Structural Studies and Modelling of Oxygen Transport in Barrier Materials for Food Packaging

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**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 work, evaluation and main part of writing the manuscript
Related work by the same author


## List of abbreviations and nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOIR</td>
<td>Ambient Oxygen Ingress Rate</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflection</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$c_i$</td>
<td>Initial concentration</td>
</tr>
<tr>
<td>$c_f$</td>
<td>Final concentration</td>
</tr>
<tr>
<td>CPVC</td>
<td>Critical Pigment Volume Concentration</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$D_{ff}$</td>
<td>Diffusion coefficient in the flake filled polymer matrix</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Diffusion coefficient in the polymer</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>EVOH</td>
<td>Ethylene vinyl alcohol</td>
</tr>
<tr>
<td>FIB</td>
<td>Focus Ion Beam</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>$F_x$</td>
<td>Flux in x direction</td>
</tr>
<tr>
<td>FV</td>
<td>Free Volume</td>
</tr>
<tr>
<td>$g(l)$</td>
<td>Probability distribution function of size l</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Heat of vaporization</td>
</tr>
<tr>
<td>$\bar{l}$</td>
<td>Average of flake size</td>
</tr>
<tr>
<td>$L_0$</td>
<td>Infinite dilution mobility coefficient</td>
</tr>
<tr>
<td>$l_i$</td>
<td>Size of flakes</td>
</tr>
<tr>
<td>$m_i$</td>
<td>Number of flakes</td>
</tr>
<tr>
<td>OTR</td>
<td>Oxygen Transmission Rate</td>
</tr>
<tr>
<td>$P$</td>
<td>Permeability</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>PVC</td>
<td>Pigment volume concentration (clay)</td>
</tr>
<tr>
<td>PVDC</td>
<td>Polyvinylidene chloride</td>
</tr>
<tr>
<td>$p_{atm}$</td>
<td>Atmospheric pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Hildebrand solubility parameter</td>
</tr>
<tr>
<td>$S$</td>
<td>Solubility</td>
</tr>
</tbody>
</table>
\( s \)  
Order parameter  

SEM  
Scanning electron microscopy  

\( T \)  
Temperature  

\( t_i \)  
Initial time  

\( t_f \)  
Final time  

\( t_l \)  
Lag time  

TGA  
Thermo Gravimetric Analysis  

TIP  
Thermodynamics Irreversible Process  

\( V \)  
Volume  

\( V_m \)  
Molar volume  

XRD  
X-Ray Diffraction  

\( \alpha \)  
Aspect ratio  

\( \alpha_c \)  
Degree of crystallinity  

\( \beta \)  
Plasticization factor  

\( \theta \)  
Angle from basal plane  

\( \kappa \)  
Orientation factor (Kaolin)  

\( \mu_i \)  
Chemical potential of species i  

\( \sigma \)  
Slit shape / Pore aspect ratio  

\( \tau \)  
Thickness of sample  

\( \phi \)  
Loading level in volume  

\( \phi_c \)  
Crystalline volume fraction  

\( \omega_j \)  
Mass fraction of species j
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1 Objectives

Food packages are provided with barrier coatings to prevent mass transport of gas, moisture, and liquid. The development of barrier coatings is driven both by practical experience and scientific advances. Moreover, many of the barrier coatings in commercial use are petroleum-based, which means that it would be beneficial to replace these with renewable coatings. Thus, there is plenty of motivation to focus research efforts in this area.

This work investigates how the structure of barrier coatings influences barrier performance. Computer modelling and experimental characterisation of well-controlled model barrier coatings allowed for the comparison of barrier materials. These models are intended to improve the understanding of the mass transport processes and allow for the prediction of how structural changes influence performance. In a longer perspective, this study provides knowledge that can be used to customize renewable barriers.
2 Background

2.1 Food packaging

Food needs to be packed in order to be transported and to maintain the quality all the way to the consumer. As much as 50% of produced food can perish on its way to the consumer (FAO, 2013). Regulations also stipulate that food packaging should deter tampering, further ensuring that food is not contaminated or spoiled. Thus, packaging material must provide adequate protection for all food quality aspects.

Today, food is stored in packages made of many materials, such as glass, metal, plastics, paper, and paperboards (Figure 1-3) (for a more detailed description, see sections 2.1.1 – 2.1.4). Furthermore, packaging material can be combined in order to achieve desired properties of the packages. The energy used to produce the different materials varies (Figure 3).

**Figure 1.** Global packaging by end use in 2012; total market size US$400b (EY, 2013).

**Figure 2.** Global packaging by type in 2012; total market size US$400b (EY, 2013).

**Figure 3.** Energy used in production of the different materials. TOE = ton of oil equivalent (NMBU).
2.1.1 Glass

Between about 3000 BC and 1200 BC, ceramics and leather were used to package food (Hagerman and Gabrielson, 2011) and since around 3000 BC glass has been used to pack food (Marsh and Bugusu, 2007). Glass is a good packaging material because it is rigid, provides good insulation, can be reused and recycled, and is almost impermeable to gases and vapours. However, because glass is heavy, it is expensive to transport and this transportation has environmental consequences. In addition, glass can break easily during transport as well as due to internal pressure, thermal shock, or other impacts (Marsh and Bugusu, 2007).

2.1.2 Metal

Packages made of metals can provide physical and chemical protection. Aluminium and steel are the most common metals used in food packages. Although these packages can be recycled, recycling affects the quality of aluminium as the recycle process increases white dross (Bruckard and Woodcock, 2009). Some of metal packages need to be treated before filling as some untreated metals can affect food. Although metal packaging offers some advantages, its environmental impact and production costs are drawbacks (Marsh and Bugusu, 2007).

2.1.3 Plastics

Plastics are polymeric materials that may require industrial additives such as plasticisers and slip additives. Polymers, such as the natural polymer cellulose, are long chain molecules made from monomers. Polyethylene (PE), a synthetic polymer and one of the most common plastics, is made from the monomer ethylene. Polymeric materials are used because they are flexible and they can be used at the processing site. In addition, polymeric packages are easy to print, heat sealable, lightweight, and inexpensive. However, packages made from
polymeric materials might be permeable to gases, vapours, and low molecular weight molecules (Barlow and Morgan, 2013, Marsh and Bugusu, 2007).

### 2.1.4 Paper and paper board

Paper is made from disintegrated cellulose fibres formed into sheets that are pressed and dried. Because paper is inexpensive, it is often used to make bags and wrap the short shelf life food. Flexible packaging was first used in China (200 BC) and in 19th century the flexible packages came to Europe. In beginning of 20th century the paperboard packages was developed (Hook and Heimlich, Jerkeman, 2000). Paperboard provides a better physical barrier than paper, it does not provide good chemical protection. Therefore, paperboard is usually combined with other materials such as aluminium foil and plastics.

