Structure-Performance
Relations of Oxygen
Barriers for Food Packaging

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Food packaging is required to secure the safety and quality of food, as well as minimize spoilage and simplify handling. Barrier coatings are generally used to meet the demands placed on fiber-based food packages, as these have the ability to regulate the amount of gases that can enter them. Some gases are detrimental to food quality: oxygen, for example, initiates lipid oxidation in fatty foods. This thesis focuses on the mass transport of oxygen in order to gain deeper knowledge of, and thereby optimise, the performance of barrier coatings. This experimental study, together with computer modelling, characterized the structure of barrier materials with respect to the mass transport process. The performance of the barriers was evaluated based on the parameters of environmental impact and product costs. As the long-term aim is to use non-petroleum-based barrier coatings for packaging, these should be evaluated by assessing the properties of the material in question, its functionality and its environmental impact to provide more insight into which materials are desirable as well as to develop technology.

The results from this study indicate that several parameters (the orientation, concentration and aspect ratio of the clay and the polymer crystallinity) influence the properties of a barrier. Using this knowledge, researchers and food packaging engineers can work toward improving and customising renewable barriers.
Appended Papers


IV. Nyflött, Å., Meriçer, Ç., Minelli, M., Moons, E., Järnström, L., Lestelius, M., and Giacinti Baschetti, M., *Influence of moisture content on polymer structure in dispersion barrier coatings of polyvinyl alcohol and its effect on oxygen mass transport* Submitted for publication

V. Venkatesh, G., Nyflött, Å., Bonnerup, C., and Lestelius, M., *An economic-environmental analysis of selected barrier coating materials used in packaging food products – A Swedish case study* Submitted for publication
Authors Contribution

I. Principal Author. Performed the experimental work, evaluation and main part of writing the manuscript

II. Principal Author. Performed the experimental work, evaluation and main part of writing the manuscript

III. Principal Author. Performed the computer model and the experimental work, evaluation and main part of writing the manuscript

IV. Principal Author. Performed the experimental work, the computer model work, evaluation and main part of writing the manuscript

V. Joint planning, collected the data and performed the life cycle analysis. Contributed to writing the manuscript
Related Work by the Same Author


List of Abbreviations

AOIR: Ambient oxygen ingress rate
ATR: Attenuated total reflection
CBA: Cost-benefit analysis
CPVC: Critical pigment volume concentration
DSC: Differential scanning calorimetry
EIA: Environmental impact assessment
E-LCA: Environmental life cycle analysis
EoS: Equation of state
EVOH: Ethylene vinyl alcohol
FDA: Food and drug administration (USA)
FIB: Focused ion beam
FTIR: Fourier transform infrared spectroscopy
LCC: Life cycle cost
GHG: Greenhouse gas
NaPAA: Sodium polyacrylate acid
NELF: Non-equilibrium lattice fluid
NET-GP: Non-equilibrium thermodynamic model for glassy polymers
OTR: Oxygen transmission rate
PALS: Position annihilation lifetime spectroscopy
PE: Polyethylene
PET: Polyethylene terephthalate
PHA: Polyhydroxyalkanoates
PLA: Polylactic acid
PP: Polypropylene
PS: Polystyrene
PVAc: Polyvinyl acetate
PVC: Polyvinyl chloride (plastic) or pigment volume concentration (filler)
PVD: Polyvinylidene chloride
PVOH: Polyvinyl alcohol
RH: Relative humidity
S-LCA: Social life cycle analysis
SEM: Scanning electron microscope
TGA: Thermogravimetric analysis
wt%: weight per cent
v%: volume per cent
XRD: X-ray diffraction
List of Nomenclature

A: Boundary condition or a constant
α: Filler aspect ratio
β: Geometric factor
b: Relation between permeability in different phases
c: Cohesive energy density
C: Concentration
C₀: Initial concentration
Cₛ(z): Concentration distribution through the coating
D: Diffusivity
∂: Hildebrand solubility
∂ₐ: Cohesive energy of dispersion
∂ₚ: Cohesive energy of polar-polar
∂ₗ: Cohesive energy of hydrogen bonding
Eₐ: Activation energy
Fₓ: Flux in x direction
ΔH: Heat of vaporization
ΔHᶠ: Enthalpy of fusion
ΔHᶠρ(Tm): Enthalpy of fusion of totally crystalline polymer
κ: Filler orientation factor
kᵢⱼ: Binary parameter
l: thickness
Lₐₐₘ: Mobility of amorphous polymer
Lₘ: Mobility of semicrystalline polymer
m: Mass
M: Molar mass
p: Pressure
p*: Characteristic pressure
Δpᵢⱼ*: Binary parameter
P: Permeability
Pᶠ: Permeability of flake filled system
Pₛ: Permeability semicrystalline polymer
Pₑᶠ: Effective permeability
pₐₜₐₘ: atmospheric pressure
ρ*: Characteristic density
ϕ: Loading level (concentration of filler)
ϕᵥ: Crystallinity
ϕᵢ: Volume fraction
Ψᵢⱼ: Binary parameter
R: Universal gas constant
r: Molar average number of lattice sites occupied
rᵣ: Control parameter
rᵣₒ: Number of lattice sites occupied
S: Solubility
s: Orientation of impermeable particles
Sam: Solubility amorphous polymer
Ssc: Solubility semicrystalline polymer
σ: Pore aspect ratio /openness of the structure
T: Temperature
T*: Characteristic temperature
Tg: Glass transition temperature
t: time
tl: Lag time
τ: Tortuosity
µ: Chemical potential
µNE: Chemical potential of species in the non-equilibrium glass
V: Volume
Vm: Molar volume
Vgas(STP): Volume of gas at standard temperature and pressure
ν*: Average closed-packed per molar volume in mixture
ν*: Volume occupied by mole of lattice sites
w: weighting factor
ω: Mass fraction
x: Distance
xi: Lattice site
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1 Background

Foodstuffs require packaging in order to uphold the quality and safety of the food, as well as to minimize spoilage and simplify handling the food supply chain in modern society. Furthermore, the packaging used should be light in weight and easy to transport. Foodstuffs that contain lipids are sensitive to oxygen, which oxidize them and is therefore detrimental to quality of the food [1-3]. One packaging material cannot fulfil all of these requirements, making different combinations of materials necessary.

Fibre-based packaging are often comprised of paperboard layered with a barrier material of plastics and aluminium. The paperboard provides the mechanical properties the packaging needs in order to withstand mechanical stresses, e.g. during transportation and storage, but it does not have the ability to prevent the mass transport of gases, grease, water or other molecules from the surrounding environment into the packed food and vice versa. Therefore, various barrier materials are added to paperboard, resulting in a layered structure with plastics and sometimes also aluminium.

Plastics are used because they are flexible and easily processed. Polymeric materials are often simple to print on, heat sealable, lightweight and inexpensive. They may, however, be permeable to gases, vapours, and molecules of low molecular weight [4, 5].

Aluminium provides physical and chemical protection and is therefore a common material used in food packaging. Although aluminium material can be recycled, the recycling process affects its quality because it increases white dross [6]. Since aluminium cannot be totally cleaned in this process, it is not reused in packaging for food.

The environmental demand made on the world’s industries and societies increases, while CO₂ emissions and the waste material that are
produced are considered a threat to the continued life and wealth of humankind on Earth. Plastics in the oceans and seas pose a threat to wildlife, as they are often non-degradable. Plastics that are thrown away outdoors are decomposed by the sun into microscopic particles, and thereby become a threat to wildlife. Fibre-based paperboard material, as opposed to the polymeric and metal-coated parts of a packaging, can be degraded completely outdoors and is thus not an overhanging threat to the environment.

The recycling process for fibre-based packaging starts by soaking the packaging in water to remove the barriers from the paperboard. The board is dissolved, which reverts it back to pulp, before being deinked. Thus the fibres can be reused, while the polymeric material is either recycled or burned to provide energy and the aluminium is reused in other industrial applications. The materials, and their properties, that can replace the petroleum-based polymeric material and aluminium, need to be fully understood and developed to be competitive.

1.1 Aim and objectives

Fibre-based packaging aimed for foodstuffs are provided with barrier coatings to prevent the mass transport of gas, moisture and liquid. The barrier coatings used today are mainly petroleum-based, and the demand for replacing them with renewable coatings are high. Their development is driven by practical experience and scientific advances. Replacing petroleum-based barrier coatings with renewable coatings requires that the properties of the barrier are understood completely. There is therefore no lack of motivation for focussing research efforts in this area.

The aim of this work was to investigate replacing petroleum-based material in food packaging with renewable and/or bio-based material. The way in which the structure of barrier coatings influences the performance of the barrier was examined and permeability, based on
the mechanisms of mass transport, was predicted. A well-known barrier coating was used to investigate the connection between the production settings and the properties of the material, down to the level of polymeric stricter and interaction with filler particles. Experimental characterisation of a well-controlled model allowed for the comparison of barrier coatings. Papers I and II investigated the structure and composition of dispersion barrier coatings in relation to permeability. These studies focused on monitoring the structural properties for scientific and industrial applications with the aim of understanding the process of oxygen mass transport.

Furthermore, a general model was developed in Papers III and IV to describe the mass transport through filled polymer coating. The barrier coating models were used to verify the computer model that was developed. The model and the model system were used to improve understanding of the mass transport processes. The computer model can be used to predict how structural changes influence the performance of the barrier.

A life cycle analysis of existing barrier coatings, both renewable and non-renewable, was made in Paper V. The environmental and economic aspects of four different barrier coatings were compared. A cradle-to-grave perspective was used when the various constituents of the coating materials were assessed.

Viewed with a longer perspective, this study provides knowledge that can be used to customize renewable barriers.
2 Food Packaging

As much as 50% of the food that is currently produced perishes on its way to the consumer [7]. Regulations stipulate that food packaging should deter tampering to ensure that the contents are not contaminated or spoiled further. Thus, packaging material must provide adequate protection for all aspects of food quality. These packaging require barriers not only to ensure safety and quality but also minimize spoilage; furthermore, they should also be easy to handle and transport. These properties are expected by both the business-to-business part of the value chain, where perhaps a greater focus lies on transport and protective performance, and the end-consumer in the latter part of the value chain. Here, the focus is on information and the actual handling of the packaging, and is also where a substantial part of the food loss arises [8].

Today, food packaging can be made of many materials: glass, metal, plastics, paper and paperboard. The different types of packaging are used for different purposes, and the relative amount of each therefore differs, Figure 1. Furthermore, different materials can be combined, e.g. plastics and paperboards, in order to achieve the properties desired in the packaging. The production of materials requires energy, with aluminium consuming the most and glass the least, Figure 2.

![Figure 1. Global packaging by type in 2012: total market size US$400b [9].](image1)

![Figure 2. Energy used in the production of various materials. TOE = ton of oil equivalent [10].](image2)
2.1 Paper and paperboard

Disintegrated wood raw material, i.e. cellulose fibres, forms paper sheets that are pressed and dried. These fibres are renewable material that is inexpensive and flexible. Paper can be used to make bags and wrappings for food with a short shelf life. Packaging similar to paper was first used in China (200 BC); flexible packaging came to Europe in the 19th century and, at beginning of the 20th century, paperboard packaging was developed [11, 12]. Although paperboard provides a better physical barrier than paper, it does not provide good protection against chemicals. Paperboard is therefore usually combined with other materials, such as plastics and/or aluminium foil, which provide a suitable barriers.

Producing fibre-based packaging material in a sustainable way starts in the forest, Figure 3. Trees are planted in generations so that some trees always remain when others are harvested: this generate a cycle of continuous growth in the forest. Some of the trees that are harvested are used in the paper mills, which turn them into fibres by different processes (chemical, mechanical or a combination of both). The resulting product, called pulp, can then be used to make paper or paperboard. The pulp and paperboard production process releases CO₂ which, in turn, can be bound by photosynthesis in the forest.

Figure 3. The production cycle of paper and paperboard (Courtesy of Stora Enso).
3 Barrier Materials

Gases, liquids, grease, aromas and light are various environmental conditions that can act to destroy the nutritional values of packed food.

The techniques used for applying barrier materials to paperboard packaging materials are laminating with a film, extrusion coating with a polymer or solution/dispersion coating. In extrusion coating, the polymer is melted in an extruder and either coated directly or laminated off-line, in the form of a film, onto the paperboard. The most common way of producing a barrier on the market today is by extrusion coating: this off-line process is not, however, as efficient as on-line coating due to the transportation between machines. Water-borne polymer solutions or dispersion coatings containing polymer, additives and maybe even plasticizers can be applied on-line in the paperboard machine, which lowers the environmental impact made, due to the minimized transportation, and increases the value of the paperboard.

The desired performance of the barrier is obtained by customizing the solution/dispersion coating through choice of material and thickness. The properties of the polymer, such as degree of crystallinity, flexibility of the chain, and branching points, affect the final properties of the barrier coating. Moreover, the polymer can interact with the additives, allowing slightly different properties of the dried barrier to be obtained compared to a polymer solution.

3.1 Environmental life cycle analysis of barrier coatings

Barriers are added to packaging board in many ways to endow it with different properties, aimed at producing a suitable food packaging. The value of the barrier added to the board is functionality by conferring upon it, for instance, the ability to withstand moisture and gases. This turns both the barrier and the food packaging into a service rather than a product. In order to move towards a service-oriented perspective, the
values of the product must be made visible to the customer. For example, improvements made to the product, such as source reduction and productivity, should be communicated. However, making such intangible attributes visible to the consumer is not easy. The value created by the barrier layer of a packaging is hidden, and it is actually only visible when the layer malfunctions and the foodstuff packed within get spoiled or leak out of the packaging, the fact that said value existed till that point in time, is appreciated [13]. Consumers simply take these functions for granted. The function of barriers varies, depending on the end-use. Barriers are used to prevent mass transport and thereby facilitate the packaging of the foodstuffs in the first place; they prolong the shelf-life of the product contained. In the context of business-to-business relationships, it is important that the barrier material can be used and the runnability can be predicted. When the value of a packaging (with the barrier coating used) is to be communicated, both the end-users and the intermediate businesses are potential targets.

