halloysite mixed with 10 % benzyl alcohol(left), PLA coated with MMT-K10 and PEI (middle) and PLA coated with bentonite and PEI, both mixed with 10 % ethanol.*

The pictures show the PEI and nanoclay-coatings for comparison. The MMT-K10 and halloysite gave uneven coating with aggregates on the surface which looked rough. The bentonite-coating was even but had some irregularities at the bottom of the substrate.

## 4.6 Gas barrier measurements

### 4.6.1 OTR and CO<sub>2</sub>TR for PLA



*Figure 27: Overview of the OTR-measurements for PLA. The figure shows the mean OTR-values for uncoated and coated PLA measured with Dualperm 8001 and based on AOIR. The lines above/on each bar represent the std.*

The measurements performed with AOIR show a reduced OTR after coating, while the measurements performed with Dualperm 8001 show an increased OTR after coating. The reason for this is not clear as a coating should reduce the OTR-value, as shown in other studies. Inaccurate preparation of samples may be the reason for these results, or cracks in the coating during the handling of the coated samples. Originally, a trilayer was supposed to be used by adding polyacrylic acid (PAA) in the dip-cycle. According to Hagen et.al (2014) a 10 trilayer-coating with PEI, MMT and PAA, had better gas barrier properties than 20 bilayers of PEI and MMT on a polyethylene terephthalate (PET)-substrate. In this work, 10-bilayer of PEI and bentonite was used, which is few layers compared to studies where improved barrier properties were achieved.

#### 4.6.2 Air permeance for carton

The gas barrier properties of the carton qualities can be partly assigned to their thickness. Invercote Duo was the thickest substrate, which can have affected the gas barrier together with the coating. In general, the carton qualities did not show good barrier properties. This was expected, as the gas barrier of fiber-materials are a challenge due to their porous structure (Li et al., 2019). After the air permeation measurements of uncoated carton, the Invercote Duo was considered the substrate with the “best” gas barrier properties. Invercote Duo was therefore used for further coating-experiments with PEI and bentonite. These results are shown in **Table 8**.

**Table 8: Air permeance (ml O<sub>2</sub>/min) for Invercote Duo uncoated and coated with PEI and bentonite.** *The table shows the mean air permeance in ml O<sub>2</sub>/min for four replicates of Invercote Duo coated with ten bilayers PEI and bentonite.*

<b>Invercote Duo 450g</b>		
	<b>Uncoated</b>	<b>Coated</b>
<b>Mean (ml O<sub>2</sub>/min)</b>	1,341	0,431
<b>Std</b>	0,139	0,053

Invercote Duo coated with 10 bilayers of PEI and bentonite had improved gas barrier properties compared to the uncoated one. The coating reduced oxygen permeability per minute of the coated substrate with 68 %. But this improvement do not mean that this coated carton has a good gas barrier property. The O<sub>2</sub>- and CO<sub>2</sub>-% was measured every third minute for about 90 minutes, but after this time the amount of O<sub>2</sub>- and CO<sub>2</sub> was the same inside and outside of the cell. For the uncoated Invercote Duo-substrates this amount was reached after about 30 minutes.

## 5 Conclusion

The purpose of this thesis was to study if the barrier properties of biopolymer-substrates could be improved by using a layer-by-layer method through dip-coating with PEI-solution and nanoclay suspensions. During the studies there were several challenges, so adjustments of the experimental design were done to solve these challenges. The work presented in this thesis shows that a reduced OTR was obtained for one carton quality (Invercote Duo), but for PLA there were no significant changes in OTR. The dip-coating in alternating 0,1 % PEI-solution and 1 % bentonite resulted in an even coating on the surface of the substrates.