Packaging is often composed of paperboard layered with barrier material. The paperboard provides the mechanical properties the packaging needs to function properly, but does not have the ability to stop mass transport from the surrounding environment into the packed food and vice versa. Therefore, different barrier materials are added to paperboard, resulting in a layered structure. Figure 4 illustrates a schematic structure of packaging material and Figure 5 shows an optical microscope view of a cross section of a paperboard.

![Figure 4](image1.png)

**Figure 4.** Schematic figure of the layer structure of barrier coatings on paperboard.

![Figure 5](image2.png)

**Figure 5.** Cross section of board with mineral coating on the top of the image and barrier coating in the bottom of the image. (Source: Stora Enso)
Food packages, made from either polyethylene (PE), renewable resources, or both (Figure 7), require barrier properties to ensure food safety and quality, and to minimize spoilage; furthermore, the package should also be easy to handle and transport (Figure 6). These properties are expected both by the business-to-business part of the value chain, where perhaps a greater performance focus lies on transport and protective performance, and by the end consumer, where perhaps the focus is on information and handling of the package. Nonetheless, both producers and consumers require packages that are easily opened, easily recycled, and leak proof. Barriers have the ability to regulate the transport of moisture, grease, and gas, which can destroy the product in different ways.

Oxygen is detrimental to the quality of packed food, especially if the food contains lipids (Lopez-Cervantes et al., 2003, Guynot et al., 2003). Lipid oxidation is one of the most common reasons for poor food quality (Huis in't Veld, 1996). Therefore, the mass transport of molecules needs to be hindered, which can be done by adding different polymeric barrier materials.

The technique for applying the barrier materials is either by extrusion of the polymer to the paperboard or by coating the paperboard with a dispersion (defined as water-borne coating) polymer solution mixed with particles) that contains polymer, fillers, and maybe a plasticizer. In extrusion coating, the polymer is melted in the extruder and coated directly or later laminated to the paperboard. The most common technique on the market today is extrusion-coated barriers, but this process needs to be done off-line, which can be rather inefficient. Because coating dispersions can be applied on-line, they have a lower environmental impact, increasing the value of the paperboard.

To provide the desired properties, barrier coatings for food packages consist of a water-borne polymer and additives. The polymer properties, such as degree of crystallinity, chain flexibility, and branching points, affect the final properties of the barrier coating. Moreover, since the polymer can interact with the additives, slightly different properties of the dried barrier can be obtained, compared to the polymer solution.
2.2 Common barrier materials

Paperboard can be combined with aluminium and polymers to make barrier materials. For products that have a long shelf life, an aluminium barrier is used because it is impermeable to most gases, vapours, molecules, and light. By combining paperboard with a thin aluminium film a lower environmental impact can be achieved compared to using solely aluminium as packaging material. The low weight but high stiffness of paperboard in combination with barrier properties of the aluminium film produces good barrier performance of packaging material.

Several polymers are used to make packaging: polyolefins, polyesters, polyvinyl chlorides, polyvinylidene chlorides, polyamides, and ethylene vinyl alcohols (Table 1) (Marsh and Bugusu, 2007). Polyethylene and polypropylene (PP) are the most common polyolefins used in food packages. These polymers are good barriers against moisture and other molecules. Polyethylene terephthalate (PET) is the most common polyester used for packing food. PET is used for carbonated liquids. Polyvinyl chloride (PVC) is a good barrier against grease/oil and is resistant to acids and bases. Polyvinylidene chloride (PVdC) is used as a general barrier against water vapour, gases, and grease/oil. Polyamide, such as
nylon, is used because it resists chemical corrosion and gas permeation. Ethylene vinyl alcohol (EVOH) is a good barrier against grease/oil and oxygen.

The barrier coatings can be combined in order to achieve the wanted properties. In addition, some of the polymers degrade when exposed to moisture although being good barriers to gases, so they need some protective coating against the moisture in the air.

Table 1. Gas permeability of nitrogen, oxygen, and carbon dioxide in different polymeric material (Finnigan, 2011)

<table>
<thead>
<tr>
<th>Material</th>
<th>Permeability / ml 20μm m² day⁻¹ atm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>0.6-0.8</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>1.1-4.1</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>20-41</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>51-71</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>31-51</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>51-800</td>
</tr>
<tr>
<td>Ethylene vinyl alcohol</td>
<td>0.002-0.2</td>
</tr>
<tr>
<td>Polyvinylidene chloride</td>
<td>0.002-0.03</td>
</tr>
</tbody>
</table>

2.3 Barrier performance

The permeation of gaseous molecules through a barrier coating can occur by diffusion and solubility processes as well as by flow through cracks and pinholes. In the dried state, the barrier material can have different structural phases that can influence the mass transport through the material. A crystalline phase will force gas molecules to take a more tortuous path compared to an amorphous phase.

The transport of mass can occur along different pathways: in the basal plane direction, in the normal plane direction of the barrier, or in both planes. Before transport through the barrier material, the molecules have to be adsorbed at the surface of the material, and some of these molecules are then absorbed. Finally, following the permeation, the molecules are desorbed into the package, where they can affect the packed food. As mentioned before, permeation during the
crystalline phase is different from permeation during amorphous phase and both fillers and additives affect permeation.

Describing the process physico-chemically, the permeation, $P$, is a combination of the diffusion, $D$, and the solubility, $S$ (see Equation 2.1):

\[ P = D \cdot S. \] (2.1)

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

Brownian motion describes the random diffusion of molecules in a barrier coating. Adolf Fick was first to describe the phenomenon of diffusion (1855), which he adopted from the mathematics of the heat transfer described by Jean-Baptiste Joseph Fourier (1822). The result was Fick’s First Law: the flow rate through a cross section of a matrix is proportional to a concentration gradient (Crank, 1979) (Equation 2.2):

\[ F_x = -D \frac{\partial C}{\partial x}. \] (2.2)

where $F_x$ is the flux in $x$ direction, $C$ the concentration, and $x$ the distance. From Fick’s First Law, the time dependent ($t$) concentration can be described with the flux, which is described in one dimension by Equation 2.3:

\[ \frac{\partial C}{\partial t} = - \frac{\partial F_x}{\partial x}. \] (2.3)

A constant diffusion coefficient results in Fick’s Second Law in one dimension, which is presented in Equation 2.4:

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right). \] (2.4)

If the diffusion coefficient is constant in the material and for a planar system, Equation 2.4 can be used (Crank, 1979):
where \( A \) is the boundary condition at \( x=0 \) and \( t=0 \), \( A = \int_{-\infty}^{0} Cdx \).