One way of discovering the value of barriers is to perform an environmental life cycle analysis (E-LCA) [14], in which different barrier solutions can be compared. E-LCA is a method that can be applied to analyse and assess the environmental impact of materials, products and services. A complete E-LCA embraces everything from the raw material extraction to waste management at the end-of-life of a product; including electricity/energy use and inter-stage transport [15]. E-LCA can use defined limits: it therefore starts with a definition of the scope and goal of the analysis, is followed by an inventory of the resources consumed in the life-cycle, these resource flows are used to calculate different environmental impacts and concludes with analysis of data [16]. E-LCA supports the decisions that are to be made, and can compare materials or identify any environmental improvements that are necessary [17]. The focus of E-LCA is on environmental impacts, which should be minimised. The results obtained from the data analysis can be used to visualise environmental impacts and also for advertisement purposes: to show the environmental impact of a product, often in comparison with another.
There is a standard for E-LCA (ISO 14000) that describes the different phases that should be included [17], namely defining the scope, goal and framework, followed by an inventory analysis and an environmental impact assessment.

The starting point for E-LCA is identifying goal and scope, as does the framework, Figure 4. The goal and scope of the E-LCA should tell for whom and why the E-LCA should be performed. The inventory is used to analyse the inflows/requirements of materials and energy and the outflows of products, by-products, reusables/recyclables and emissions. Every product or service utilised by the system is essentially a culmination of a set of processes, each of which interacts with and impacts the environment – so-called indirect environmental impacts of the studied system. Further, there are processes within the system that by virtue of emissions to the environment account for its direct environmental impacts. The data used in the E-LCA can be obtained by making measurements, modelling or from information provided by external companies/databases. The data should then be processed to environmental impacts, which should have been defined. Depending on the goal and scope the E-LCA can be processed in different ways, as indicated by Figure 4. So, the inventory analysis became an impact assessment and finally interpretation of results, a complete E-LCA is accomplished. Related to the E-LCA are economic analysis, Life-cycle costing (LCC) and social life-cycle analysis (S-LCA), which are all included in the domain of sustainable development [16].
Cost-benefit analysis (CBA) is a method which is used to analyse alternatives from an economic perspective [18]; the results of a CBA are presented as a net benefit. Ideally, CBA must be integrated with E-LCA, when environmental impacts are determined [19]. Environmental impact assessment (EIA) is based on environmental and other non-monetary concerns; it is used in the process of planning projects [20, 21]. EIA includes identification, prediction, evaluation and mitigation of the effects of the project. This constitutes a framework for conducting assessments, whilst E-LCA is a method for analysis. Generally speaking, EIA has more details of impacts, whereas E-LCA provides a more reliable quantification of the net environmental impact in areas and regions [22].

In this thesis, an E-LCA and a simple economic analysis have been carried out, for four different barriers: PE, EVOH+kaolin, latex+kaolin and starch. E-LCA enables the analyst to identify environment-friendlier alternatives and ways of preventing pollution, as well as enabling different materials designated for the same end-use to be compared [23]. Global warming is the environmental impact considered in the study, along with the cost of the product: while the former enables one to compare on the basis of greenhouse gas (GHG) emissions, the latter is useful when alternatives have to be ranked on the basis of how expensive (or affordable) they are. The value for the customer is the functionality of the barrier in combination with the environmental impacts which with E-LCA can be easier communicated to the end-consumers. The E-LCA is discussed further in Section 9.

### 3.2 Common barrier materials

Polymers, such as polyolefins, polyesters, polyvinyl chlorides, polyvinylidene chlorides, polyamides and ethylene vinyl alcohols (Table 1) [5] are used on fibre-based packaging to form barriers. The barrier functions and usage of various polymers can be summarized as:
• Polyolefins, such as polyethylene (PE) and polypropylene (PP), make good barriers against moisture and other molecules.

• Polyesters, such as polyethylene terephthalate (PET), make good moisture and oxygen barriers. Commonly used for carbonated liquids.

• Polyvinyl chloride (PVC) is a good barrier against grease/oil, acid and bases.

• Polyvinylidene chloride (PVdC) is a good barrier against general water vapour, gases and grease/oil.

• Polyamides are good chemical and gas barriers.

• Ethylene vinyl alcohol (EVOH) is a good grease/oil and oxygen barrier.

<table>
<thead>
<tr>
<th></th>
<th>Permeability / ml μm m⁻² day⁻¹ atm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen</td>
</tr>
<tr>
<td>PET</td>
<td>60-80</td>
</tr>
<tr>
<td>PVC</td>
<td>100-400</td>
</tr>
<tr>
<td>High density PE</td>
<td>2000-4000</td>
</tr>
<tr>
<td>Low density PE</td>
<td>5000-7000</td>
</tr>
<tr>
<td>PP</td>
<td>3000-5000</td>
</tr>
<tr>
<td>PS</td>
<td>5100-80000</td>
</tr>
<tr>
<td>EVOH</td>
<td>0.2-20</td>
</tr>
<tr>
<td>PVdC</td>
<td>0.2-3</td>
</tr>
</tbody>
</table>

Polymer coatings can also be used as barriers in plastic packaging; the percentage share of the global market is presented in Figure 5 [25]. PVdC, which has a majority on the global market, is used mainly for fresh food due to its general barrier properties. Metallised plastics are used for products that need a good oxygen and light barrier, e.g. snack food. Plastic treated with AlOx are used mainly for retortable pouches and film lids for fresh food.
3.3 Barrier performance

Mass transport through a barrier coating is combination of diffusivity and solubility, the result of permeability. If the coating is not perfect, mass transport occurs through cracks and pinholes. The polymer structure of the coating influences the mass transport through it: crystalline regions have a lower rate of diffusion for gas molecules than amorphous regions due to the order of the polymer chains, which is impermeable for oxygen. Additives affect the structure; an impermeable filler, for example, forces gas molecules to take a tortuous path, which lowers the permeation process.

Before mass transport can take place, the molecules need to be adsorbed at the surface, although some of them are absorbed into the barrier. Then, the molecules can diffuse along different pathways. In general, this process is driven by the overall difference in partial pressure on either sides of the barrier layer. Finally, following
permeation, the molecules are desorbed into the packaging, where they can affect the food packed within.

Describing the process physico-chemically, the permeation, $P$, is a product of the diffusivity, $D$, and the solubility, $S$ (Equation 3.1):

$$ P = D \cdot S. $$  \hfill (3.1)

Diffusivity and solubility depend on the characteristics of the barrier material as well as the characteristics of the molecules available for permeation. For example, permeation can be affected when hydrogen bonding occurs between oxygen and a hydroxyl group on the polymer.

Diffusion is described as the random movement of molecules in a barrier coating, also known as Brownian motion. Adolf Fick was the first person to describe the phenomenon of diffusion (1855), which he adopted from the mathematics of heat transfer as described by Jean-Baptiste Joseph Fourier (1822). The result was Fick’s first law: the rate of flow through a cross-section of a matrix is proportional to a concentration gradient [26] (Equation 3.2):

$$ F_x = -D \frac{\partial C}{\partial x}. $$  \hfill (3.2)

where $F_x$ is the flux in the $x$ direction, $C$ is the concentration, and $x$ is the distance. Using Fick’s first law, the time dependent ($t$) concentration can be described with the flux which, in turn, is described in one dimension by Equation 3.3 thus:

$$ \frac{\partial C}{\partial t} = -\frac{\partial F_x}{\partial x}. $$  \hfill (3.3)
A constant diffusion coefficient results in Fick’s second law in one dimension, presented below in Equation 3.4:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right). \quad 3.4$$

If the diffusion coefficient is constant in the material, and the system is planar, Equation 3.5 can be used [26]:

$$C = \frac{A}{\sqrt{\pi}} e^{-x^2/4Dt}, \quad 3.5$$

where $A$ is the boundary condition at $x=0$ and $t=0$, $A = \int_{-\infty}^{\infty} C dx$.

The structure of the barrier material affects the mass transport through it: it is therefore important to measure the time resolution (dynamics) of the mass transport. The dynamics of the mass transport provide information about the structure of the barrier, as well as the different states of mass transport: the steady and the non-steady-states. The non-steady-state gives information about the lag in time. The steady-state phase is achieved when the diffusion of permeant through the material is constant (i.e. the time lag before this state) and can be determined using a linear relationship. The time lag, $t_l$, can be calculated using Equation 3.6:

$$t_l = \frac{\int_0^l \int_0^l c_s(x) d^2x}{\int_0^{C_0} D(x) dx}, \quad 3.6$$

where $c_s(x)$ is the concentration distribution through the coating in the steady-state, $l$ is the thickness of the sample ($0<x<l$) and $C_0$ is the initial concentration, Figure 6.
Permeability is defined by the parameters of diffusivity and solubility (Equation 3.1). The solubility of small molecules, such as oxygen, depends on the interactions between the molecule and the polymer. The large difference in the solubility parameters of both the molecule and polymer, the lower the solubility of the molecule in the polymer. Low solubility indicates that the constituents are less compatible [27]. The Hildebrand solubility parameter, \( \partial \), can be used to calculate the solubility:

\[
\partial = \sqrt{c} = \left[ \frac{\Delta H - RT}{V_m} \right]^{1/2},
\]

where \( c, \Delta H, R, T \) and \( V_m \) are the cohesive energy density, heat of vaporization, universal gas constant, temperature, and molar volume, respectively. The Hansen solubility parameter [28] is an expansion of the Hildebrand solubility parameter. The cohesive energy is divided into three parts that correspond to the dispersion, polar-polar and hydrogen bonding forces thus:

\[
\partial^2 = \partial_d^2 + \partial_p^2 + \partial_h^2.
\]

The Hansen solubility for polyvinyl alcohol (PVOH) shows that while the polar-polar and dispersion forces are close to that of water, the hydrogen bonding forces differ, Figure 7. This indicates that, although PVOH is soluble in water, the hydrogen bonding force is different: it
therefore dissolves slowly at room temperature, but can be increased by raising the temperature of the water.

![Figure 7. Hansen solubility for PVOH and water shown in 3D.](image)

The solubility of the penetrant depends on the properties of the solid material, such as voids, free volume, crystallite size, and degree of crystallinity.

### 3.4 Polymer properties

The building blocks in polymers are monomers, which are repeating units. The monomers build long chains; it is their size that determine the molecular weight of the polymers. Polymers containing more than one type of monomer are known as co-polymers and block co-polymers, Figure 8.
The molecular weight affects the polymer’s properties, e.g. density which, in turn, affect the properties of the barrier. The arrangement of the polymer chains with respect to each other affects the mechanical and chemical properties of the polymer. The polymer’s properties affect its potential use, since different applications require different properties. Mechanical properties are of importance in the manufacturing process and also in the handling of the packaging. Chemical properties affect the interaction of the polymer chains, which can affect the mechanical properties of the polymeric material. For example, glass transition of the polymer affects the stiffness of the chain and the formation of crystalline phases. The free volume in a polymeric material is linked to mass transport [26]: the more flexible the chains the greater the free volume, which increases the mass transport of molecules. Free volume are affected by the degree of crystallinity of the barrier.

Polymers can be divided into categories according to the source used for production and possible biodegradation: petroleum-based/bio-based and non-biodegradable/biodegradable, Figure 9. All plastics are degradable because it is possible for them to be broken down. Plastics that are biodegradable can be broken down by the metabolism of micro-organisms: compostable plastic is biodegradable and will break down under certain conditions [29]. Compostable plastic is a subset of biodegradable plastic, and biodegradable plastic is a subset of degradable plastic: the opposite does not, however, apply.
Increased awareness of the environment forces industry to make choices that are environment friendly. Plastics were historically based on petroleum but nowadays more plastics are produced from bio-based resources [30]. The degradability of plastics will be more important in decreasing the amount of non-degradable plastics present in the environment. Both petroleum and bio-based polymers can be non- and biodegradable, which gives an indication of whether nature can take care of polymer degradation itself or not.

![Figure 9. The categories of polymers.](image)

Today, research is focused on replacing petroleum-based polymers with bio-based in order to reduce the environmental impact; an overview of bio-based polymers can be seen in Figure 10. Some of the polymers used for barriers are being produced from renewable resources, such as cellulose and polysaccharides, whilst others are biodegradable and bio-based, such as polylactate (PLA) and polyhydroxyalkanoates (PHA).
3.5 Composites

Two or more components that are mixed together form one material that is called a composite. A composite can be comprised of a polymer matrix and fillers, such as fibres and clays. Depending on the properties desired, different ways of mixing can be utilized. Should both the polymer and the fillers be water soluble, then the mixing take place in water with a mixer; if using water is not an option, then an extruder is used, Figure 11. The plastic granules and fillers are fed from the hopper in to the barrel of the extruder. Here, the material is melted gradually by mechanical energy generated by the screws and heaters. The molten polymer is forced into a die, which forms the polymeric film that is coated on the paperboard.

Figure 11. Cross-section of a plastic extruder.
The purpose of a composite is to provide characteristic properties and/or more economical material. The characteristic properties, whether physical or chemical, are often not the same as the different components. The compatibility of the constituents is of importance in minimizing phase separation. Phase separations can result in a higher mass transport through the material, and lower mechanical strength. In this thesis, the composite under study comprises a polymer matrix with impermeable particles such as clay, Figure 12.

Figure 12. Illustration of the mass transport of oxygen (black and white) through the polymer composite (grey), which has amorphous and crystalline regions filled with impermeable particles such as clay (black).