The thickness and the contact angle of the substrates were measured. The thickness of the substrates increased after being coated. For PLA, the thickness increased from 305  $\mu\text{m}$  to 343 $\mu\text{m}$  after coating. The thickness of Invercote Duo increased from 515,89 $\mu\text{m}$  to 649 $\mu\text{m}$  after coating. The thickness-measurement method was inaccurate, so it was difficult to evaluate the thickness properly. After the contact angles were measured, a UVC-treatment of PLA and CrownBoard Craft was performed. The contact angle was measured to obtain information about the wettability before the dip-coating. PLA and one carton quality (CrownBoard Craft) had poor wettability so a UVC-treatment was performed. The wettability of these two substrates was altered successfully with the UVC-treatment. The contact angle was reduced from 99,68° to 79,31° for PLA and from 103,87° to 91,52° for CrownBoard Craft.

After initial measuring and adjustments, the dip-coating was performed. PEI and three nanoclay suspensions were used. The two first ones, MMT-K10 and halloysite were not fitted for these experiments because they deposited as uneven layers on the substrates. Adjustments, like adding benzyl alcohol/ethanol to the liquids and surface treatment of the substrates were done to improve the coating. The last coating combination, with PEI and bentonite resulted in an even coating and the substrates coated with this combination was therefore chosen for gas barrier measurements. The improvement of gas barrier properties showed various results. The OTR for coated PLA was increased from 106,75 ml O<sub>2</sub>/m<sup>2</sup>\*day to 109,8 ml O<sub>2</sub>/m<sup>2</sup>\*day when measured with Dualperm 8001, but was reduced from 115,8 ml O<sub>2</sub>/m<sup>2</sup>\*day to 114,8 ml O<sub>2</sub>/m<sup>2</sup>\*day when measured with the AOIR-method. These results are not significant. The air permeation of Invercote Duo was reduced from 1,341 ml O<sub>2</sub>/ min to 0,431 ml O<sub>2</sub>/ min. This equals a reduction of almost 70 %. The substrates and the last coating-combination used in this thesis showed promising results, but should be examined further.

## 6 Future work

The experiments performed in this thesis show that there was no significant change in OTR for PLA, but the OTR-reduction was significant for carton. These varying results makes more research necessary. Further adjustments of the experimental design should be done to obtain better gas barrier properties.

Proposals for adjustments are to change the ratio of the PEI-solution and nanoclay suspensions to examine how different concentrations affect the barrier properties. The dip-coating process is time-intensive, and it would be interesting to see if good results could be obtained by reducing the immersion- and drying-time. The drying time in the oven could also be reduced to see if the effect would be the same, or if higher temperatures can be used to reduce the time. Not all experiments are suited for large scale production. It would therefore be interesting to see if the results could be replicated in an upscaled version.

More detailed information about the samples as they were made could be useful for further work, so a scanning electron microscopy (SEM) could be used to see the structure of the coating and inspire to further adjustments to improve the properties.

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## 8 Appendix

### Appendix 1 Thickness measurements

All samples are measured in  $\mu\text{m}$

<b>CrownBoard Craft</b>	<b>Sample</b>			
<b>Measurement</b>	<b>1</b>	<b>2</b>	<b>3</b>	
<b>1</b>	425	412	408	
<b>2</b>	435	423	428	
<b>3</b>	428	421	413	
<b>Mean</b>	429,33	418,67	416,33	<b>421,44</b>

<b>Invercote G</b>	<b>Sample</b>			
<b>Measurement</b>	<b>1</b>	<b>2</b>	<b>3</b>	
<b>1</b>	497	495	489	
<b>2</b>	492	487	500	
<b>3</b>	494	484	504	
<b>Mean</b>	494,33	488,67	497,67	<b>493,56</b>

<b>Invercote Duo</b>	<b>Sample</b>			
<b>Measurement</b>	<b>1</b>	<b>2</b>	<b>3</b>	
<b>1</b>	512	513	525	
<b>2</b>	517	522	515	
<b>3</b>	515	512	512	
<b>Mean</b>	514,67	515,67	517,33	<b>515,89</b>

<b>PLA</b>	<b>Sample</b>			
<b>Measurement</b>	<b>1</b>	<b>2</b>	<b>3</b>	
<b>1</b>	273	293	332	
<b>2</b>	287	297	319	
<b>3</b>	333	297	315	
<b>Mean</b>	297,67	295,67	322,00	<b>305,11</b>