The steady-state phase is achieved when the permeant diffuse constant through the material (i.e., the time lag before this state) is achieved and can be determined using the linear relationship. The time lag can be calculated using Equation 2.6:

\[
t_t = \frac{\int_{0}^{1} \int_{0}^{1} C_s(x)dzdx}{\int_{0}^{1} D(u)du}.
\]  

(2.6)

Permeability is defined by diffusion and solubility parameters (Equation 2.1). The solubility of small molecules depends on the interactions between the molecule and the polymer: the larger difference in solubility parameters of the molecule and the polymer, the less solubility. That is, they are less compatible (Hedenqvist, 2002). The permeant can interact with the material, affecting solubility. This process can defined by the Hildebrand solubility parameter, \( \partial \), and calculated using Equation 2.7:

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

(2.7)

where \( c, \Delta H, R, T, \) and \( V_m \) are the cohesive energy density, heat of vaporization, universal gas constant, temperature, and the molar volume, respectively. The Hansen solubility parameter (Hansen, 1967) is an expansion of Hildebrand solubility parameter. The cohesive energy is divided into three parts that correspond to the dispersion, polar-polar, and hydrogen bonding forces. The solubility also depends on the voids found in the otherwise solid material, free volume, crystallite size, and degree of crystallinity.

2.4 Composites

A composite is a material that consists of two or multiple components, where the smaller part is the filler material and the larger part is the matrix material. The aerospace, car, and computer industries use composites made from plastic
polymeric material filled with particles (e.g., clay, cellulose, and glass fibres). The polymer and the particles must be compatible to minimize phase separation, since this can result in higher mass transport through the material. In this thesis, the composite under study consists of a polymer matrix with impermeable particles such as clay and nano fibrillated cellulose (NFC) fibres.

The free volume of a polymeric material (i.e., voids) is linked to mass transport (Crank, 1979): the more flexible the chains, the greater the free volume, thereby increasing the mass transport of molecules. Voids are affected by the degree of crystallinity of the barrier. Free volume is not the same as the occupied and unoccupied state of the polymer.

2.4.1 Pigment volume and the critical volume concentration

Mineral pigments, typical fillers, often are used to improve surface and optical properties. The pigment volume concentration (PVC) in the polymer matrix affects the mechanical properties of the material. The polymers need to sufficiently cover the pigments to be embedded. If the material is filled with so much pigment that the pigment cannot be totally covered with the polymer, the critical pigment volume concentration (CPVC) has been exceeded. Above the CPVC, voids will be introduced in the matrix, negatively affecting packing (Andersson, 2008). The CPVC is affected by other parameters as well, such as optimal lattice packing, type of polymer and additives, and the state of dispersion or agglomeration (i.e., how much the pigments interact) (Asbeck and Loo, 1949).

2.4.2 Tortuosity

Polymer filled with impermeable particles will force the gas molecules to take a tortuous pathway (Equation 2.8) (Nielsen, 1967) (Figure 8):

\[
\frac{D_0}{D_{eff}} = \frac{1 + \frac{\alpha_2 \phi}{2}}{1 - \phi}
\]

(2.8)
where $\alpha$ is the aspect ratio and $\phi$ is the loading level.

The aspect ratio, defined as $d/h$ (Figure 8), and the concentration of the particles contribute to the shape of this pathway. Particles with high aspect ratio will result in a longer path compared to particles with smaller aspect ratio at the same volume fraction. The orientation of the particles is also significant, since the particles that are oriented in the basal plane of the barrier will increase tortuosity (Lape et al., 2004, Lape et al., 2002, Minelli et al., 2011). Openness of the structure depends on the slit shape, which is defined as the distance between the platelets (Figure 8).

![Figure 8. Tortuosity factor from impermeable platelets (grey) in a polymer matrix (black). The * indicates a more open structure while the x indicates a more closed structure.](image)

### 2.4.3 Polymer-filler interface

The polymer matrix is affected by the fillers, the molecular mobility, the free volume, the crystallinity, and the diffusion coefficient, which depends on the interactions with the fillers in the dried state. In the wet state, the polymer binds water, which affects the mobility of the chains. The interactions in the polymer matrix (Turi, 1981) depend on a number of factors:
1. Adsorption and wetting. To achieve complete adsorption and wetting, the surface energy of the fillers needs to exceed surface energy of the matrix.

2. Inter diffusion. The interaction between filler and polymer matrix is enhanced by diffusion of molecules from one to the other.

3. Electrostatic charge. The interfacial bonding is increased by electrostatic differences between the filler and the polymer.

4. Chemical bonding. Covalent bonds between polymer and filler promote the interfacial interaction (Table 2).

5. Mechanical adhesion. Mechanical interlocking can enhance the matrix interconnection (Table 2).

Table 2. Forces of bonding and peel energy of topography on copper surface (Kinloch, 1987, Arrowsmith, 1970)

<table>
<thead>
<tr>
<th>Type</th>
<th>Bond energy / kJmol(^{-1})</th>
<th>Peel energy / kJm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic bond</td>
<td>600-1100</td>
<td></td>
</tr>
<tr>
<td>Covalent bond</td>
<td>60-700</td>
<td></td>
</tr>
<tr>
<td>Metallic bond</td>
<td>110-350</td>
<td></td>
</tr>
<tr>
<td>Hydrogen bond</td>
<td>10-40</td>
<td></td>
</tr>
<tr>
<td>Permanent dipole-dipole interactions</td>
<td>4-20</td>
<td></td>
</tr>
<tr>
<td>Dipole-induced dipole interactions</td>
<td>&lt;2</td>
<td></td>
</tr>
<tr>
<td>Dispersions (London) forces</td>
<td>0.08-40</td>
<td></td>
</tr>
<tr>
<td>Flat topography</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>Flat topography + 0.3 µm dendrites</td>
<td></td>
<td>0.67</td>
</tr>
<tr>
<td>Flat topography + 0.3 µm dendrites + oxidation</td>
<td></td>
<td>0.77</td>
</tr>
<tr>
<td>3 µm tall pointy pyramids</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>2 µm tall blunt pyramids + 0.3 µm dendrites</td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>2 µm tall blunt pyramids + 0.3 µm dendrites + oxidation</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>3 µm tall pointy pyramids + 0.3 µm dendrites + oxidation</td>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>Nickel foil with club shaped protruding structures</td>
<td></td>
<td>2.3</td>
</tr>
</tbody>
</table>

The interaction between the fillers and the matrix is favourable when the polymer covers the surface of the particles; furthermore, this condition reduces polymer mobility. If the particles are not well embedded in the matrix, there
will be a void around the particles, and this unoccupied volume leads to an increase in the free volume (Paul and Robeson, 2008). Semi-crystalline materials follow the same theory as the composite materials, since the crystalline regions can be considered as impermeable fillers (Solovyov and Goldman, 2008).