3.5.1 Additives and fillers

Additives and fillers can be used to adjust the properties in the wet state or in the dry state, for example adjust the mechanical properties and compatibility of the components in the composite. Plasticizers make the polymer chains more flexible and may even reduce the cracks and pinholes that are always present in a barrier coating. Moreover, the altered rheology that additives cause can make processing easier and thereby reduce costs. Plasticizers, which soften the polymer matrix, are used to minimize mechanical failure. Enzymes and other additives
provide compounds that are detrimental either to the packaging material itself or the goods contained within scavenging capacity. Fillers such as clays, on the other hand are added to increase the length of the pathways through the polymer matrix.

The surface and optical properties can be improved with mineral pigments, which are typically fillers. The mechanical properties of the coating are affected by the pigment volume concentration (PVC) in the polymer matrix. The pigments need to be embedded in the polymer matrix and, if they are not totally covered, the critical pigment volume concentration (CPVC) is exceeded. Negative packing effects of the fillers arise above the CPVC since voids are introduced into the matrix [31]. Parameters such as optimal lattice packing, type of polymer and additive, and state of dispersion or agglomeration (i.e. how much the pigments can interact) affect the CPVC [32].

The fillers are often impermeable to gases, the molecule of which are therefore forced to take a tortuous path. Tortuous pathways have been described in many ways; one of the first tortuosity models is described by Nielsen 1967 [33] (Section 4.4):

\[
\frac{P}{P_{ff}} = \frac{1 + \alpha \phi}{1 - \phi},
\]

where \(P\) is the polymer permeability, \(P_{ff}\) is the filled polymer permeability, \(\alpha\) is the aspect ratio and \(\phi\) is the level of loading (concentration of filler). The aspect ratio can be defined either by the ratio diameter divided by the thickness of the platelets (often specified by the suppliers for their products and often applied in two dimensional models for permeability (as in Eq. 3.8)) or the ratio of the surface area of the normal plane divided by surface area of the side plane, which is applied in three-dimensional permeability models [34]. A tortuous pathway can be achieved by having a high aspect ratio, high concentration of filler and well-orientated filler platelets (i.e. in the basal plane of the barrier) [34-36].
3.6 Interfaces

Differences in material can be on macroscopic and microscopic levels. The microstructural difference in materials is an interface, such as that between a polymer-filler and amorphous-crystalline polymer regions, and the contact between the barrier and the surrounding. In this section, the different interfaces will be reviewed and discussed.

3.6.1 Polymer-filler interface

The polymer-filler interface is of importance since the adsorption of the polymer onto the filler affects the degree of packing and density around the fillers. The properties of the polymer and the surface of the filler are important because the polymer can be adsorbed one of three ways at an interface: by competitive, cooperative and independent adsorption, Figure 13 [37].

![Figure 13. Polymer adsorption onto a clay interface.](image)

Competitive adsorption can take place if two macromolecules compete for the same adsorption site; it results in the adsorption of one of them, while the other remains in the solution. Cooperative adsorption occurs when one macromolecule is adsorbed onto the surface and the second one interacts with it, i.e. the second macromolecule is adsorbed on top of the first. Independent adsorption occurs when the macromolecules adsorb at different sites, e.g. one macromolecule is adsorbed onto the
basal plane while the other is adsorbed onto an edge, and is probably due to some reaction preference.

### 3.6.2 Water interface

Water acts as a plasticizer for some polymers, e.g. PVOH. In PVOH, water can be in three different states: non-freezing, freezing and free [38]. Non-freezing water binds strongly to the hydroxyl groups on PVOH and the temperature of the phase transition is indistinct. One water molecule can attach to the PVOH monomer, giving a maximum of 29 wt% non-freezing water. The non-freezing water cannot undergo phase transition when the temperature drops below 0°C (at 1 atm) due to the insufficient structural order, Figure 14. Freezing water interacts with either the polymer chains or the non-freezing water and forms aggregates with sufficient structural order to undergo phase transition at temperatures below 0°C. Free water is presumed to be located in the free volume within the polymer.

![Phase diagram for water.](image)

*Figure 14. Phase diagram for water.*
The plasticizing effect of water on PVOH comes mainly from non-freezing water and is due to the interaction between the water and the hydroxyl group on the polymer chains. The water progressively turns the crystalline region into being amorphous, by increasing the size of side groups and destroying the hydrogen bonds in the PVOH system. Water, however, cannot destroy intact crystallites [39]. The solubility of water in PVOH depends on the relative humidity, Figure 15 [40, 41].

![Graph showing water solubility in PVOH at different RH. The grey rhombus (*) are from Hauser and McLaren 1948 [41] and black line is from the model presented in Section 10.](image)

Figure 15. Water solubility in PVOH at different RH. The grey rhombus (*) are from Hauser and McLaren 1948 [41] and black line is from the model presented in Section 10.

The properties of the filler depend on the way in which its interaction with water occurs. In this study kaolin (Al$_2$Si$_2$O$_5$(OH)$_4$), which is a non-swelling clay, was used (see Section 5.2): it has the ability to bind water onto its hydrophilic parts, i.e. silanol and aluminol sites [37, 42].

The interaction between PVOH and water is mainly due to hydrogen bonding and solvation forces: physisorption. It is, however, strongly dependent on the molecular weight and degree of hydrolysis. Gases, such as oxygen and carbon dioxide, exhibit weak interaction with
PVOH. The interaction between PVOH and kaolin is electrostatic and is probably due to hydrogen bonds [42, 43]. The barrier is affected by humidity so it is also important to know how oxygen and water bond together; studies have shown that they bond weakly, i.e.by van der Waals forces. All of the interactions are weak, so they can therefore interact easily with each other.

Some of the oxygen molecules that are adsorbed onto the barrier are desorbed at the surface. Molecules diffuse through the barrier to the surface at the side of low concentration, where they desorb. The same procedure also happens with water molecules, and the oxygen interacts with the water as well. This means that the number of interaction sites for oxygen increases, and thereby affects permeability.

3.6.3 Barrier-air interface

The interface between the barrier and the surroundings (i.e. the air) includes oxygen, water and other molecules and is important since it affects the mass transport. Adsorption occurs when molecules from a gas or solution phase binds in a condensed layer onto a solid or liquid phase; desorption occurs as the adsorbed layer dissociates from the interface [44].

There are two different types of adsorption: physisorption and chemisorption. In the former, the adsorptive bond is due to van der Waals interaction; it is the weakest form of adsorption. The latter is characterized by a chemical reaction between the adsorbed particle and the surface. The adsorption energy can be used to determine which kind of sorption occurs: chemisorption has a higher energy than physisorption, due to the type of bond involved.
4 Modelling

The producers of fibre-based food packaging should decrease their use of petroleum-based polymers and aluminium foil is to reduce the total emission of CO₂ per packaging. Therefore, it is important to gather more knowledge of barriers that can be used in fibre-based packaging solutions in order to understand what properties are needed for bio-based polymers. Mathematical modelling of mass transport processes can be used to predict the barrier performance of new combinations of bio-based polymers. Models describing (mathematically) the mass transport of gaseous molecules can be divided into those for sorption, diffusion, and trans-membrane mass transport [45] (Table 2). Empirical models are then developed from experiments and are based on interpolation to fit experimental data; semi-empirical models combine theories with experimental data in order to simplify calculations, and theoretical models use physical and chemical theories.
<table>
<thead>
<tr>
<th>Model</th>
<th>Classification of model</th>
<th>Number of Permeating Components</th>
<th>Glassy</th>
<th>Polymer Type Semi-crystalline</th>
<th>Cross-linked</th>
<th>Rubbery</th>
<th>Co-polymers</th>
</tr>
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<tr>
<td>Sorption</td>
<td></td>
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<tr>
<td>Langmuir and Henry's Law Isotherms</td>
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<td>Single</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
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<td>x</td>
<td></td>
<td>x</td>
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<tr>
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<td>Semi-Empirical</td>
<td>Binary</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>Semi-Empirical</td>
<td>Multi</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
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<tr>
<td>UNIFAC</td>
<td>Theoretical</td>
<td>Multi</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
<td></td>
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<tr>
<td>ASOG-FV</td>
<td>Semi-Empirical</td>
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<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
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<tr>
<td>Entropic-FV</td>
<td>Semi-Empirical</td>
<td>Multi</td>
<td>x</td>
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<td>x</td>
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<td></td>
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<tr>
<td>modified NRTL</td>
<td>Semi-Empirical</td>
<td>Binary</td>
<td>x</td>
<td></td>
<td>x</td>
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<tr>
<td>ENSIC</td>
<td>Semi-Empirical</td>
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<td>x</td>
<td></td>
<td>x</td>
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<tr>
<td>Molecular Simulation for Sorption</td>
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<td>Binary</td>
<td>x</td>
<td></td>
<td>x</td>
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<tr>
<td>Empirical Diffusion Coefficients</td>
<td>Empirical</td>
<td>Multi</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<tr>
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<td>Binary</td>
<td>x</td>
<td></td>
<td>x</td>
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<tr>
<td>Dual Sorption</td>
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<td>Binary</td>
<td>x</td>
<td></td>
<td>x</td>
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<tr>
<td>Molecular Simulation for Diffusion</td>
<td>Theoretical</td>
<td>Binary</td>
<td>x</td>
<td></td>
<td>x</td>
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<tr>
<td>Mass Transfer</td>
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<tr>
<td>Empirical Model by Franke</td>
<td>Empirical</td>
<td>Multi</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<tr>
<td>Solution-Diffusion Model</td>
<td>Semi-Empirical</td>
<td>Multi</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
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<tr>
<td>Semi-Empirical Model after Meyer-Blumenroth</td>
<td>Semi-Empirical</td>
<td>Binary/Ternary</td>
<td>x</td>
<td></td>
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<tr>
<td>Q-Model</td>
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<td>Binary</td>
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<td></td>
<td>x</td>
<td></td>
<td></td>
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<tr>
<td>Process-specific Permeability Functions</td>
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<td>Binary</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
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<tr>
<td>Thermodynamic of Irreversible Processes (TIP)</td>
<td>Semi-Empirical</td>
<td>Multi</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
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<tr>
<td>Stephan-Maxwell Theory</td>
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<td>Ternary</td>
<td>x</td>
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<td>Pore Flow Model</td>
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<td>Binary</td>
<td>x</td>
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<td>x</td>
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<tr>
<td>Pseudophase-Change Solution-Diffusion Model</td>
<td>Theoretical</td>
<td>Binary</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
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</tr>
</tbody>
</table>
4.1 Models for sorption

Sorption models can describe the behaviour of permeant molecules at the interface of the surroundings and the barrier coatings. These models can also describe the solubility of the permeant in the material.

Many researchers have studied the sorption of different systems empirically [46-51]. There are two empirical models: the Langmuir adsorption isotherm model and Henry’s law [52, 53]. These describe a single permeant and can be used for different states of a polymer in a barrier. Henry’s law is used for rubbery polymers whilst Langmuir’s isotherm model is used for crystalline polymers [54]. Therefore, both models can be used to compare the sorption of different states of a polymer matrix in order to develop its properties and thereby achieve the performance desired. Nevertheless, this is not always sufficient and a combination with other theories is often necessary to obtain a complete description [45].

Semi-empirical models include the solubility parameter theory, Flory-Huggins, universal quasi chemical (UNIQUAC), analytical solution of group (ASOG-FV), entropic-FV, modified non-random two liquid (NRTL) and engage species induced clustering (ENSIC). These models address the sorption process whereby each theory describes the polymer state and the permeant components, although not fully. The model for the solubility parameter describes the energy required to overcome the intermolecular forces when separating the molecules [55]. The Flory-Huggins model predicts the concentration profile and the sorption selectivity [56-58]. UNIQUAC is used to predict phase equilibrium, and has been extended to be combined with hydrogen bonding and free volume [59]. ASOG-FV is an alternative method that is directly related to UNIQUAC, UNIFAC, and the Flory-Huggins theory and includes the free volume [60]. The entropic-FV is also similar to UNIQUAC and UNIFAC, to which the free volume is added [61, 62]. The modified NRTL calculates the phase equilibria and, in certain cases, being part of the Flory-Huggins theory [63]. ENSIC describes sorption as a mechanical anisotropic process [64].
Current theoretical models used for sorption are UNIFAC and molecular simulation. UNIFAC is used for a system lacking experimental data and can predict the phase equilibria [65]. This model has been extended to include free volume theory and to capture the different phases of the polymer (i.e. crystalline, semi-crystalline, and amorphous) and cross-linked polymers. The molecular simulations for sorption are solved using the chemical potential [66-68].

The non-equilibrium lattice fluids (NELF) model can be used to model solubility in the polymer matrix [69] and is based on chemical potential combined with mixing theories. NELF describes the solubility of the gas in a glassy polymer: there are non-equilibrium systems and have a higher specific volume that the equilibrium state. NELF is based on the fact that the Gibbs free energy of the glassy polymers can be described by the density of the polymers and it is thermodynamically treated as a variable of an internal state. The Gibbs free energy for polymer mixtures or humid polymers can determined by Sanchez and Lacombe’s lattice fluid theory [70]. The solubility of gas is calculated from equilibrium conditions, and requires that the chemical potential of the penetrant in the glassy polymer is equal to the external gaseous phase. Equation of state (EoS) models are efficient for calculating the solubility of gases and vapours in glassy polymers [69]. The non-equilibrium thermodynamic model for glassy polymers (NET-GP) [69, 71] determines the extension required of EoS below T_g, which conventional EoS models are not able to describe.

4.2 Models for diffusion

Diffusion models describe the random path of the diffusant in the polymer matrix. These models can be used to analyse and predict diffusion but are, however, specified for a certain type of system and not for general application.
The empirical diffusion coefficient model needs a diffusion coefficient at infinite dilution as a reference value and uses approximations for the calculations [72, 73]. It is suitable for use in process and material design.