## Appendix 2 Contact angle measurements after UV-treatment

Treatment time (min)		1	
Replicate	PLA	CrownBoard Craft	
	1	88,09	101,8
	2	85,76	98,3
	3	89,31	95,67
<b>Mean</b>		87,72	98,59

Treatment time (min)		5	
Replicate	PLA	CrownBoard Craft	
	1	86,12	97,21
	2	76,83	93,59
	3	76,82	96,09
<b>Mean</b>		79,92	95,63

Treatment time (min)		10	
Replicate	PLA	CrownBoard Craft	
	1	73,01	90,50
	2	81,6	85,65
	3	82,28	100,88
	4	80,38	89,06
<b>Mean</b>		79,32	91,52

Treatment time (min)		30	
Replicate	PLA	CrownBoard Craft	
	1	78,22	91,62
	2	80,98	91,97
	3	92,11	97,1
	4	84,57	101,96
<b>Mean</b>		83,97	95,66

### Appendix 3 Air permeance calculation

Calculation of air permeance for Invercote Duo

Sample	Oxygen-level in decimals		% of 276		Time (m)	Diff ml
	Start	Stop	Start	Stop		
1	0,00322	0,162	0,88872	44,712	97	43,82
2	0,00254	0,151	0,70104	41,676	98	40,97
3	0,00233	0,137	0,64308	37,812	102	37,17
4	0,00341	0,172	0,94116	47,472	95	46,53

Air permeance for Invercote Duo

Sample	Invercote Duo	
	Uncoated MI O <sub>2</sub> /min	Coated MI O <sub>2</sub> /min
1	1,415	0,452
2	1,131	0,418
3	1,416	0,364
4	1,4	0,490
Mean	1,341	0,431

## Appendix 4 Contact angle measurements

Contact angle for benzyl alcohol side 1

<b>Benzyl alkohol</b>					
<b>PLA</b>	<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>	
<b>Drop</b>					
<b>1</b>	55,69	46,16	46,79	50,71	
<b>2</b>	43,7	47,67	42,45	53,73	
<b>3</b>	50,23	48,64	50,83	42,19	
<b>4</b>	53,49	51,91	54,83	48,74	
<b>Mean</b>	50,78	48,6	48,73	48,84	49,235
<b>Invercote 285g (side 1)</b>					
<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>					
<b>1</b>	20,69	20,25	21,1	27,8	
<b>2</b>	20,25	17,33	22,06	21,34	
<b>3</b>	21,55	19,32	21,14	22,54	
<b>4</b>	21,67	19,65	21,82	21,54	
<b>Mean</b>	21,04	19,14	21,53	23,31	21,253125
<b>Invercote 380g (side 1)</b>					
<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>					
<b>1</b>	28,22	22,47	22,37	23,22	
<b>2</b>	24,93	25,25	23,31	22,91	
<b>3</b>	24,54	25,01	25,8	23,27	
<b>4</b>	22,37	24,85	24,42	22,96	
<b>Mean</b>	25,02	24,4	23,98	23,09	24,11875
<b>Invercote duo 450g (side 1)</b>					
<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>					
<b>1</b>	21,65	23,08	24,91	23,04	
<b>2</b>	23,4	24,6	24,19	24,9	
<b>3</b>	22,43	23,43	25,05	25,07	
<b>4</b>	24,18	24,74	23,74	22,65	
<b>Mean</b>	22,92	23,96	24,47	23,92	23,81625