### 2.5 Polymers

Today, most research focuses on the polymer in order to replace the petroleum-based polymer with bio-based polymers. An overview of bio-based polymers can be seen in Figure 9. Some of the polymers used for barriers (see Chapter 2.2) are being produced from renewable resources, such as cellulose and polysaccharides, others can be biodegradable and renewable, such as polylactate and PHA.

![Figure 9. Overview of bio-based polymers (Johansson et al., 2012).](image)

A polymer is built from many repeating units that build chains and the length of the chain determines a polymer's molecular weight. The polymer's physical properties, such as density, and barrier properties are affected by the length of the polymer chain up to a certain polymer chain length. A polymer can have different repeating units and thus build what is known as a co-polymer and block co-polymer chains, which can be used to produce a barrier layer. The morphology, such as crystallinity, is affected by the arrangement of the polymer (i.e., how polymers are arranged with respect to each other). Different polymer arrangements have different mechanical properties and chemical properties. Glass transition of the polymer affects the stiffness of the chain and the
formation of crystalline phases. Mechanical properties are important in the manufacturing process and in the handling of packages. Chemical properties affect the interaction of the polymer chains, which can affect the mechanical properties of the polymeric material.

2.6 Additives and fillers

Cracks and pinholes can be adjusted by adding additives to make the barrier more flexible and to improve its ability to be transported. Additives have different purposes, such as processability and decreased cost. Plasticization of the polymer is used to minimize mechanical failure. Enzymes and other additives produce scavenging capacity of detrimental (to the package material itself or the packed goods) compounds. Fillers, such as clays, are added to increase the pathway in the polymer matrix.
3 Modelling

3.1 Background

Petroleum-based barriers have been used for a long time; however, the packaging and food industries want to replace petroleum-based barriers with bio-based barriers, a transition that will require more research. Researchers can use modelling to examine how different bio-based barriers perform under various conditions.

Today, the fibre-based food package industries are looking for ways to decrease the use of aluminium foil and petroleum-based polymers and to increase the share of the fibre-based packages in the food industry. Therefore, it is important to gather more knowledge about fibre-based barriers in order to understand what properties are needed for bio-based polymers. Modelling can be used to predict the barrier performance of new combinations of bio-based polymers. Chapter 3.2 provides an overview of the theories that ground the modelling of mass transport.

3.2 Theories for modelling of mass transport

Models describing (mathematically) mass transport of gaseous molecules can be divided into models for sorption, diffusion, and trans-membrane mass transfer (Lipnizki and Trädgårdh, 2001) (Table 3). Empirical models are developed from experiments and are based on interpolation of the experimental data. Semi-empirical models combine theories with the experimental data. The theoretical model uses physical and chemical theories.
3.2.1 Models for sorption

The Langmuir adsorption isotherm model and Henry’s Law can be used to develop an empirical model for sorption. Such a model can also be used to describe the different polymer states and describe a single permeant. Many researchers have studied the sorption for different systems (Schmittecker, 1987, Stephan, 1993, Meckl, 1994, Enneking, 1995, Staudt-Bickel, 1995, Hladik, 1995). Henry’s law is used for rubbery polymers and Langmuir isotherm model is used for crystalline polymers (Prausnitz et al., 1986). Therefore, both models can be used to compare permeability of polymer matrix in order to develop the
polymer matrix properties to achieve the wanted performance. However, this is not always sufficient and a combination with other theories is often needed for a complete description (Lipnizki and Trädgårdh, 2001).

Semi-empirical models include 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 are not able to capture the whole permeation process since each theory incompletely describes the polymer state and the permeant components.

The solubility parameter model describes the energy for separating molecules in order to overcome the intramolecular forces (Nijhuis et al., 1993). Flory-Huggins model predicts the concentration profile and the sorption selectivity (Mulder, 1984, Nijhuis, 1990, Mulder, 1991). UNIQUAC is used to predict phase equilibrium, and it has been extended to be combined with hydrogen bonding and free volume (Abrams and Prausnitz, 1975). ASOG-FV is an alternative method that is directly related to UNIQUAC, UNIFAC, and Flory-Huggins theory (Wilson and Deal, 1962). The entropic-FV is also an alternative method that is similar to UNIQUAC and UNIFAC, however, the free volume is not added (Elbro et al., 1990, Kontogeorgis et al., 1993). The modified NRTL calculates the phase equilibria and in certain cases the theory ends up being part of the Flory-Huggins theory (Wu et al., 1996). ENSIC describes the sorption as a mechanical anisotropic process (Favre et al., 1993).

The theoretical models are UNIFAC and molecular simulation. UNIFAC is used for a system without experimental data and the model can predict the phase equilibria (Fredenslund et al., 1975). This model has been extended to include free volume theory and to capture the different phases of the polymer (i.e., crystalline, semi-crystalline, or rubbery polymer) and cross-linked polymers. The molecular simulations for sorption are solved using the chemical potential (Tamai et al., 1995, Fritz and Hofmann, 1997, Fritz and Hofmann, 1998).
3.2.2 Models for diffusion

The empirical diffusion coefficient needs a diffusion coefficient at infinite dilution as a reference value and uses approximations for the calculations (Böddeker, 1986, Mulder and Smolders, 1984). This model is suitable for process and material design.

Free volume, dual sorption, and molecular simulation of diffusion are theoretical models for diffusion. The free volume theory describes the mass transfer based on molecule movements; this means that the model is a physical description of the diffusion (Fujita, 1961). This theory has been modified to capture diffusion in semi-crystalline and rubbery polymers as well as cross-linked polymers. Dual sorption theory is similar to free volume theory; the model describes the diffusion based on free spaces, micro-voids, in the structure (Vieth et al., 1976, Vieth and Sladek, 1965). Molecular simulations describe the permeating component in the polymer matrix using chemical potentials (Meares, 1988, Hofmann et al., 1997, Howell, 1993).

All the empirical, semi-empirical and theoretical models can be used to analyse and predict diffusion; however, the models are specified for a certain type of system and not for general application, indicating that more research is needed.