Free volume, dual sorption, and molecular simulation are all theoretical models for diffusion. The free volume theory describes the mass transport based on molecule movements, making it a model that gives a physical description of diffusion [74]. This theory has been modified to capture diffusion in semi-crystalline and rubbery polymers as well as cross-linked polymers [45]. Dual sorption theory is similar, but restricted to glassy membranes. This theory describes diffusion based on the free spaces, i.e. free volume, present in the structure [75, 76]. Molecular simulations describe the permeating component in the polymer matrix using chemical potentials [77-79].

Fick’s law describes the diffusional behaviour of the penetrating molecules, (see Section 3.3). The size of the penetrant and the availability of diffusion sites in the polymer (e.g. free volume [74, 80]) is linked directly to the diffusion coefficient.

4.3 Models for mass transport

Mass transport models combine both the solubility and diffusivity of the permeant, thereby providing a complete description of the mass transport. However, they are developed to consider only certain conditions, such as constant pressure, independent of temperature or porous media.

Empirical models do not use physico-chemical relations, although they do assume that the concentration of permeate is independent of temperature. The effect of temperature on permeability can be
described by an Arrhenius relation, where free permeate flow under constant pressure is presumed [81].

Semi-empirical models for mass transport include solubility-diffusion, a semi-empirical model after Meyer-Blumenroth, the Q-model, a process-specific permeability functions, the Thermodynamic of Irreversible Process (TIP), and the pore-flow model. The solubility-diffusion model is divided into three steps: the first is absorption of the permeate, the second is diffusion through the rubbery polymer system based on the gradient in the chemical potential and the third is desorption of the permeate [82]. The semi-empirical model after Meyer-Blumenroth extends the solubility-diffusion model by including the effect of coupling up to three fluxes. It applies to pressure rather than concentration being a driving force, which is associated with chemical potential [83, 84]. The Q-model is also based on the coupling of fluxes to describe the permeability and difference in chemical potential [85]. Process-specific permeability functions use coupling in the solubility-diffusion model by dividing the permeability into empirically-determined permeability functions [86]. The TIP model describes the coupled diffusion and coupled fluxes [87]. Mainly for use with porous materials, the pore-flow model describes straight cylinders in the polymer distributed throughout the layer [88, 89].

The Maxwell-Stefan theory and pseudophase-change solubility-diffusion model are both theoretical models. The former theory is based on irreversible thermodynamic processes: driving force, gradient of the chemical potential and interaction forces, which are described by friction forces [47]. The latter model assumes that permeation can be described by the solubility-diffusion theory. The system is in thermodynamic equilibrium and any changes in the phases of permeate occur in the layer. The process is isothermal and the pressure is described as an adjacent applied pressure [90, 91].

A combined model comprising solubility, diffusivity and tortuosity has been presented in Nyflött, et al. 2016 [92] and expanded further to
include humidity Nyflött, et al. 2016 [93]; a flow diagram of the model’s strategy can be seen in Figure 16. The model is discussed in Section 10.

![Flow diagram of the model strategy.](image)

*Figure 16. Flow diagram of the model strategy. SL-EoS: Sanchez & Lacombe Equation of state, L: mobility, τ: tortuosity. Subscripts (apply to all components): am = amorphous, SC = semi crystalline, eff = effective.*

### 4.4 Models for tortuosity

Adding impermeable particles to a polymer matrix forces the penetrant to take a tortuous path around them. The concept of a tortuous path has been explained by different research groups; Table 3 shows some of the equations that have been developed to describe its effect on permeability.

The tortuosity model proposed by Nielsen 1967 [33] has been expanded following the observation that platelets can orientate as two-dimensional periodic arrays [94]. The model was also extended to embrace many flake layers [95].

The orientation of the platelets is another factor that can be included: theories are either exponential functions [96] or order parameters [97]. Molecular simulations for platelet-filled systems have also been developed further [98, 99].
<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell 1873 [100]</td>
<td>$\frac{P}{P_{ff}} = \frac{1-\phi}{1+\alpha \phi}$</td>
<td>$\phi$ loading level, $\alpha$ aspect ratio</td>
</tr>
<tr>
<td>Volume fraction [33]</td>
<td>$\frac{P}{P_{ff}} = (1 - \phi)^2$</td>
<td></td>
</tr>
<tr>
<td>Nielsen 1967 [33]</td>
<td>$\frac{P}{P_{ff}} = \frac{1-\phi}{1+\alpha \phi}$</td>
<td></td>
</tr>
<tr>
<td>Aris 1986 [94]</td>
<td>$\frac{P}{P_{ff}} = \left(1 + \frac{(\alpha \phi)^2}{1-\phi} + \frac{\alpha \phi}{\sigma} + \frac{4 \alpha \phi \ln \left(\frac{\pi \alpha^2 \phi}{\sigma (1-\phi)}\right)}{\sigma (1-\phi)}\right)^{-1}$</td>
<td>$\sigma$ pore aspect ratio</td>
</tr>
<tr>
<td>Cussler, et al. 1988 [95]</td>
<td>$\frac{P}{P_{ff}} = \left(1 + \frac{(\alpha \phi)^2}{1-\phi}\right)^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Fredrickson and Bicerano 1999 [101]</td>
<td>$P_{ff} \approx F_m \left(\frac{\pi}{\ln(\alpha \phi)}\right)$</td>
<td>$F_m(x) = \left(\frac{1}{m} \sum_{j=1}^{m} \frac{1}{1+\alpha x}\right)^2$</td>
</tr>
<tr>
<td>Bharadwaj 2001 [97]</td>
<td>$\frac{P}{P_{ff}} = \frac{1-\phi}{1+\alpha \phi^2 (5+\frac{1}{2})}$</td>
<td>$S = 0$</td>
</tr>
<tr>
<td>Gusev and Lusti 2001 [102]</td>
<td>$\frac{P}{P_{ff}} = \exp \left(- \left(\frac{\alpha \phi}{x}\right)^{\beta}\right)$</td>
<td>$\beta$ geometric factor, $\beta = 0.71, x = 3.47$</td>
</tr>
<tr>
<td>Lape, et al. 2002 [36]</td>
<td>$\frac{P}{P_{ff}} = \frac{1-\phi}{\left(1+\frac{2}{3} \alpha \phi\right)^2}$</td>
<td></td>
</tr>
<tr>
<td>Moggridge, et al. 2003 [103]</td>
<td>$\frac{P}{P_{ff}} = \left(1 + \frac{2 (\alpha \phi)^2}{27 (1-\phi)}\right)^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Minelli, et al. 2009 [104]</td>
<td>$\frac{P}{P_{ff}} = \frac{\alpha \phi}{\sigma} \left(1 + \frac{\sigma}{a}\right)^2 + \frac{(\alpha \phi)^2 (1+\frac{\sigma}{a})^4}{1-\phi (1+\frac{\sigma}{a})}$</td>
<td>$\sigma$ openness of the structure</td>
</tr>
<tr>
<td></td>
<td>$+ \frac{\alpha \phi}{\sigma} \left(1 + \frac{\sigma}{a}\right)^2 \ln \left(\frac{1-\phi (1+\frac{\sigma}{a})}{\phi \sigma (1+\frac{\sigma}{a})^2}\right)$</td>
<td>$r_t = \frac{\alpha - \phi (a+\sigma)}{\phi (a+\sigma)^2}$.</td>
</tr>
</tbody>
</table>

The models have been developed for different purposes so the mathematical description of the filler commonly used in each model can differ slightly. The permeability behaviour can thus differ even, though the aspect ratio and concentration of the filler are used, see...
Figure 17. All of the models used are semi-empirical; experimental results are therefore it is important in order to obtain the best models for the material studied.

Figure 17. Effect of tortuosity on permeability with different aspect ratio ($\alpha$), a: $\alpha=1$, b: $\alpha=10$, c: $\alpha=50$, d: $\alpha=100$. 
5 Materials

5.1 Polyvinyl alcohol

PVOH was prepared for the first time in Germany, in 1924, by Herrmann and Haehnel [105]. PVOH is produced by the hydrolysis of polyvinyl acetate (PVAc) in an alcohol solution, via a free radical process or suspension polymerization. PVOH exists as different grades of hydrolyse characterized by the amount of acetate groups that remain after the conversion has taken place:

\[
[\text{CH}_2\text{CH(OAc)}]_n + \text{C}_2\text{H}_5\text{OH} \rightarrow [\text{CH}_2\text{CH(OH)}]_n + \text{C}_2\text{H}_5\text{OAc}.
\]

It is a well-controlled process that, due to the removal of acetate groups, can produce partly or fully hydrolysed PVOH. The structure of PVOH, which has the same degree of polymerization as PVAc, is a saturated hydrocarbon backbone with side chains of hydroxyl groups, Figure 18. Although the chains are rather flexible, they have low amount of branching and this which influences the crystallisation process. The side chains contribute to water solubility, which is important for water-borne dispersion barriers. Above 98% PVOH is considered as being fully hydrolysed, and has an expected crystallinity of 40-50% [106]. A lower degree of hydrolysis produces a lower degree of crystallinity, because the acetate groups hinder both crystallization and inter-chain hydrogen bonding. The amount of plasticizer added also affects also crystallinity, as does the type of catalysed production process (i.e. acid or base) that is used. The polar alcohol groups (OH) produce crystalline regions that reduces the degree of water solubility but increase the solvent resistance, tensile strength and adhesion to hydrophobic surfaces [106].
PVOH has a carbon backbone that can degrade. Degradation can cause discolouring and crosslinking due to the removal of hydroxyl and acetate side groups. Non-plasticized PVOH degrades above 180°C due to the removal of water from its structure. Depending on the degree of crystallinity the crystalline melting point is 180-240 °C: it can, however, be regulated by the adjusting the degree of hydrolysis in the polymerization process. The presence of acetate groups also affects the degree of degradation: the liberation of acetic acid during degradation catalyses the degradation process. PVOH does not leave toxic residues during degradation: the end-products are biomass, carbon dioxide and water [106].

When formed, PVOH is a water soluble rubbery synthetic polymer, which is characterized by excellent film-forming, emulsifying and adhesive properties. PVOH has good flexibility, good gas barrier and good solvent resistance properties. Low crystallinity is linked to lower strength and increased water solubility. The adhesion and the coating performances mean that PVOH is often used in packaging industry. Moreover, PVOH is barrier against gases (Table 4), grease (animal, vegetable and mineral) and organic solvents (aromatic and aliphatic hydrocarbons, esters, ethers and ketones). All these properties are affected by the degree of polymerization and degree of hydrolysis [107]. The gas permeability is increasing with humidity, lower degree of hydrolysis, higher temperature, lower $T_g$ and lower crystallinity.

In addition, the diffusion process is affected by the orientation and size of the crystalline regions. The crystalline regions have a similar effect
on the mass transport as impermeable particles (such as clay), forcing the oxygen molecules to take a tortuous pathway [108]. Molecular simulation of oxygen diffusion in PVOH has shown that oxygen displacement occurs preferentially along the backbone [109]. The crystalline regions can capture oxygen molecules for a short time and thereby introduce a lag time: the time it takes the oxygen to diffuse through the barrier is thus prolonged. The lag time for oxygen is related to the free volume in, and the chain movements of the polymeric material [110]. Tightly-packed chains with high local alignment, such as crystalline regions, reduce the diffusion of oxygen even if the free volume remains constant [111].

Table 4. Gas permeability of PVOH for different gases.

<table>
<thead>
<tr>
<th>Gas permeability</th>
<th>mL cm (cm² s cm Hg)^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{H2}</td>
<td>$6.6 \times 10^{-13}$</td>
</tr>
<tr>
<td>P_{O2}</td>
<td>$6.24 \times 10^{-17}$</td>
</tr>
<tr>
<td>P_{F2}</td>
<td>$&lt; 10^{-13}$</td>
</tr>
<tr>
<td>P_{N2}</td>
<td>$10^{-11}$</td>
</tr>
<tr>
<td>P_{CO2}</td>
<td>$10^{-13}$</td>
</tr>
</tbody>
</table>

In this research, polymer grades from Kuraray (Frankfurt, Germany) were chosen, namely atactic, Poval (Mowiol) 15-99, Poval (Mowiol) 6-98, Mowiol 6-88, Poval 5-74, Poval 20-98 and Poval 56-98. Poval 15-99 grade was chosen because it is widely accepted as being suitable for use with food (e.g., it is FDA approved). The polymer grade chosen has a hydrolysation degree of 99% and a viscosity of 15 Pas in water at 4% concentration. Poval 6-98, 6-88 and 5-74 were chosen due to their similar molecular weight (30 000 – 50 000 g/mol) for studies of the hydrolysis degree (98%, 88% and 74%). Poval 6-98 (47 000g/mol), 20-98 (125 000 g/mol) and 56-98 (195 000 g/mol) were chosen for studies of molecular weight; all of the samples had a hydrolysis degree of 98%.
5.2 Kaolin

Kaolin (Al₂Si₂O₅(OH)₄) is a 1:1 layered clay: one layer is tetrahedral and the next is octahedral. The molecular structure of kaolin is shown in Figure 19. Furthermore, it is non-expandable in water. The cohesive energy between one of the layers and the oxygen atoms in the adjacent layer is mainly electrostatic, van der Waals interaction and hydrogen bonding between hydroxyl groups. Kaolin has a low cation exchange capacity, usually between 1-10 meq per 100g [112], and a density of 2.63 g cm⁻³ [113]. Kaolin is the most common type of clay used in barrier materials because its aspect ratio is high and the platelets orientate in the basal plane with very little need for great forces to be applied. This clay was chosen due to its rather thin and long platelets (high aspect ratio) and its ability of being detectable in SEM.