Contact angle for benzyl alcohol side 2

<b>Benzyl alcohol</b>					
<b>Invercote 285g (side 2)</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	
<b>Drop</b>					
<b>1</b>	22,8	11,96	16,83	15,21	
<b>2</b>	15,13	13,21	11,23	12,31	
<b>3</b>	21,71	8,48	12,27	10,66	
<b>4</b>	16,82	15,12	17,05	14,35	
<b>Mean</b>	19,12	12,19	14,35	13,13	14,7
<b>Invercote 380g (side 2)</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	
<b>Drop</b>					
<b>1</b>	18,91	15,5	18,72	14,15	
<b>2</b>	18,4	13,23	17,36	12,68	
<b>3</b>	18,84	15,84	18,35	17,14	
<b>4</b>	19,06	13,85	20,17	14,99	
<b>Mean</b>	18,8	14,61	18,65	14,74	16,7
<b>Invercote duo 450g (side 2)</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	
<b>Drop</b>					
<b>1</b>	23,62	27,71	34,81	23,51	
<b>2</b>	22,96	23,56	27,79	23,4	
<b>3</b>	22,44	23,4	24,61	23,22	
<b>4</b>	23,22	23,07	24,31	21,7	
<b>Mean</b>	23,06	24,44	27,88	22,96	24,58

Contact angle for water, side 1

<b>Water</b>						
<b>PLA</b>	<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>						
	1	99,68	90,89	103,69	104,36	
	2	103,57	97,96	100,16	94,51	
	3	87,38	90,26	100,31	97,96	
	4	106,46	112,11	106,22	99,4	
<b>Mean</b>		99,27	97,81	102,6	99,06	<b>99,6825</b>
<b>Invercote 285g (side 1)</b>	<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>						
	1	105,9	100,98	106,33	131,09	
	2	101,48	103,42	88,99	106,99	
	3	105,42	103,38	101,19	106,75	
	4	98,35	106,21	102,12	93,44	
<b>Mean</b>		102,79	103,5	99,66	109,57	<b>103,8775</b>
<b>Invercote 380g (side 1)</b>	<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>						
	1	75,58	76,12	73,8	71,13	
	2	74,24	67,68	74,92	76,53	
	3	78,39	75,74	77,95	74,35	
	4	78,29	78,15	75,35	79	
<b>Mean</b>		76,63	74,42	75,51	75,25	<b>75,45125</b>
<b>Invercote duo 450g (side 1)</b>	<b>Area 1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>						
	1	74,92	73,81	81,13	75,35	
	2	74,07	75,17	80,26	75,44	
	3	73,81	75,92	79,31	72,65	
	4	72,82	72,11	74,96	75,71	
<b>Mean</b>		73,91	74,25	78,92	74,79	<b>75,465</b>

Contact angle for water side 2

<b>Water</b>						
<b>Invercote 285g (side 2)</b>						
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>						
	<b>1</b>	106,24	109,77	106,65	105,91	
	<b>2</b>	105,22	107,55	107	103,01	
	<b>3</b>	101,48	108,16	108,75	104,75	
	<b>4</b>	106,47	109,19	103,04	109,99	
<b>Mean</b>		104,85	108,67	106,36	105,92	<b>106,45</b>
<b>Invercote 380g( side 2)</b>						
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>						
	<b>1</b>	102,94	102,39	96,24	94,98	
	<b>2</b>	103,09	94,58	104,1	97,99	
	<b>3</b>	102,01	102,57	105,7	98,96	
	<b>4</b>	103,43	98,46	95,59	92,48	
<b>Mean</b>		102,87	99,5	100,41	96,1	<b>99,72</b>
<b>Invercote duo 450g (side 2)</b>						
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>		
<b>Drop</b>						
	<b>1</b>	89,84	79,63	79,89	79,98	
	<b>2</b>	80,56	80,24	78,14	78,74	
	<b>3</b>	78,06	77,83	78,71	77,54	
	<b>4</b>	79,07	80,1	82,45	77,71	
<b>Mean</b>		81,88	79,45	79,8	78,49	<b>79,91</b>

## Appendix 5 Specification sheets for chemicals and substrates

Specification sheet for Montmorillonite K10

# Specification Sheet

**SIGMA-ALDRICH**

<b>Product Name</b>	Montmorillonite, K 10, powder
<b>Product Number</b>	69866
<b>Product Brand</b>	ALDRICH
<b>CAS Number</b>	1318-93-0