3.2.3 Models for mass transfer

Empirical models do not use physical-chemical relations although they assume permeate concentrations independent of temperature. The effect of temperature on permeability can be described by the Arrhenius equation, where one side of the equation describes the free permeate flow under constant pressure (Franke, 1990).

Semi-empirical models for mass transfer include Solubility-Diffusion, semi-empirical model after Meyer-Blumenroth, Q-model, Process-specific permeability functions, thermodynamic of Irreversible process (TIP), and Pore-flow model.
The Solubility-diffusion model is divided into three steps: absorption of permeate, diffusion through the rubbery polymer system based on the gradient in chemical potential, and desorption of permeate (Graham, 1866). The semi-empirical model after Meyer-Blumenroth extends the solubility-diffusion model by coupling fluxes, applies to pressure rather than concentration, and relates to driving forces associated with chemical potential (Meyer-Blumenroth, 1989, Rautenbach et al., 1991). Q-model is also based on the coupling of fluxes to describe the permeability and difference in chemical potential (Klatt, 1993). Process-specific permeability functions use coupling in the solubility-diffusion model by dividing the permeability into permeability functions (Vier, 1995). The TIP model describes the coupled diffusion and coupled fluxes (Kedem, 1989). Mainly for use with porous materials, the Pore-flow model describes straight cylinders in the polymer distributed through the layer (Okada and Matsuura, 1988, Okada and Matsuura, 1991).

The Maxwell-Stefan theory and pseudophase-change solubility-diffusion models are theoretical models. The Maxwell-Stefan theory is based on irreversible thermodynamic processes by the driving force, gradient of the chemical potential, and interaction forces, described by friction forces (Stephan, 1993). The pseudophase-change solubility diffusion model assumes that the permeation can be described by solubility-diffusion theory, the system is in thermodynamic equilibrium, any phase changes of permeate occur in the layer, the pressure is adjacent applied pressure, and the process is isothermal (Shieh and Huang, 1998a, Shieh and Huang, 1998b).

The non-equilibrium lattice fluids (NELF) model can be used to model the mass transport through the polymer matrix (Doghieri and Sarti, 1996) and is based on the chemical potential combined with mixing theories.

### 3.2.4 Theories for tortuosity

If polymer matrix includes impermeable particles such as clay, the theory needs to be extended since the oxygen is forced to take a tortuous pathway through the system (Figure 8). The tortuous path has been explained by different research groups. The oldest theory for the pathway is a theory proposed by Nielsen (1967):
\[ \frac{D_0}{D_{ff}} = \frac{1+\frac{\alpha \phi}{2}}{1-\phi}, \]  
\( (3.1) \)

where \( \alpha \) is the aspect ratio and \( \phi \) is the loading level. The theory was expanded because the platelets could orient as a two-dimensional periodic array (Aris, 1986):

\[ \frac{D_0}{D_{ff}} = 1 + \frac{\alpha^2 \phi^2}{4(1-\phi)} + \frac{\alpha \phi}{2\sigma} + \frac{2\alpha \phi}{\pi(1-\phi)} \ln \left[ \frac{\pi \alpha^2 \phi}{4\sigma(1-\phi)} \right], \]  
\( (3.2) \)

where \( \sigma \) is the pore aspect ratio. This expansion of the Nielsen model gave a slightly different model compared to Equation 3.2 (Wakeham and Mason, 1979):

\[ \frac{D_0}{D_{ff}} = 1 + \frac{\alpha^2 \phi^2}{4(1-\phi)} + \frac{\alpha \phi}{2\sigma} + 2(1-\phi) \ln \left[ \frac{1}{\sigma \phi} \right] \]  
\( (3.3) \)

Equation 3.2 was extended for a polymer matrix with many layers of flakes (Cussler et al., 1988):

\[ \frac{D_0}{D_{ff}} = 1 + \frac{\alpha^2 \phi^2}{4(1-\phi)} + \frac{\alpha \phi}{2\sigma} \]  
\( (3.4) \)

The difference between Equation 3.2 and Equation 3.3 is because the fourth term on right hand side in Equation 3.4 can be neglected (Cussler et al., 1988). Another research group demonstrated that the third term could also be excluded when \( 1/\sigma \ll \alpha \phi \) (Falla et al., 1996). The flake distribution in the layer is important; if the flakes are uniform and randomly placed, the model changes (Cussler et al., 1988):

\[ \frac{D_0}{D_{ff}} = 1 + \frac{\alpha^2 \phi^2}{\beta(1-\phi)}, \]  
\( (3.5) \)

where \( \beta \) is the geometric factor. The randomly placed flakes and mono-disperse flakes can be accounted for (Lape et al., 2004):

\[ \frac{D_0}{D_{ff}} = \frac{(1+1/3\alpha \phi)^2}{1-\phi}. \]  
\( (3.6) \)
The model was expanded to include all terms in order to capture the effect of the tortuous pathway (Minelli et al., 2009):

\[
\frac{D_0}{D_{ff}} = \begin{cases} 
1 & r \leq 1 \\
\frac{\alpha \phi (1 + \frac{\sigma}{\alpha})^2 + \frac{(\alpha \phi)^2 (1 + \sigma / \alpha)^4}{1 - \phi (1 + \sigma / \alpha)} + \frac{\alpha \phi}{\pi/4} \left(1 + \frac{\sigma}{\alpha}\right)^2 \ln \left(\frac{1 - \phi (1 + \sigma / \alpha)}{(\pi/2) \sigma \phi (1 + \sigma / \alpha)}\right)}{r} & r \geq 1 + \frac{\alpha \phi}{\sigma} + \frac{\alpha \phi}{\pi/4} \left(1 + \frac{\sigma}{\alpha}\right)^2 \ln \left(\frac{\sigma (1 + \sigma / \alpha)}{\sigma (\pi/2)}\right) 
\end{cases}.
\]

(3.7)

where \(\sigma\) is the openness of the structure and \(r = \frac{\alpha - \phi (\alpha + \sigma)}{\phi (\alpha + \sigma)^2}\).

For poly-disperse flakes with discrete size distribution (Lape et al., 2004), this equation is used:

\[
\frac{D_0}{D_{ff}} = \frac{1}{1 - \phi_{tot}} \left(1 + \frac{\phi_{tot} \sum_i m_i l_i^2}{3 \sum_i m_i l_i}\right)^2,
\]

(3.8)

where \(m_i\) and \(l_i\) is the number and the size of the flakes in the \(i\)th class. For systems having continuous size distributions, the expression is as follows (Lape et al., 2004):

\[
\frac{D_0}{D_{ff}} = \frac{1}{1 - \phi_{tot}} \left(1 + \frac{\phi_{tot} \int_0^l l^2 g(l) dl}{3 \int_0^l l g(l) dl}\right)^2,
\]

(3.9)

where \(g(l)\) is the probability distribution function of sizes and \(\bar{l}\) is the average flake size.