![Figure 19. Molecular structure of kaolin.](image)

Kaolin often contains a dispersant agent such as sodium polyacrylate acid (NaPAA) [114], this can affect the polymer crystallinity. Therefore, kaolin platelets were cleaned, as described in Jarnstrom, et al. 1987 [115], and summarized in Figure 20.
Figure 20. The procedure used to the kaolin

5.3 Renewable material, starch and hemicellulose

Starch is based on amylose, which is a linear polymer, and amylopectin, a branched polymer. The structure of starch is basically a backbone based on glucose units linked together by α-1,4-glucosidic bonds; the branches in amylopectin are linked by α-1,6-glucosidic bonds, Figures 21 and 22. Starch tends to bond by intra-molecular hydrogen bonding to form a helical structure. Amylose has good film-forming properties and binds to surfaces with polar groups. Unmodified starch has a high molecular weight and a high viscosity and requires modifying to make it more suitable for use in coatings, usually by oxidation or adding a functional group. A granule of potato starch, which is comprised of 21 % amylose and 79 % amylopectin [116], has a diameter of around 30 μm. In this study, hydroxypropylated and oxidized potato starch were used (Solcoat P 55, Solam, Kristianstad, Sweden). Oxidation introduces carboxyl and carbonyl into the starch, and these act as an internal plasticizer. The chain length become reduced, which lowers the viscosity of the starch solution, making it more suitable for use as a barrier coating. Hydroxypropylated starch has improved film-forming properties and enhanced strength [116, 117].
Hemicellulose binds to cellulose and lignin and exists in various forms in trees and plants: it is removed from the cellulosic fibres in alkaline conditions after the lignin has been extracted. The alkaline conditions make the polymer insoluble in water but can be modified by for example esterification, etherification and methacrylation. This allows the solubility and thermal, as well as the film-forming properties to be modified [118, 119]. The degree of polymerization depends on the type of hemicellulose in question, and varies between 80 and 200. Xylan, Figure 23, is one type of hemicellulose. It is comprised of a β(1→4)-D-xylopyranose backbone with side groups, and has a typical degree of polymerization of 3 to 5. In this thesis, xylan from beech wood was used (X4252, Sigma Aldrich)

In order to produce films from starch and hemicellulose a plasticizer has to be used to make the polymer matrix more flexible and less brittle. The plasticizer replaces some of the hydrogen bonds between the polymer (both intra- and intermolecular hydrogen bonds) and polymer:water [120–123]. The polymer chains become more flexible upon addition of plasticizer and can crystallize more easily. The
amount of plasticizer is important since too much will eventually lead to phase separation [124]. In this study, sorbitol (D-sorbitol, Sigma Aldrich), which is a sugar alcohol, was used as the plasticizer since it is approved for food contact.

5.4 Preparation of the polymer solution and dispersion

PVOH was dissolved in deionized water at 95°C under gentle stirring for 1.5 - 3 hours, depending on the grades used: PVOH with a low degree of hydrolysis needed to be heated for a longer period of time. The polymer solution was cooled to room temperature before the film was prepared. The concentration of the final PVOH solution was measured before film preparation or mixing with kaolin, and was between 10 - 15 weight% (wt).

The kaolin was dispersed in deionized water at room temperature during high shear mixing for 30 min, and had a final concentration of 60 wt%. The dispersion was then diluted to the concentrations required. Prior to mixing the pH of the PVOH and kaolin were checked and adjusted to pH 7.3 (Paper I) and 6.3 (Paper II) by adding NaOH. The PVOH solution and the kaolin dispersion were mixed in different ratios.

The starch was dissolved in deionized water at 95°C under vigorous mixing for 45 min to a final concentration of 10 wt%. Prior to film preparation, the starch solution was cooled down to room temperature whilst being stirred. The plasticizer was then added to the starch solution, which was kept at room temperature [125].

Xylan was dissolved together with sorbitol in deionized water at 95°C with magnetic stirring for 15 min until the final concentration of the xylan was 10 wt%. The solution was cooled down and later diluted by re-heating it for 15 min to reach a final concentration of 2.85 wt% [125].
6 Methods for Characterizing Properties of Barrier Material

In this section the method used to characterize the barrier material is described further. The common methods that are available for characterizing barrier coatings are described together while the material-specific properties are described separately.

6.1 Barrier coatings

Barrier coatings were prepared on PET substrate with a bench rod coater (K202 Control Coater, RK Print Coat Instruments Ltd., Royston, UK) with different wire-wound rods in order to obtain coating of varying thickness. The PET substrate was used to make coating with even thickness and the high adhesion strength between the PET and PVOH [126]. They were subsequently dried in heating chamber at a specified temperature (60°C, 95°C or 160°C). Some barrier films were also prepared by pouring the polymer solution or dispersion into Petri dishes made in polystyrene (PS), to make free-standing films, which were dried in 23°C and 50 RH% for up to one week.

The temperature of the barrier coating dried in the heating chamber was determined by an IR temperature sensor (Thermopoint TPT 62, FLIR System AB, Danderyd, Sweden). The water content in the films was also measured, using a contactless NIR moisture sensor (FIBRO MCA 1410, FIBRO System AB, Hägersten, Sweden).

The thickness of the coating was measured with a mechanical profilometer (STFI thickness profilometer, THT-Teknik AB, Järfälla, Sweden) or a mechanical thickness micrometer (App 141, Lorentzen & Wettre, Stockholm, Sweden) and a micrometer screw.
The barrier coating was studied in an optical microscope and a scanning electron microscope (SEM), which was used to study the structure in more details.

The films were also equilibrated in a climate chamber (CTS C+ 10/200, Hechingen, Germany) prior to some of the measurements named below being made (DSC and FTIR).

### 6.2 Characterization of kaolin

The kaolin used in this thesis was characterized by size distribution, organic compound and composition. The particle size of the dispersed kaolin was analysed using the sedimentation method (LUMiSizer, LUM GmbH, Berlin, Germany) according to ISO 13318-2. Its composition was analysed with X-ray diffraction XRD (D8 Advance, Bruker AXS, Karlsruhe, Germany) with Cr K (alpha) source, and 2θ was measured between 2-65°, Figure 24.

![Figure 24. The XRD instrument](image)
The organic compounds present in the kaolin were analysed using thermogravimetric analysis (TGA) (TGA/SDTA851e, Mettler-Toledo, Schwerzenbach, Switzerland). The kaolin was imaged with SEM (Zeiss EVO MA10, Carl Zeiss Microscopy GmbH, Jena, Germany), Figure 25.

6.2.1 Orientation of the kaolin

The platelets in the kaolin are important: its tortuosity is strongly dependent on their orientation (see Chapter 4.5). Orientation can be determined by image analysis of SEM images or by Fourier transform infrared spectroscopy (FTIR) (Thermo Nicolet FTIR Nicolet iS10, Madison, US).

SEM was used to image the barriers, the cross-sections in particular, as this provided information on distribution and orientation of the filler. Moreover, the thickness of the barrier coating could also be observed. SEM was operated at high vacuum (10^-5 – 10^-6 mbar), Figure 26. The cross-section was prepared by using either focussed ion beam (FIB) procedure or embedding it in epoxy. The FIB technique required first placing the coated films between two glass plates (Bellco cover-slips).
The cross-sections were then prepared with an ion-beam cutter (Hitachi IM4000), which sputtered the samples with argon ions for seven hours (acceleration voltage of 3 kV, discharge voltage of 1.5 kV and gas flow of 0.08 cm³min⁻¹). Finally, the cross-sections were sputtered with carbon before the images were captured. The barrier films were embedded in epoxy (Epofix) and left to harden for 12 hours. The embedded films were polished in four steps: 1) SiC paper #500; 2) MD largo with DP-spray with grind size 5μm; 3) MD Dur with DP-spray with grind size of 3μm and, finally, 4) MD Nap with DP-spray with grind size of 1μm. The sample were rinsed with ethanol and dried in between each step. The embedded films were coated with gold to prevent charging effects from affecting the samples.

The cross-section images were analysed with image analysis to estimate the orientation, size and area distributions in the kaolin [127] and was based on the structure tensor method [128]. Before the orientation of the platelets can be determined, the images need to be pre-processed: Gaussian filter, segmentation, normalization and threshold were applied to the images, Figures 27 and 28. The angle is presented in the unit circle, which shows the angles of the platelets used in the image analysis. Figure 28 shows results from both the co-
variance matrix method (which did not produce usable results in all cases) and the structure tensor method (which was applicable in all cases) [127].

Figure 27. Pre-processing process of the SEM image.

Figure 28. Examples of results from the image analysis

FTIR is vibration spectroscopy that identifies molecules by the vibration frequencies of specific chemical bonds, Figure 29: the electromagnetic field (aligned in the direction of the bond) excites the bond and thereby produces a vibration. FTIR can also be used to identify phases, the crystallinity of the polymer and the orientation of the kaolin according to the rules of specificity and excitation [129]. Spectra are often depicted with absorbance (or transmittance) as a function of wavenumber [cm\(^{-1}\)] (inversely proportional to frequency) based on the use of the Michelson-Morely interferometer found in modern instruments. The degree of crystallinity of the polymer and the orientation of kaolin can be studied using FTIR in transmission mode and attenuated total reflection (ATR) mode [130].
Kaolin has characteristic vibrations in the 3600-3700 cm\(^{-1}\) region that represent dipole oscillation of the OH bonds, Figure 30. Here, kaolin has four peaks of which three (3670, 3652, and 3620 cm\(^{-1}\)) represent bonds orientated at a shallow angle to the basal plane of the kaolin platelets and one (3695 cm\(^{-1}\)) represents the perpendicular bond [131, 132]. The orientation factor of kaolin, \(\kappa\), can be calculated from the ratio of the peak area at 3695 cm\(^{-1}\) and 3620 cm\(^{-1}\) [131]:

\[
\kappa = \frac{\text{peak intensity } 3695\text{cm}^{-1}}{\text{peak intensity } 3620\text{cm}^{-1}}. 
\]

A low value of \(\kappa\) means that the orientation of the kaolin platelets is mainly in the basal plane of the barrier coating.
Figure 30. FTIR spectrum of the kaolin used.

6.3 Characterization of PVOH

The PVOH was characterized by crystallinity and free volume, which are described in detail below.

6.3.1 Degree of crystallinity

The degree of crystallinity can be determined using FTIR and a differential scanning calorimeter (DSC) (DSC Q2000, TA Instrument, Newcastle, USA).

FTIR spectra can be used to determine the degree of crystallinity of PVOH. The ratio between the crystalline and amorphous regions in the PVOH can be calculated from the FTIR peaks, Figure 31: both the regions can be studied by examining the C-O stretch vibrations in the 1090-1150 cm\(^{-1}\) region [133-135]. The degree of crystallinity, \(\phi_c\), can be calculated from the ratio of the peak intensity in the crystalline region (1140-1145 cm\(^{-1}\)) to that in the amorphous region (1090-1096 cm\(^{-1}\)) [134] thus:
\[ \Phi_c(\%) = -13.1 + 89.5 \cdot \frac{\text{crystalline peak intensity}}{\text{amorphous peak intensity}} \]

Figure 31. FTIR spectrum of the crystalline and amorphous regions in the PVOH used.

The DSC can be used to detect the crystallization mechanism in polymer systems [136]. The calorimeter is used to study the heat transfer during both physical and chemical processes, Figure 32.

Figure 32. Schematic DSC curve illustrating the three zones of a polymer.
The enthalpy is measured at constant pressure or constant volume. Equation 6.3 can then be used to calculate the crystallinity [137]:

\[
\phi_c(\%) = \frac{\Delta H_f(T_0 - T_f)}{\Delta H_f^0(T_m)(1 - m_f)} \times 100\%,
\]

where \(\Delta H_f(T_0 - T_f)\) is the enthalpy of fusion of the sample between temperature \(T_0\) and \(T_f\), \(\Delta H_f^0(T_m)\) is the enthalpy of the totally crystalline polymer and \(m_f\) is the mass fraction of the filler. For PVOH, the enthalpy of the totally crystalline polymer is \(\Delta H_f^0(T_m) = 138.6 \, J/g\) [138].

### 6.3.2 Free volume

The vacancy of an atom represents a local free volume. Free volume are made by the segmental motion of atoms; they are important for diffusion in polymeric material and are detectable by positron annihilation lifetime spectroscopy (PALS), Figure 33. PALS is used to determine the local electron density and electrostatic interaction sites at the atomic level. The radiation of the positrons can be measured using time resolution and energy spectra. The structure of the material can be investigated in terms of, for example vacancies (missing atoms), clusters of atoms and size of free volume [139].
The positron source ($^{22}\text{Na}$) is placed in between the three pieces on each side of the sample, giving it a sandwich geometry. Two scintillation detectors are used: one for detecting the birth of positrons and one for annihilation. The decays from the positron source produce a positron and a $\sim1.27$ MeV $\gamma$-quantum, which acts as a start-signal for the detector. The positrons diffuse thermally into the material and during their lifetime (few hundreds of picoseconds), they interact with the defects. The stop signal for the detector comes from the annihilated positron, which produces two 511 keV $\gamma$-quantums. The time difference between the start and stop signals is the lifetime of the positron, Figure 34.

![Figure 33. The PALS instrument used.](image)

![Figure 34. Positron annihilation lifetime of PVOH with different degrees of hydrolysis and molecular weights. PVOH 1: hydrolysis degree 98% $M_w=47000$; PVOH 2: hydrolysis degree 74% $M_w=40000$; PVOH 3: hydrolysis degree 88% $M_w=37000$; PVOH 4: hydrolysis degree 98% $M_w=195000$; and PVOH 5: hydrolysis degree 98% $M_w=125000$.](image)
7 Methods for Measuring Permeability

Different methods were used to determine the permeability of the barrier films and are described in detail below.