### **TEST**

**APPEARANCE (COLOR)**

**APPEARANCE (FORM)**

**PH**

**PH (METHOD)**

**LOSS ON IGNITION**

### **SPECIFICATION**

Off White to Faint Grey

Powder

3.0 - 4.0

10 % IN H<sub>2</sub>O

REPORT RESULTS

# Specification sheet for halloysite

**SIGMA-ALDRICH®**

*sigma-aldrich.com*

3050 Spruce Street, Saint Louis, MO 63103, USA

Website: [www.sigmaaldrich.com](http://www.sigmaaldrich.com)

Email USA: [techserv@sial.com](mailto:techserv@sial.com)

Outside USA: [eurtechserv@sial.com](mailto:eurtechserv@sial.com)

## Product Specification

Product Name:  
Halloysite nanoclay

Product Number: **685445**  
CAS Number: 1332-58-7

$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2 \text{H}_2\text{O}$

Formula:  $\text{H}_4\text{Al}_2\text{O}_9\text{Si}_2 \cdot 2 \text{H}_2\text{O}$   
Formula Weight: 294.19 g/mol

TEST	Specification
Appearance (Color)	White to Tan
Appearance (Form)	Powder
Loss on Drying	
Specification: Report Results	
Miscellaneous Supplier Data	
BHT Surface Area	
Specification: Report Result	
Miscellaneous Assay	Conforms
Pore Volume; 1.26-1.34 ml/gm	
Bulk Density	
Specification: Report Results	
Units: lbs/ft <sup>3</sup>	
pH	Conforms
4.5-7.0	
Diameter	Conforms
30-70 Nanometers	
Length	Conforms
1-3 microns	
Product of Supplier	Conforms
Product of Applied Minerals, Inc.	
ICP Major Analysis	Confirmed
Confirms Al and Si Components	
Trace Metal Analysis	
Specification: Report Results	
Specification: PRD.4.ZQ5.10000027252	

# Specification sheet for hydrophilic bentonite

**SIGMA-ALDRICH**<sup>®</sup>

[sigma-aldrich.com](http://sigma-aldrich.com)

3050 Spruce Street, Saint Louis, MO 63103, USA

Website: [www.sigmaaldrich.com](http://www.sigmaaldrich.com)

Email USA: [techserv@sial.com](mailto:techserv@sial.com)

Outside USA: [eurtechserv@sial.com](mailto:eurtechserv@sial.com)

## Product Specification

Product Name:  
Bentonite

**Product Number:** 285234  
**CAS Number:** 1302-78-9  
**MDL:** MFCD00130611

$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$

### TEST

### Specification

Appearance (Color)

Conforms to Requirements

White to Grey

Appearance (Form)

Powder

Loss on Drying

≤ 8.0 %

pH

7.0 - 10.5

c = 4g/200mL, H<sub>2</sub>O

Specification: PRD.1.ZQ5.10000004741

# Specification sheet for polyethyleneimine

**SIGMA-ALDRICH**<sup>®</sup>

[sigma-aldrich.com](http://sigma-aldrich.com)

3050 Spruce Street, Saint Louis, MO 63103, USA

Website: [www.sigmaaldrich.com](http://www.sigmaaldrich.com)

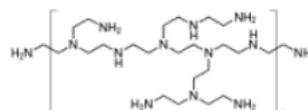
Email USA: [techserv@sial.com](mailto:techserv@sial.com)

Outside USA: [eurtechserv@sial.com](mailto:eurtechserv@sial.com)

## Product Specification

Product Name:

Product Number: **408727**  
CAS Number: 9002-98-6  
MDL: MFCD00084427



### TEST

### Specification

Appearance (Color)	Colorless
Appearance (Form)	Viscous Liquid
Infrared spectrum	Conforms to Structure
Water Content	≤ 1.0 %
Viscosity mPa.s	13000 - 18000

Specification: PRD.0.ZQ5.10000033911





**Norges miljø- og biovitenskapelige universitet**  
Noregs miljø- og biovitenskapelige universitet  
Norwegian University of Life Sciences

Postboks 5003  
NO-1432 Ås  
Norway