The orientation of the flakes is another factor that can be included and the theories are either exponential functions (Lusti et al., 2004) or order parameters (Bharadwaj, 2001). Molecular simulations for flake filled systems have been further developed (Eitzman et al., 1996, Swannack et al., 2005).
4 Materials and methods

In this section, the experimental materials and methods used in the studies comprising this thesis are described. In addition, some of the underlying theories for the materials' constitution and measurement and analysis principles are discussed. Some measurement and analysis methods have also been developed further within the frame of the thesis project.

4.1 Materials

4.1.1 Polyvinyl alcohol

Polyvinyl alcohol (PVA) is a hydrophilic polymer with excellent film forming and adhesive properties as well as a high tensile strength. PVA is often used as a barrier material due to low diffusion of gases and aromas through the material. PVA is produced by polymerizing vinyl acetate and the polyvinyl acetate (PVAc) is then hydrolysed to PVA. PVA exists as different hydrolyse grades that are characterized by the amount of acetate groups that are left after the conversion:

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

Its structure consists of a saturated hydrocarbon backbone with hydroxyl groups as side chains (Figure 10). The chains are rather flexible but straight, which influences the crystallisation process. The side chains contribute to water solubility, which is important for water-borne dispersion barriers. In addition, the diffusion process is affected by the orientation and the size of the crystalline regions. The crystalline regions have a similar effect on the mass transport as impermeable particles such as clay force the oxygen molecules to take a torturous pathway (Solovyov and Goldman, 2008). Molecular simulation of the oxygen diffusion in PVA has shown that oxygen displacement preferentially occurs along the backbone (Karlsson et al., 2004). The crystalline regions can capture oxygen molecules for a short time and thereby introduce a lag time (i.e., the delay time can be prolonged). The lag time for oxygen is related to the free
volume in and the chain movements of the polymeric material (Takeuchi, 1990). Tightly packed chains with local high alignment, such as crystalline regions, will reduce the diffusion of oxygen even if the free volume remains the same (Takeuchi et al., 1990).

In this research, a polymer grade from Kuraray (Frankfurt, Germany) was chosen, Mowiol 15-99. This polymer grade was chosen because it is widely accepted as being suitable for use with food (e.g., it is FDA approved). The chosen polymer grade has a hydrolyzation degree of 99% and a viscosity of 15 Pas in water at a 4% concentration.

![Figure 10. Three-dimensional molecular structure of Poly(vinyl alcohol); hydrogen is white, oxygen is red, and carbon is black.](image)

### 4.1.2 Kaolin

Kaolin (Al₂Si₂O₅(OH)₄) is a 1:1 layered clay, which means that one layer is tetrahedral and the next layer is octahedral and is non-expandable in water (Figure 11). The cohesive energy between one of the layers and the oxygen atoms of the adjacent layer is mainly electrostatic with increased van der Waals interaction and hydrogen bonding between hydroxyl groups. Kaolin has a low cation exchange capacity, usually between 1-10 meq per 100g (Van Olphen, 1977). The density of kaolin is 2.63 g cm⁻³ (Grim, 1968). Kaolin is the most common type of clay used in barrier materials since the aspect ratio is high and the platelets orient almost in the basal plane without high applied forces. This clay was chosen due to its rather thin and long platelets (high aspect ratio) and the possibility to be detected in SEM.
4.1.3 Preparation of dispersion

PVA was dissolved in ionized water at 95°C under gentle stirring for 1.5 hours. The polymer solution was cooled to room temperature before film preparation. The concentration of the final PVA solution was measured before mixing with kaolin. The kaolin was dispersed in ionized water during stirring to a concentration of 60 wt% and afterwards diluted to the needed concentrations. The PVA solution and kaolin dispersion were both adjusted to pH around 7 by adding NaOH before mixing the two components together. The PVA solution and the kaolin dispersion were mixed in 1:1 ratio with respect to wet weight (Figure 12).
4.2 Barrier coatings

The dispersions were coated onto polyethylene terephthalate (PET) sheets by a bench coater (K202 Control Coater, RK Print Coat Instruments Ltd., Royston, UK) using a wire-wound cylindrical rod and subsequently dried at a certain temperature (Figure 13). The coatings were dried until a 5% moisture content was achieved; the water content was measured with a moisture sensor (FIBRO MCA 1410, FIBRO System AB, Hägersten, Sweden). The temperature of the barriers was measured with an IR temperature sensor (Thermopoint TPT 62, FLIR system AB, Danderyd, Sweden). The thickness of the dry coatings was measured with a mechanical thickness profilometer (STFI thickness profile meter, TJT-Teknik AB, Järfälla, Sweden).

Figure 13. A SEM image of the coating. The dashed line indicates where the dispersion is and image above the dashed line is the PET film.

4.3 Characterization of kaolin

The kaolin 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°. The organic compounds in the kaolin were analysed using thermogravimetric analysis (TGA) (TGA/SDTA851e, Mettler-Toledo, Schwerzenbach, Switzerland). The particle size of dispersed kaolin was analysed using the sedimentation method (LUMiSizer, LUM GmbH, Berlin, Germany) according to ISO 13318-2. The particle size of dispersed kaolin was also measured using the laser diffraction technique (Mastersizer 3000, Malvern Instrument Nordic AB, Uppsala Sweden) according to ISO 13320. Figure 14 is an SEM image of the kaolin.

![SEM image of the kaolin](image)

Figure 14. SEM image of the kaolin.