7.1 Oxygen transmission rate

The oxygen transmission rate (OTR) was measured according to ASTM D3985 with OxTran 2/21 (MOCON, Minneapolis, US), Figure 35. Two chambers are separated by the barrier material to be tested, Figure 36 and the sample is flushed with nitrogen. One side contains the test gas, in this case oxygen, which is absorbed by the sample. The oxygen is transported through the sample and desorbed on the other side; the other chamber contains the carrier gas, nitrogen, which transports the oxygen to the sensor. Although the climate in the instrument can be adjusted in terms of moisture and temperature, it needs to be stabilized before the measurements are made. This method determines the permeability at steady-state, which represents the equilibrium of the mass transport through the barrier coating. The constraints of measuring the steady-state permeability by this method limits the information of the structural influence on the mass transport process that can be extracted from the experimental data obtained.
7.2 Ambient oxygen ingress rate

Permeability can also be measured by applying another method: the instrument PermMate (Systech, Illinois, US) can be used to measure ambient oxygen transmission rate (AOIR). This method is quite flexible since the samples can be mounted either in a cell or between two cells. It can also measure directly the permeability of packaging that are filled to their headspace. A needle is placed into the cell or packaging to extract a sample of gas, which is then transported to the sensor. This extracted gas can be returned into the packaging again or else nitrogen can be entered, Figure 37. This method provides information about the mass transport in the initial as well as the steady-state phase, because the time resolution provided by the extraction procedure and oxygen sensor is much faster (around 5 s) than that of the MOCON equipment.

![Figure 37. Image of the AOIR method (Courtesy of Systech, Illinois).](image)

AOIR can also be used to calculate the OTR [140, 141]. The measurement obtained of the increase in oxygen concentration can be used to calculate permeability, \( P \):

\[
P = \left( \frac{dp}{dt} \right)_{t \to \infty} \frac{V \cdot l}{p_{atm}} = \left( \frac{dc}{dt} \right)_{t \to \infty} \frac{V \cdot R \cdot T \cdot l}{V_{gas(STP)} p_{atm} A}
\]

7.1

where \( V \) is the volume of the sample cell, \( p \) is pressure, \( t \) is time, \( l \) is the thickness of the sample, \( p_{atm} \) is the oxygen pressure, \( c \) is concentration, \( R \) is the gas constant, \( T \) it the temperature, \( V_{gas(STP)} \) is the volume for the gas at standard condition and \( A \) is the area.
The AOIR method allows the lag time, $t_l$, to be extracted from the data due to the low concentration at the beginning, Figure 38. The lag time can be used to calculate the diffusion coefficient, $D$, of the barrier material being studied:

$$D = \frac{\pi^2}{6t_l}. \tag{7.2}$$

The solubility, $S$, of the barrier material can be calculated using the permeability and diffusion, according to Henry’s law (Equation 7.3):

$$S = \frac{p}{D}. \tag{7.3}$$

Figure 38. An example of AOIR experiment results obtained in this study, displayed as concentration versus time. Extraction of the lag time and data from the permeability calculations (Equations 7.1-7.2) are shown.
7.3 Permeometer

The time resolution of the mass transport of oxygen through the barrier can also be measured, using a permeometer. The method is based on a standard ASTM D 1434 and has two set-ups: one for dry conditions, Figure 39 [142], and one for humid, Figure 40. The sample is mounted in the sample holder and kept under vacuum to remove dissolved substances before measurements are made. The pressure sensors PI 01 and PI 02 are used to check that the dissolved substances are removed prior to measuring, and to check the pressure difference during the measuring procedure. The downstream volume calibrated previously is closed during measurements, so the increase in gas in the downstream volume is the results of permeation through the coating.

Figure 39. Schematic diagram of a dry permeometer (Courtesy of Bologna University, DICAM).

Figure 40. Schematic diagram of a humid permeometer (Courtesy of Bologna University, DICAM)
8 Results and Discussion – The Permeability of Barrier Coatings

The permeability of the barrier coatings was analysed under different conditions in order to determine how structure and the interaction between the coating constituents themselves affect permeability [114, 141]. Moreover, permeability was measured for different relative humidity, temperatures and pre-treatments of the barrier. The studies are summarized in the following sections, starting with the choice and development of the experimental method. This is followed by accounts of the impacts of the filled polymer (PVOH) matrix, crystallinity of the polymer (PVOH) and the relative humidity on permeability, and concludes with some parallel studies carried out in the master thesis on renewable materials (starch and hemicellulose) suitable for barrier applications.

8.1 The influence of time resolution

The method for measuring permeability is crucial since different methods produce different results. In this thesis the permeability was measured using OTR, AOIR and two permeometers (see Section 7). OTR provides steady-state permeability while AOIR and the permeometer give time-resolved and steady-state permeability.

The OTR method is the one most commonly used for measuring steady-state permeability, for several reasons: the sensitiveness of the sensor, the independency of the operator and the ASTM standard. However, it cannot provide the time resolution of the permeability. The time-resolved AOIR was measured by discrete sampling as well as by continuous measurement. Discrete AOIR samples were collected by removing the needle that supplies the sensor with gas samples, and refilling the cell with nitrogen when needed. A pressure difference might be introduced during the measurement before the refill of nitrogen so, in order for this to be minimized, the refilling is done at regular sampling intervals. The continuous measurement is performed in a closed system: the volume taken to the sensor is reinserted into the
cell, and has the same pressure during the duration of the measurement. The difference in set-up give a similar-steady-state permeability, Figure 41. However, the time resolution for the two AOIR set-ups differs: the discrete sampling shows a combination of pressure-driven permeability and refilling of nitrogen, and it therefore has a faster increase than the continuous sampling, Figure 42. The discrete sampling does not give a satisfying time resolution, but it might be possible to improve this by using the closed system, as with the continuous sampling.

Dry and humid permeometers show a difference at dry conditions. In the dry conditions it is important that the system is completely dry: this is not the case for the humid permeometer because it has a water reservoir and humidifier, so the system cannot be totally dried out. The AOIR cell can be dried out and controlled by silica gel. The AOIR set-up uses surrounding air, which is not dried before entering the system. At dry conditions, AOIR and the dry permeometer show slightly different results: oxygen could, however, be used instead of air in AOIR

Figure 41. AOIR of a PET sample obtained from two different sampling method. The black squares (■) for discrete measurements and the solid line (—) for continuous measurements.
(with a different set-up), which would reduce the difference between them.

This introduces a difference in the permeability obtained by the different methods. A comparison of the humid permeometer and AOIR shows good agreement at 50 % relative humidity (RH), Figure 42: the deviations between the measurements are probably due to the detection limit of the sensors and their errors (see Section 7).

![Figure 42. Comparison of the results obtained by the humid permeometer and AOIR at 50 %RH, open rhombus (◊) measured with permeometer and cross (x) measured with AOIR.](image)

The choice of method affects the determination of permeability due to the different sensors used. However, steady-state permeability is often comparable independent of the method used. The differences between the methods are linked to the resolution of the sensors. Time-resolved permeability is more sensitive to the instrumental set-up and can provide structural information of the material. It is therefore important to gather adequate knowledge of the pros and cons of the different methods and their precision in detecting time-resolution permeability.
8.2 The influence of kaolin content

Kaolin, when used in barrier applications, is known to produce a tortuous pathway for diffusing molecules in a polymer matrix. In this study, the kaolin concentration was varied from 0 to 75 wt%, where 63 wt% is the CPVC (see Section 3.5.1). Above CPVC, the polymer cannot cover all the platelets and therefore introduces voids in the barrier coating, which becomes brittle as it dries. This results in the formation of cracks and, eventually, the loss in capacity to act as a barrier. It was noticed that the film that formed during drying was not as good as under CPVC, Figure 43.

*Figure 43. Barrier coatings with 5.8 wt% kaolin. Thickness: 11.1 ± 2.2 μm [141].*

Steady-state permeability is lowered by the addition of kaolin, Figure 44. Thinner samples do not show a decrease permeability with the addition of kaolin, however, because of the confined space and introduction of free volume.
Figure 44. OTR results for the samples, all coated on PET and dried at 60 °C. Open black square symbols (□) average thickness 5.3 μm and closed black square symbols (■) average thickness 1.8 μm.

The kaolin platelets orientate themselves in the coating to produce an angle of main axis relative to the plane of the coating (see Section 6.2.1 and Figure 28), which depends on the concentration of the kaolin, drying conditions and confined space [114]. The kaolin can also have different aspect ratios and this affects the decrease in permeability in different ways, Figure 45. The modelling of the permeability (see Section 10) shows the prediction of the different aspect ratios: aspect ratio 1 is spheres or cubes, and higher ratios represent flakes. Cleaned kaolin (see Section 5.2) has an aspect ratio of 9 whilst that of pre-treated kaolin is 16: both show that permeability is lowered with increasing concentration of kaolin. The deviation seen up to 1 volume% (v) depends on the pre-treatment of the kaolin: clean kaolin shows good agreement with the model. The pre-treated kaolin shows a deviation from the model, because pre-treatment affects its crystallinity [92].
Figure 45. The calculated effect on the oxygen permeation rate (lines) as a function of filler concentration ($\phi_c=0.2$). The black cross (x) are the experimental values for the pre-treated filler with $\alpha = 16$; the black open rhombus (◊) are the experimental values for the cleaned filler with $\alpha = 9$; the light gray solid line (—) is the Maxwell model; the black line (—) is the Minelli model with $\alpha = 16$ and the dashed black line (---) is the Minelli model with $\alpha = 9$ [92].

8.3 The influence of crystallinity

The nucleation of crystalline regions is affected by the drying conditions, confined space, additives used and interactions between polymers [30, 141]. A difference could be detected between PVOH dried on PET and PS by comparing the coated samples and the free standing films [114] and is due the interactions between PVOH-PET and PVOH-PS [135]. The PVOH polymer chains arrange themselves differently, depending on the possibility to bond with the other components. The order of the polymer chains of the PVOH in a kaolin-filled coating is affected not only by interactions with the kaolin but also whether or not a dispersant agent is used. The formation of crystalline regions is affected by the addition of dispersant agents and the concentration of the kaolin added, Figure 46. Kaolin, which often contains a dispersant
agent such as NaPAA [114], reduces crystallinity: kaolin without a dispersion agent shows higher crystallinity than kaolin with NaPAA. This is due to the interactions that occurs in the material and the chain conformation of the polymer (see Section 3.6.1). Clean kaolin acts as a nucleation agent with a maximum at 3 wt% for material with less than 50 %RH, whereas kaolin with NaPAA has a maximum at 5 wt%. Humidity lowers the degree of crystallinity, because the water molecules diffuse into the crystalline regions, weaken the hydrogen bonds and, eventually, dissolve the crystals [43, 93].

Figure 46. Difference in the crystallinity of kaolin without a dispersant agent and with NaPAA versus the concentration of kaolin at different humidities. Positive values show that kaolin without a dispersant agent has high crystallinity and vice versa.

The confined space and the drying conditions also affect how the PVOH can crystallize [141]. These are linked strongly: a less confined space and a constant drying temperature mean slower drying, resulting in higher crystallinity. The process parameters are connected to each other, e.g. the drying rate is linked to the confined space, drying temperature and moisture content.
8.4 The influence of hydrolysis degree

A lower degree of hydrolysis means that there are more acetate side groups: this disturbs the crystallinity of the polymer. The degree of hydrolysis also affects the free volume in the material, whereas the molecular weight does not, Table 5.

Table 5. Free volume size of the free volume in PVOH with various molecular weights and degree of hydrolysis.

<table>
<thead>
<tr>
<th>Mw</th>
<th>Hydrolysis / %</th>
<th>Free volume / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVOH 1</td>
<td>47000</td>
<td>98</td>
</tr>
<tr>
<td>PVOH 2</td>
<td>40000</td>
<td>74</td>
</tr>
<tr>
<td>PVOH 3</td>
<td>37000</td>
<td>88</td>
</tr>
<tr>
<td>PVOH 4</td>
<td>195000</td>
<td>98</td>
</tr>
<tr>
<td>PVOH 5</td>
<td>125000</td>
<td>98</td>
</tr>
</tbody>
</table>

The degree of hydrolysis of PVOH results in differences in permeability, Figure 47. The main difference is the diffusion coefficient, which is dependent on the degree of hydrolysis and is captured by the model. The difference in diffusion coefficient is due to the free volume size [108]: PVOH with a hydrolysis degree of 88% has a free volume size of 0.48 nm, while that with a hydrolysis degree of 98% has a free volume size of 0.42 nm. The diffusion coefficient of PVOH with a hydrolysis degree 88% is $3 \times 10^{-11}$ and for 98% it is $1 \times 10^{-11}$ [43]. The PVOH with the lower hydrolysis degree does not have the possibility of crystallizing as the PVOH with the higher degree: the side groups disturb the orientation of the polymer chains and affects the packing of the polymer chains.
Figure 47. The calculated oxygen permeation (line), as a function of crystallinity, $\phi_c$, and the experimental data (symbols). The solid line (—) and crosses (x) are PVOH with an 88% hydrolysis degree; the dashed line (--) and filled rhombus (♦) are PVOH with a 98% hydrolysis degree.

8.5 The influence of relative humidity

The fact that water plasticize PVOH is well known and it is therefore interesting to study the material under humid conditions. Kaolin introduces free volume into the material, since the permeability increases up to 50 %RH, Figure 48. The polymer chains become more flexible under humid conditions, which is visible as increased permeability. PVOH coatings exhibit good performance at low RH: at 80%RH, however, the barrier function is lost due to its sensitivity to water [39, 41, 109, 143]. Permeability is increased initially by the addition of kaolin, levelling out at higher concentrations: at 80 %RH no significant difference between the concentrations of kaolin can be detected.
8.6 The influence of renewable materials

Renewable materials, such as starch and hemicellulose, have a great potential of being used as barrier coatings [30]. Such renewable materials are often brittle: amylopectin, for example, becomes brittle due to its branched structure, Figure 22, preventing the molecule from forming hydrogen bonds [31]. A plasticizer may, however, be used to improve mechanical properties. Water can act as a plasticizer and can be crucial for the performance of a barrier. The moisture uptakes for starch and hemicellulose have been compared with that of PVOH, Figure 49. The figure shows that starch equilibrated rapidly at 66% compared to PVOH and hemicellulose. The water uptake for PVOH increased slowly and did not stabilize, while that for hemicellulose increased rapidly at the beginning and soon reached a stable content. At 66 %RH, the barrier function of the different materials is affected in different ways, depending on the polymer and its hydrophilic properties, Table 6.
At 85 %RH, PVOH is able to take up more water than starch and hemicellulose, even though, the latter is not in equilibrium. The water uptake for the various polymers depends on the interaction between water and the polymer: PVOH has more sites than starch and hemicellulose for hydrogen bonding with water, making it possible for PVOH to take up more water before the film breaks [125].

![Figure 49. Water uptake of PVOH, starch and hemicellulose at different levels of humidity (50, 66 and 85 %RH).](image)

Plasticizers such as sorbitol (as used in this study) lower the glass transition temperature [125]. Sorbitol is an internal plasticizer: it is co-polymerized into the structure and disturbs the order of the polymer chains so that they cannot be as close to each other as before [144]. The fact that glass transition temperature is lowered demonstrates that the plasticizers form interactions (probably hydrogen bonding), which is only present if no phase separation occurs [145, 146].

The permeability of the PVOH, starch and hemicellulose that were used, and their varying contents of sorbitol, are summarized in Table 6. The large variation in thickness is reflected in the permeability
results, so the permeance is therefore stated. The difference seen for the films made of hemicellulose and starch is a disagreement with the AOIR and OTR methods: this is linked to structural differences resulting from the same sample not being measured by the different instruments.

Table 6. Thickness and permeance of free-standing films of PVOH, starch and hemicellulose measured with OTR and AOIR.

<table>
<thead>
<tr>
<th></th>
<th>Thickness</th>
<th>$P_{\text{AOIR}}$</th>
<th>$P_{\text{OTR}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVOH</td>
<td>408 ± 73</td>
<td>1.3 ± 0.5</td>
<td>1.4 ± 0.6</td>
</tr>
<tr>
<td>PVOH + 10 wt% Sorbitol</td>
<td>319 ± 68</td>
<td>1.4 ± 0.4</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>PVOH + 20 wt% Sorbitol</td>
<td>152 ± 38</td>
<td>1.5 ± 0.2</td>
<td>2.2 ± 1.8</td>
</tr>
<tr>
<td>Starch</td>
<td>228 ± 75</td>
<td>1.6 ± 0.8</td>
<td>Out of range</td>
</tr>
<tr>
<td>Starch + 10 wt% Sorbitol</td>
<td>247 ± 31</td>
<td>1.5 ± 0.1</td>
<td>1.3 ± 0.6</td>
</tr>
<tr>
<td>Starch + 20 wt% Sorbitol</td>
<td>240 ± 67</td>
<td>4.0 ± 1.0</td>
<td>Out of range</td>
</tr>
<tr>
<td>Hemicellulose + 30 wt% Sorbitol</td>
<td>67 ± 27</td>
<td>1.6 ± 0.4</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Hemicellulose + 40 wt% Sorbitol</td>
<td>91 ± 28</td>
<td>2.0 ± 1.2</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>Hemicellulose + 50 wt% Sorbitol</td>
<td>74 ± 24</td>
<td>1.5 ± 0.2</td>
<td>3.0 ± 0.7</td>
</tr>
</tbody>
</table>
9 Results and Discussion – Environmental Life Cycle Analysis

The E-LCA performed in this thesis, comprises the production of the materials for the coating, their transport to Sweden (city of Karlstad) and application to the board. The production of the raw materials used for producing the coating material is, however, not included, as accurate data are not available to the authors at the time of this analysis. The end-of-life of the material is also analysed but the lifetime of the packaging is not included, because the focus here is to compare the various materials. Changing the barrier of packaging will affect its contents (i.e. food): this, in turn, will affect the environmental impact it causes, since a greater food loss would imply a higher environmental impact [147]. Different barriers have different uses, e.g. aluminium is an excellent barrier against light, gases, grease, moisture and other molecules [148] and cannot therefore be compared on the basis of environmental impact alone. The performance of the barrier in question needs to be included if the comparison is not to be misleading [8, 149].

E-LCA performed on aseptic liquid packaging coated with aluminium, shows that aluminium has the highest CO\textsubscript{2} impact even though it is lightest in weight. It would then be preferable to substitute the aluminium for a polymer with less CO\textsubscript{2} emission, such as polyamide [149]. However, the mixture of plastics also affects the environmental impact: the highest impact comes from the production of the material, e.g. when fossil fuels are used [150, 151]. Petrochemical polymers affect global warming more than biodegradable polymer due to end-of-life handling, which, although easier to handle not perform well in the contexts of acidification and eutrophication [152, 153]. Bioplastics have been shown previously to a have great potential in reducing not only the consumption of fossil fuels but also the emission of CO\textsubscript{2} [149].

Another possibility for reducing environmental impact is to recycle the materials [154], although the material is often not clean enough to be
reused in food packaging. The separation and recycling of aluminium used in packaging is difficult [149]. The plastics used as barriers are not easily recycled either, and are therefore often incinerated to simply recover energy. A combination of barrier materials is thus not advisable from a recycling perspective [150]. Nevertheless, multi-layered barrier films are often used to provide the barrier performance necessary to minimize food waste and prolong shelf-life [155].

Four different barrier materials are compared, with the end-application being packaging for frozen food, e.g. fish sticks [154]. The barriers are: EVOH mixed with 50 wt% kaolin (from USA and UK), latex mixed with 50 wt% kaolin (from USA and UK), starch and PE. It is assumed that all barriers are applied to identical paperboard, which is therefore excluded from the comparison. PE is applied by extrusion coating in an off-line operation, whereas the others are applied by on-line dispersion coating. The barrier solutions are compared by their contribution to global warming and their respective economics. The global warming effects (in kg-CO₂ equiv.) of the different barrier coatings with an end-of-life in the form of incineration or recycling can be seen in Figure 50. Starch is a biological polymer in origin and its incineration releases biogenic carbon dioxide (assuming complete combustion in the incinerator) [154]. Aerobic composting of starch may release some carbon to the air as biogenic carbon dioxide but since most of the carbon is added to the soil, its end-of-life handling is assumed to be carbon-neutral [154]. In comparison, starch affects global warming the least and latex + kaolin the most.

The different possible origins of kaolin imports to Karlstad, give a slight difference in the global warming potential, owing to different transportation distances to Sweden. The end-of-life scenarios result in greater differences: the recycling of polymers is preferable to incineration. It is assumed that recycling is possible in all cases.
The reference case in Figures 51 and 52 is polyethylene. The aggregated value is:

\[ Score = \frac{\text{Cost}_I}{\text{Cost}_{PE}} \cdot W_{\text{cost}} + \frac{\text{GHG}_I}{\text{GHG}_{PE}} \cdot W_{\text{GHG}} \]

where \( w \) is the weighting factor for cost and GHG. PE has thus the score of 1 for the entire range of weighting factors. A sensitivity analysis can be performed using data from the plots, Figures 51 and 52, which considers the ranking of the materials with different weighting factors: making a comparison of the different barrier solutions is thus simplified since only one number is presented. Both starch and EVOH + kaolin are more environment-friendly than PE, while latex is less so. The economic aspect shows that both EVOH + kaolin and latex + kaolin are more expensive than PE, which can act as a guide for companies when choosing between different alternatives.

Figure 50. Global warming effects of PE, EVOH + kaolin (USA and UK), latex + kaolin (USA and UK) and starch for two end-of-life scenarios. Black: recycling and grey: incineration.
Figure 51. Normalized global warming for incineration and cost versus PE for all barrier solutions.

Figure 52. Normalized global warming for incineration and cost versus PE for all barrier solutions.
A very costly product with a very small carbon footprint would have a higher weighting factor for the economic aspect, compared to a cheaper product with a larger carbon footprint. This would simply mean that producers with higher production costs are motivated to reduce the same, while producers whose products have higher carbon footprints, are driven towards truncating them. Producers should aim for both a low production cost and a low carbon footprint at the same time. The motivating factor here is sustainability using it as a means of competing and for promoting a new way of thinking.
10 Results and Discussion – The Model Developed

A combined model for permeability has been developed in order to capture the polymer’s crystallinity, filler tortuosity and humidity. The model is described briefly below: all equations are stated in Section 10.1 [92, 93].

A description of the solubility of various solutes in polymer systems can be obtained by using several modelling approaches [156]. The EoS model has proven to be an effective method for calculating the solubility of gases and vapours in amorphous polymers: these have a peculiar non-equilibrium behaviour that must be taken into account. This is done in the NET-GP model [69, 71], which has extended the EoS approach below $T_g$, and is used in this work in combination with the lattice fluid EoS model developed by Sanchez and Lacombe [70]. This combination gives rise to the NELF model [69], which represents the solubility of gases and vapours in amorphous glassy polymers.

The diffusional behaviour of the penetrating molecules also has to be analysed and described by an appropriate transport model. The thermodynamic model for diffusivity was chosen because it was convenient to use the same base as for solubility. The lattice fluid model is combined with a simple transport model to describe the diffusion of gas through the barrier layer: a method often used for various different polymer/penetrant systems [157-164].

At humid conditions, water is included in the thermodynamic description by treating the humid PVOH as a pseudo-component. The characteristic parameters of the pure and the pseudo-components are determined by Sanchez and Lacombe’s EoS. Water not only acts as a plasticizer, increasing the mobility of the polymer chains, but it also affects all of the regions, sometimes negatively at high moisture contents. This is accounted for by the Maxwell binary equation, which introduces regions where the polymer chains are more flexible and permeation is faster [165-167].
Semi-crystalline polymers contain crystalline regions that need to be added to the description. The crystalline regions are impermeable to penetrants such as gases, because there make the path tortuous for the penetrant. This has been described by the Maxwell tortuosity model, which has been proven to be useful in other cases [100].

Fillers that are platelet-like in shape enhance the performance of a barrier by presenting the penetrant with a tortuous pathway. The theory of tortuosity has been studied extensively by many research groups, Section 4.4. Two main parameters are relevant in such models: the volume fraction of the inclusions, $\phi$, and their aspect ratio, $\alpha$.

The combined model show good agreement with the experiments on the addition of kaolin with different aspect ratio, Figure 53 (see also Section 8.2). Cleaned kaolin (see Section 5.2) has an aspect ratio of 9 whereas pre-treated kaolin has 16: both show that permeability is lowered with increasing concentration of kaolin. The clean kaolin shows a good agreement with the model, so the deviation seen (of up to 1 v%) depends on the pre-treatment of the kaolin, which affects crystallinity [92]. This shows it is possible to combine different theories in to one model in order to predict the mass transport in filled polymeric material.
Figure 53. The effect on the oxygen permeation rate (lines) calculated as a function of the concentration of the filler ($\phi_c=0.2$). The black cross (x) are experimental values for the pre-treated filler ($\alpha=16$); the black open rhombus (◊) are experimental values for the cleaned filler ($\alpha=9$); the grey solid line (—)= Maxwell model; the black line (—)= Minelli model ($\alpha=16$); the dashed black line (- -)= Minelli model ($\alpha=9$).

Crystallinity is also captured by the combined model, Figure 54 (see also Section 8.4). The increase in crystallinity enhances the tortuous pathways for the penetrant and thereby lowers permeability. The model assumes that the distribution of crystallites is homogeneous throughout the barrier coating. This might not be the case for the experiments, however, which explains the deviation of the results obtained. Permeability also depends on the degree of hydrolysis, Figure 54: a higher degree reduces permeability since the diffusion coefficient differs. The model describes this very nicely.
The influence of humidity on filled polymeric layers also shows good agreement with the model, Figure 55. The discrepancies observed, especially at 20 %RH, can be due to a slight difference in crystallinity resulting from plasticization induced by the water molecules present in the experiments. The model showed lower permeability than the experiments at 20 %RH, which is probably linked to the underestimation of the solubility of water and the increased diffusivity induced by the water.
Figure 55. Parity plot of permeability determined experimentally vs by model, at different levels of humidity.

The combined model shows that the permeation of oxygen through a complex, filled, polymer layer at humid conditions can be predicted: it means that the combined model can be used to develop new materials for use in barrier coatings.