### 4.4 Oxygen transmission rate

The oxygen transmission rate (OTR) was measured according to ASTM D3985 with OxTran 2/21 (MOCON, Minneapolis, US) (Figure 15). Two chambers were separated by the barrier material to be tested (Figure 16). The sample was flushed with nitrogen. One side contained the test gas, in our case oxygen, which is absorbed by the sample. Oxygen is transported through the sample and desorbed on the other side; the chamber contains the carrier gas, nitrogen, which transports the oxygen to the sensor. This method determined the steady state permeability. The steady state permeability represents the equilibrium of the mass transport through the barrier coating.
4.5 Ambient oxygen transmission rate

The permeability can also be measured with another method: ambient oxygen transmission rate (AOIR) using the instrument PermMate (Systech, Illinois, US). This method is quite flexible; the samples can be mounted in a cell or between two cells. The method can also directly measure permeability of packages, which are filled to their headspace. A needle is placed into the cell or package to extract some gas and this sample is transported to the sensor. This extracted gas can be inserted into the package again. Otherwise, nitrogen can be inserted (Figure 17). This method gives information about the mass transport in the initial as well as the steady-state phase, since the time resolution provided by the extraction procedure and oxygen sensor is much faster (around 5 s) than that of the MOCON equipment.
AOIR can also be used to calculate the OTR (Larsen et al., 2000, Nyflött et al., 2014a). The measurement of the increase in oxygen concentration can be used to calculate permeability $P$:

$$P = \frac{V \cdot (c_f - c_i) \cdot \tau}{p_{atm} \cdot (t_f - t_i)},$$  \hspace{1cm} (4.1)

where $V$ is the volume of the sample cell, $\tau$ is the thickness of the sample, $c_i$ and $c_f$ are initial and final concentrations, respectively, $p_{atm}$ is the atmospheric pressure, and $t_i$ and $t_f$ are the initial and final time, respectively.

With the AOIR method, the lag time, $t_l$, can be extracted from the data due to the low concentration in the beginning (Figure 18). The lag time can be used to calculate the diffusion coefficient, $D$, of the studied barrier material:

$$D = \frac{\tau^2}{6t_l},$$  \hspace{1cm} (4.2)

The solubility, $S$, of the barrier material can be calculated with the permeability and the diffusion, according to Henry’s Law (Equation 4.3):

$$S = \frac{P}{D}.$$  \hspace{1cm} (4.3)
Figure 18. Example of AOIR experimental results from this study displayed as concentration versus time. The extraction of lag time and data for the permeability calculation (Equation 4.1-4.2) are shown.

4.6 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is vibration spectroscopy that identifies molecules by vibration frequencies of specific chemical bonds (Figure 19). FTIR can also be used to identify phases, crystallinity of the polymer, and the orientation of the kaolin.

Spectra were collected with a Thermo Nicolet FTIR Nicolet iS10 (Madison, US) (Figure 20). Spectra are often depicted with absorbance (or transmittance) as a function of wavenumber [cm⁻¹] (inversely proportional to frequency) due to the use of Michelson-Morely interferometer 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.
4.6.1 Degree of crystallinity

The ratio of the crystalline to amorphous regions of the PVA can be calculated from the FTIR peaks (Figure 21). Both the crystalline and amorphous regions in the PVA can be studied by the C-O stretch vibrations in the 1090-1150 cm\(^{-1}\) region (Peppas, 1977, Tretinnikov and Zagorskaya, 2012, Kozlov et al., 2003). The degree of crystallinity, \(\alpha_c\), can be calculated from the ratio of the peak intensity in the crystalline region (1140-1145 cm\(^{-1}\)) to the peak intensity in the amorphous region (1090-1096 cm\(^{-1}\)) (Tretinnikov and Zagorskaya, 2012):

\[
\alpha_c(\%) = -13.1 + 89.5 \cdot \frac{\text{crystalline peak intensity}}{\text{amorphous peak intensity}}.
\]

Figure 21. FTIR spectrum for the crystalline and amorphous regions of PVA used in this thesis project.
4.6.2 Kaolin orientation

Kaolin has characteristic vibrations in the 3600-3700 cm\(^{-1}\) region that represent dipole oscillation of the OH bonds (Figure 22). In this region, kaolin has four peaks of which three – 3670, 3652, and 3620 cm\(^{-1}\) – represent bonds oriented with a shallow angle to the basal plane of the kaolin platelets while one (3695 cm\(^{-1}\)) represents the perpendicular oriented bond (Elton et al., 1999, Farmer, 1964). The kaolin orientation factor, \(\kappa\), can be calculated from the ratio of the peak area at 3695 cm\(^{-1}\) and 3620 cm\(^{-1}\) (Elton et al., 1999):

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

(4.5)

A low \(\kappa\) means that the orientation of the kaolin platelets is mainly in the basal plane of the barrier coating.

![Figure 22. FTIR spectrum of kaolin used in this thesis project.](image)

4.7 Image analysis of scanning electron microscope images

Scanning electron microscopy (SEM) (Zeiss EVO MA10, Carl Zeiss Microscopy GmbH, Jena, Germany) was used to image the barriers, especially the cross sections as these provided information on filler distribution and orientation. Additionally, barrier coating thickness could also be observed. SEM was operated at high vacuum (10\(^{-5}\) – 10\(^{-6}\) mbar). The cross section was prepared by either focussed ion beam (FIB) or embedded in epoxy. The FIB technique
procedure required placing the coated films between two glass plates (Bellco Cover-Slips). Next, the cross-sections were prepared with ion-beam cutter (Hitachi IM4000), sputtering 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 capturing the images. The coated films were embedded in epoxy (Epofix) and harden for 12 hours. The embedded films were polished in four steps: 1) SiC paper #500; 2) the MD largo with DP-spray with grind size 5µm; 3) MD Dur with DP-spray with grind size of 3µm; 4) and MD-Nap with DP-spray with grind size of 1µm. Between every step, the samples were rinsed with ethanol and dried. The embedded films were coated with gold to prevent charging effects from the samples.

The cross section images were analysed with image analysis to estimate the kaolin orientation, size, and area distributions. The image analysed was based on the structure tensor method. Before the orientation of the platelets can be determined, the images need to be pre-processed (i.e., Gaussian filter, segmentation, normalization, and threshold were applied to the images) (Figure 23 and Figure 24). The angle is presented in the unit circle, which shows angles for the platelets used in the image analysis. Figure 24 shows results from both the covariance matrix method (did not produce usable results in all cases) and the structure tensor method (was applicable in all cases).

![Figure 23. Pre-processing process of the SEM image.](image1)

![Figure 24. Example of results from the image analysis.](image2)
5 Summary of papers

In this section, the most important results and conclusions from each of the individual papers are highlighted to form the basis for overall conclusions made from this thesis project.

5.1 Paper I

Dispersion barrier produced from poly (vinyl alcohol) (PVA) and kaolin blends coated onto polymeric supports were investigated using two methods that measure permeability: the oxygen transmission rate (OTR) and the ambient oxygen ingress rate (AOIR). Coatings with different thicknesses and kaolin contents were studied. FTIR and SEM were used to obtain the structure of the dispersion coating (i.e., the polymer crystallinity and kaolin orientation). The kaolin content affected the orientation and the polymer crystallinity. Higher kaolin content was accompanied by higher degree of crystallinity of PVA. The early stages, determined by AOIR, proved that the thickness was less important, although thickness was significant for the steady-state permeability. A coating with an initial lower permeability ended up with a higher steady-state permeability (Figure 25).