10.1 The model in equation form

All the equations used in the model are summarized in Tables 7 and 8, appearing in chronological order.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Definition/Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure component</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho_i^* p_i^* T_i^*$</td>
<td>Characteristic density,</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td>Equation</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>----------</td>
</tr>
<tr>
<td>$r_i^0$</td>
<td>Number of lattice sites occupied by a mole of pure component $i$</td>
<td>$r_i^0 = \frac{M_i}{\rho_i^* v_i^*}$</td>
</tr>
<tr>
<td>$v_i^*$</td>
<td>Volume occupied by a mole of lattice sites of pure substance</td>
<td>$v_i^* = \frac{RT_i^<em>}{p_i^</em>}$</td>
</tr>
<tr>
<td>$\omega_i$</td>
<td>Mass fraction of $i$ in the amorphous phase</td>
<td>$\omega_i = \frac{\omega_i^0 \rho_i^*}{\sum \omega_i \rho_i}$</td>
</tr>
<tr>
<td>$\phi_i$</td>
<td>Volume fraction</td>
<td>$\phi_i = \frac{\omega_i^0 \rho_i^*}{\sum \omega_i \rho_i}$</td>
</tr>
</tbody>
</table>

**Multi component**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho^*$</td>
<td>Characteristic density of the mixture</td>
<td>$\frac{1}{\rho^<em>} = \sum_i \frac{\omega_i \rho_i^</em>}{\rho_i}$</td>
</tr>
<tr>
<td>$p^*$</td>
<td>Characteristic pressure of the mixture</td>
<td>$p^* = \sum_i \phi_i p_i^* - \frac{1}{2} \sum_i \phi_i \sum_{j \neq i} \phi_j \Delta p_{ij}$</td>
</tr>
<tr>
<td>$\Delta p_{ij}$</td>
<td>Binary parameter</td>
<td>$\Delta p_{ij} = p_i^* + p_j^* - 2(1 - k_{ij}) \sqrt{p_i^* p_j^*}$</td>
</tr>
<tr>
<td>$\Psi_{ij}, k_{ij}$</td>
<td>Binary parameter</td>
<td>$\Psi_{ij} = 1 - k_{ij}$</td>
</tr>
<tr>
<td>$r$</td>
<td>Molar average number of lattice sites, $x_i$, occupied</td>
<td>$r = \sum \chi_i r_i$</td>
</tr>
</tbody>
</table>
Table 8. Equations used to calculate diffusion and permeability.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Definition/Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^*$</td>
<td>Characteristic temperature of the mixture</td>
<td>$T^* = \frac{p^<em>}{r} \sum_i x_i r_i \frac{T_i^</em>}{p_i^<em>} = \frac{p^</em> v^*}{r}$</td>
</tr>
<tr>
<td>$v^*$</td>
<td>Average close-packed per molar volume in the mixture</td>
<td>$v^* = \frac{RT^<em>}{\rho^</em>}$</td>
</tr>
<tr>
<td></td>
<td>Sanchez-Lacombe equilibrium EoS</td>
<td>$(\frac{\rho}{\rho^<em>})^2 + \frac{p}{p^</em>} + \frac{T}{RT} \left[ \ln \left( 1 - \frac{\rho}{\rho^<em>} \right) + \frac{\rho}{\rho^</em>} \left( 1 - \frac{1}{r} \right) \right] = 0$</td>
</tr>
<tr>
<td></td>
<td>Chemical potential of species i in the non-equilibrium glass (amorphous)</td>
<td>$\frac{\mu_{i}^{KE}}{RT} = \ln(\bar{\rho}\phi_i) - \ln(1-\bar{\rho}) \left[ \phi_i^0 + \frac{r_i^0 - r_i^<em>}{\bar{\rho}} \right] - r_i - \frac{\bar{\rho} p_i^</em>}{RT} \left[ p_i^* + \sum_{j=1}^{N_i+1} \phi_j (p_j^* - \Delta p_i^*) \right]$</td>
</tr>
<tr>
<td></td>
<td>Solubility (semi-crystalline) [157, 158]</td>
<td>$S_{S.C.} = S_{am.}(1 - \phi_C)$</td>
</tr>
</tbody>
</table>

by a molecule in the mixture

$D$  Diffusivity $D = L \frac{\partial \mu_i / RT}{\partial \ln \omega_i} \bigg|_{\omega_i \rightarrow 0}$

$L$  Mobility (amorphous) $L_{am.} = Ae^{-\frac{E_A}{RT}}$

Mobility (semi-crystalline) [157, 158] $L_{S.C.} = L_{am.}(1 - \phi_C)$
<table>
<thead>
<tr>
<th>( \tau )</th>
<th>Tortuosity [34, 95]</th>
</tr>
</thead>
</table>
| \( \tau = \begin{cases} \tau_\tau & \text{if } \tau_\tau \leq 1 \\
\frac{(\alpha \phi)^2 (1 + 1/\alpha)}{1 - \phi (1 + 1/\alpha)} + \frac{\alpha \phi}{\pi/4} \left( \frac{1 + \frac{1}{\alpha}}{2} \right) \end{cases} \) | \( \tau_\tau \geq 1 \) |

<table>
<thead>
<tr>
<th>( r_\tau )</th>
<th>Control parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_\tau = \frac{\alpha - \phi \alpha}{\phi \alpha^2} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha = \frac{S_n}{S_L} ) (in 3D)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( P_{\text{eff}} )</th>
<th>Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{\text{eff}} = (1 - \phi \epsilon)^2 L \frac{\omega_1}{p} \tau_{\text{ff}} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( P_{\text{eff, Maxwell}} )</th>
<th>binary Maxwell equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{p}{P_{\text{composite}}} = 1 + \frac{3 \mu_A}{\pi^2 n^2 - 1 - \phi} )</td>
<td></td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( b = \frac{P_{\text{water}}}{P_{\text{composite}}} )</td>
</tr>
</tbody>
</table>
11 Summary of Papers I-V

11.1 Paper I

Dispersion barrier coatings made from PVOH and kaolin blends were coated onto a polymeric support in order to determine their permeability. The barrier coatings were of different thicknesses and contained varying amount of kaolin. The oxygen permeability was measured using two different methods, namely OTR and AOIR, which showed good agreement. Structural information of the dispersion-barrier coatings was obtained by FTIR and SEM. It was revealed that the kaolin content influences both the orientation of the kaolin platelets and the degree of crystallinity of the PVOH. Increased contents of kaolin increased the alignment of the kaolin platelets to the basal plane of the coating, and thus increased the crystallinity of the PVOH. The thickness of the barrier proved to be less important in the early stage of the mass transport, while it had significant influence on the steady-state permeability. The results demonstrate that permeability is influenced by the structure (both chemical and physical).

11.2 Paper II

A more in depth analysis of the barrier coatings studied in Paper I was carried out, in order to obtain more structural information. The PVOH and kaolin blends were coated onto a polymeric support to determine the performance of the barrier. The same two methods were used as in Paper I, i.e. OTR and AOIR, to determine the oxygen permeability: this increased as the content of kaolin increased, up to about 5 wt%, where after it decreased. Above 5 wt% kaolin, the oxygen permeability decreased due to the increased effect of tortuosity. The orientation of the kaolin and crystallinity of the polymer were obtained from FTIR and SEM. The former was influenced by the drying temperature, thickness of the samples and the kaolin concentration; the latter increased with increased thickness of the sample. The thicker barriers
revealed the effect of drying temperature, while the thinner samples did not: the thicker samples, when combined with a kaolin content lower than 20 wt%, achieved a higher degree of crystallinity at lower drying temperatures.

11.3 Paper III

An extended model for the permeation of gas through a filled polymer layer was developed and applied to the permeability of oxygen through a PVOH/kaolin dispersion coating. The model is based on a description of the properties of polymers and penetrants in a thermodynamically consistent framework with the driving force for the diffusion of the penetrant gas being the chemical potential. The well-established NELF model for the polymer phase is extended to account for the additional features of the polymer-filled system, such as the concentration and aspect ratio of an inorganic filler, both of which enhance its tortuosity. The results obtained from the model of oxygen permeability through a dispersion coating layer consisting of PVOH and two types of kaolin with different aspect ratios are compared to data obtained experimentally. A good agreement is found in terms of the effect of crystallinity of the polymer, the concentration of the filler and its aspect ratio. The experimental results also indicate a complex interplay between the polymer and the filler: the permeability determined of two surface kaolin clays that were modified differently displayed slight deviations from the predictions made by the model.

11.4 Paper IV

This paper presents a study on the effect of moisture on PVOH and PVOH-kaolin dispersion barrier coatings. The permeability was measured at different levels of humidity and the material was characterized under the same conditions. The properties and microstructure of the material were also characterized by measuring
the polymer’s crystallinity at different levels of humidity and the concentration and orientation of the kaolin. The experimental results revealed that the water plasticized all the PVOH materials in a similar way regardless of the concentration kaolin. The crystallinity of PVOH was affected drastically by the humidity. The combined model presented in Paper III was developed further in order to capture the effect of moisture. The model showed good agreement with the experiments and on the overall permeability of the material.

11.5 Paper V

Barrier coatings are used primarily to extend the shelf-life of food by preserving its colour, odour, taste and quality, thereby reducing waste. Most publications hitherto have compared packaging and barrier coating materials on the basis of their environmental impacts alone. This paper presents a more holistic view by including economic aspects when four barrier coatings, namely starch, PE, EVOH+kaolin and latex+kaolin, were analysed. Two well-defined, end-of-life, handling scenarios were considered: recycling for PE, EVOH+kaolin and latex+kaolin or incineration, while starch is composted. Several environmental impacts can, of course, be analysed but only global warming is considered in this paper. Two approaches were used to combine the economic and environmental aspects: the first was normalization, weighting and aggregating and the second used a “carbon tax” to internalize the externality caused by emission of GHG. The weighting factors were obtained by carrying out a survey. When weighting factors (40.6% for environmental and 59.4% for economic) are used for both end-of-life scenarios, starch emerges as the most sustainable alternative, followed by PE. This case study, methodology and the results obtained will hopefully form a springboard for more detailed studies of this nature, under the umbrella of sustainability.
12 Conclusions

The following conclusions are drawn from the thesis project:

- **What method is used for measuring permeability is important because different set-ups can give different results:** it is therefore essential to have detailed knowledge of the method in question and its possible usage. The AOIR method provided results similar to those of OTR in the steady-state phase. The permeometer was also a possible method for detecting time-resolved permeability. However, due to the instrumental set-up, the dry permeometer has a better detection level than AOIR under dry conditions.

- **The interaction between the components, confined space, degree of hydrolization, additives to the coating dispersion and fillers,** all produced properties of the drying coating layer, such as packing of fillers and crystallinity of polymer, which were all demonstrated as having an effect on permeability. Structural information of the material must therefore be determined so that the permeability can be analysed.

- **A procedure for analysing the important properties of the material was produced.** Confined space, the addition of filler and the presence of moisture were shown to affect the crystallinity of PVOH: this was detected by the use of both FTIR and DSC, and showed comparable results. The addition of filler and its orientation is affected by the confinement of the space and the usage of dispersion agent due to the various interactions that occur within the material.

- **Renewable materials present great potential for use as oxygen barriers.** Both hemicellulose and starch had a lower uptake of water than PVOH, probably due the varying condition under which hydrogen bonding could occur. The mechanical properties and barrier performance under humid conditions of both hemicellulose and starch needs to be improved. The barrier coatings should be possible to convert without creating defects in the coating, which is possible if plasticizers are used. The
barrier should be able to use in various conditions, the moisture sensitiveness could be lowered by crosslinking the polymer.

- A model developed for permeability through a complex-filled polymeric material at humid condition was developed; agreement with the experimental data was found to be satisfactory. Knowledge pertaining to the material can be expressed and captured by modelling, with the added benefit that options are open for other materials, process development and, perhaps, eventual optimization. A combined model for permeability was developed successfully, showing that it is possible to include all the properties of a barrier. The fact that both solubility and diffusivity are calculated allows the model that was developed to contain a mathematical description of the influences had by the crystallinity of the polymer, the level of humidity, the addition of a filler and its aspect ratio on the permeability of the barrier coatings.

- E-LCA could be used to compare barrier coatings, although it is important that the boundaries of the E-LCA are known. Barrier coatings were compared, which can then act as an aid for companies not only in choosing the right material for the purpose at hand but also in forming a basis for development routes. This E-LCA study shows that it might be worthwhile putting effort into solving technical problems for these materials, so that they be deemed a more sustainable options.

Thus the thesis have analysed the structure-performance relations for barrier coatings. The developed model is possible to use for predicting permeation. The E-LCA model compare the competitiveness of sustainable solutions in a broader context than the usual E-LCA.
13 Future Perspectives

It is important that the packaging and transport aspects are fully understood. Barrier coatings need to be investigated further in terms of the interactions that happen between the different components: they not only occur between the components in the actual coating but also with the surroundings, such as air and water vapour. The characteristics of the material (e.g. the effect of additives on the polymer and its crystallinity) have been determined as playing an important role in the overall properties of the coating. The adsorption of the polymer onto the filler can vary due to the additives present on the filler’s surface (originating from production of the actual filler). This requires further investigation in order to determine if there is a less dense region around the particles.

Most packaging have a layered structure, which, in turn, introduces interfaces between the individual layers. The intersection between these materials becomes important: other researchers have found that the order of the layer plays an important role here. The indication is that these interfaces are of great importance and should therefore be studied further.

The model should be tested for more barrier coatings so that a general description is obtained. The combined model should also be tested for a variety of additives in order to improve knowledge of the behaviour of different fillers. The combined model can use any of the many different models for tortuosity that already.

Moreover, the model requires further expansion if it is to capture the interactions between the various components of coatings. In this study, hydrogen bonding was omitted, because it was possible. It was notice, however, that hydrogen bonding may have a great impact on the coating. The other interactions that take place in coatings should be included, along with the different layers of barrier coatings in the packaging to obtain a more complete depiction.
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Structure-Performance Relations of Oxygen Barriers for Food Packaging

Food packaging is required to secure the safety and quality of food, as well as minimize spoilage and simplify handling. Barrier coatings are generally used to meet the demands placed on fibre-based food packages, as these have the ability to regulate the amount of gases that can enter them. Some gases are detrimental to food quality: oxygen, for example, initiates lipid oxidation in fatty foods.

This thesis focuses on the mass transport of oxygen in order to gain deeper knowledge of, and thereby optimise, the performance of barrier coatings. This experimental study, together with computer modelling, characterized the structure of barrier materials with respect to the mass transport process. The performance of the barriers was evaluated based on the parameters of environmental impact and product costs. As the long-term aim is to use non-petroleum-based barrier coatings for packaging, these should be evaluated by assessing the properties of the material in question, its functionality and its environmental impact to provide more insight into which materials are desirable as well as to develop technology.

The results from this study indicate that several parameters (the orientation, concentration and aspect ratio of the clay and the polymer crystallinity) influence the properties of a barrier. Using this knowledge, researchers and food packaging engineers can work toward improving and customising renewable barriers.