![Figure 25a](image)

AOIR measurements of the oxygen concentration (%) versus time a) for the first 30 minutes and b) up to four days. The data points are the mean values of six measurements. The black cross: PET film; filled red square: PVA\(_t=4.4\); closed red square: PVA\(_t=10.9\); open blue rhombus: PVA\(_k=5.8\) \(t=5.2\); closed blue rhombus: PVA\(_k=5.8\) \(t=11.1\); open green triangle: PVA\(_k=38\) \(t=5.9\); closed green triangle: PVA\(_k=38\) \(t=10.7\).
5.2 Paper II

The permeability of dispersion barriers produced from poly (vinyl alcohol) (PVA) and kaolin blends coated onto polymeric supports were studied using two measurement methods: the oxygen transmission rate (OTR) and the ambient oxygen ingress rate (AOIR). The thickness and kaolin content varied. A clear effect of the kaolin on the permeability was seen up to 5.7 wt%. FTIR and SEM were used to study the effect of kaolin and showed that both the drying temperature and the thickness of the samples affected the orientation of the kaolin (Figure 26). The kaolin platelets at 20 wt% were more random compared to the other wt%. At high loading levels, the kaolin platelets oriented more in the basal plane of the coating for the thicker coatings compared to the thinner coatings. The diffusion coefficient was affected by the kaolin loading, which shows the effect of tortuosity.

![Figure 26](image_url)

**Figure 26.** Kaolin orientation for the thinnest barriers, thickness 1.8 ± 0.1 for 60 °C, 1.7 ± 0.1 for 95 °C, and 2.4 ± 0.1 for 160 °C. The samples were dried in 60 °C, 95 °C, and 160 °C.

5.3 Paper III

In paper III, a model for the diffusion process was devised for the studied systems. Apart from determining diffusivity using the model, the results were also compared to results from previous experimental studies. The model uses a combination of theory of the polymer matrix including crystalline and
amorphous regions and geometric description of impermeable flakes. This model uses Equation 5.1:

\[ D_{eff} = (1 - \phi_C)L_0e^{\beta \omega_1 \frac{\partial \mu_1/RT}{\partial \ln \omega_1}} e^{-\frac{E_a}{RT}} / v_{ff}, \]  

(5.1)

where

\[ v_{ff} = \begin{cases} \frac{2}{3} \left(s + \frac{1}{2}\right) \left(\frac{(a\phi)^2}{1-\phi(1+\sigma/\alpha)} + \frac{a\phi}{\pi/4} \left(1 + \frac{\sigma}{\alpha}\right)^2 \ln \left(\frac{1-\phi(1+\sigma/\alpha)}{(\pi/2)a\phi(1+\sigma/\alpha)}\right)\right) & \text{if } r \leq 1 \\ \frac{2}{3} \left(s + \frac{1}{2}\right) \left(\frac{a\phi}{\sigma} + \frac{a\phi}{\pi/4} \left(1 + \frac{\sigma}{\alpha}\right)^2 \ln \left(\frac{\alpha(1+\sigma/\alpha)}{\sigma(\pi/2)}\right)\right) & \text{if } r \geq 1 \end{cases} \]  

(5.2)

where \( s \) is the order parameter defined by Equation 5.3:

\[ s = \frac{1}{2} (3 \cos^2 \theta - 1) \]  

(5.3)

The amorphous volume fraction – \((1 - \phi_C)\) – is inversely proportional to the tortuosity factor of the crystalline regions (Minelli, 2014, Minelli and Sarti, 2013).

The results showed that the orientation of the flakes is important: a well ordered system decreases diffusion. The flake aspect ratio is important as high aspect ratio compared to a low aspect ratio is more influential at high concentrations (Figure 27). This model captures the effects of the structure on diffusion.

**Figure 27.** The calculated effect on the oxygen diffusion rate of the aspect ratio, \( \alpha \), as a function of loading level, \( \phi \) (\( \sigma = 0.1, \phi_C = 0.1 \) and \( \theta = 0 \)). The experimental results are from Nyflött et al. (2014a) and Nyflött et al. (2014b).
Barrier coatings were produced from poly (vinyl alcohol) (PVA) and kaolin blends that subsequently were coated onto a polymeric support. These barriers were characterized to understand how chemical and physical structures influence permeability. Scanning electron microscopy and Fourier transform infrared spectroscopy determined the kaolin orientation and the polymer crystallinity. At a low concentration of kaolin, the crystallinity of PVA decreased and the kaolin particles were oriented in the basal plane of the barrier coating for the thinner films.

The computer model combined theories for the polymer phase and for the tortuous pathway of the oxygen molecules as the result of impermeable clay particles. The model indicated that the mass transport was affected by the aspect ratio of the clay in combination with the clay concentration. The model also suggested that the crystallinity of the polymer chains affected the mass transport.

The results indicate that there are several important parameters with respect to improving barrier properties: clay orientation, clay concentration, clay aspect ratio, and polymer crystallinity. This work provides additional knowledge about mass transport processes associated with different packaging barriers and provides knowledge that can be used to customize renewable barriers.
7 Future perspectives

To minimize food spoilage, packages with good barriers should be used. Therefore, it is important to understand what happens in the permeation process. Understanding the properties of polymers and fillers will allow future investigations to develop better barriers. Future studies should investigate early-stage permeability of layered structures in different combinations. The activation energy of the polymer also needs to be investigated. The activation energy influences the initial permeability, which is often critical when discussing the permeation process.

The computer model developed in this thesis needs to be further developed to capture the whole permeability process. The solubility process needs to be inserted into the model. The model also needs to be expanded from a two-dimensional to a three-dimensional model to capture the whole permeation process, especially the layered structure. Molecular dynamic simulation might improve the understanding of the process. The model needs to be compared with experiments and needs to be checked against different systems in order to achieve a general description.
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Structural Studies and Modelling of Oxygen Transport in Barrier Materials for Food Packaging

The requirements of food packages are to ensure food safety and quality, to minimize spoilage, and to provide an easy way to store and handle food. To meet these demands for fibre-based food packages, barrier coatings are generally used to regulate the amount of gases entering a package, as some gases are detrimental to food quality. Oxygen, for example, initiates lipid oxidation in fatty foods. Bakery products may also be sensitive to oxygen. This thesis focused on mass transport of oxygen in order to gain deeper knowledge in the performance of barrier coatings and to develop means to optimize the performance of barrier coatings. This experimental study along with computer modelling characterized the structure of barrier materials with respect to the mass transport process.

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