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Diffusion of CO_2 through Polymer Membranes

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Summary:

Food industry use polymers as packaging to protect and maintain high quality and freshness of the product during distribution and storage. Polymers are permeable for gases like O_2, CO_2 and water vapor. Simulation models for the oxygen-(OTR) and the water vapour (WTR) transmission rate through different polymers and polymers layers are developed by Norner AS.

In this report, a suggestion for a model describing the diffusion of CO_2 through different polymers used in food packaging, as well as a model describing the temperature dependency for permeation is evaluated. Relevant material constants have been used from experimental work, literature and from an external test-center, Innoform Testservice.

The models were found from a theoretical study of the solution-diffusion model and simulated in MATLAB. The experimental equipment used in this thesis was a volumetric method and not suitable for polymers used as a gas barrier. Therefore, the models were based on material constants found from the literature and Innoform Testservice.

The suggested model describes the consumption of CO_2 through a single layer polymeric barrier, under steady state conditions and 0% relative humidity for different temperatures. The model can be verified using experimental values and for a more powerful model, a study using different polymers layers and the influence of the humidity should be studied.

Preface

This thesis is carried out as a fulfillment of the Master of Science degree in Process Technology at University College of Southeast Norway, during the spring of 2017. It has been carried out at the University College of Southeast Norway in co-operation with Norner AS under the supervision of Ass. Professor Marianne S. Eikeland, Professor Britt M. E. Moldestad, Business Director/Advisor Morten Augestad and Senior Researcher Irene Helland.

This thesis gives a suggestion for a mathematical model describing the diffusion of CO_2 through different polymers using material factors found experimentally or from literature. The task description can be found in Appendix A. The programs used for the experiment is LabVIEW and the result is calculated using Microsoft Excel and MATLAB.

I would like to thank University College of Southeast Norway and Norner AS for granting me the opportunity to work on this interesting topic. I especially would like to thank my supervisors Ass. Professor Marianne S. Eikeland and Professor Britt M. E. Moldestad for guiding me throughout this study, and Business Director/Advisor Morten Augestad and Senior Researcher Irene Helland for spending their valuable time with me for the meetings and giving guidance for the success of the project.

Also, I would like to give my thanks to Mathias Henriksen, Per Morten Hansen and my dear Hans Olav B. Sørenesen for the support and practical help on the experimental equipment.

Porsgrunn, 15.05.2017

Chatrine Hogseth Olsen

Nomenclature

Abbreviations	**Description**
AS	«Aksjeselskap», Limited Company
ASTM	American Society for Testing and Materials
Atm	Atmosphere
CO_2	Carbon dioxide
CO_2TR	Carbon dioxide Transmission Rate
DIN	Deutsches Institut für Normung
EVOH	Ethylene vinyl alcohol
FCM	Food Contact Materials
GDP-C	Gas permeability tester
HDPE	High-density polyethylene
ISO	International Organization for Standardization
LDPE	Low-density polyethylene
LLDPE	Linear Low-density polyethylene
MAP	Modified Atmosphere Packaging
N_2	Nitrogen
OTR	Oxygen Transmission Rate
Pa	Pascal
PA6	Polyamide
PE	Polyethylene
PEN	Polyethylene napthalate
PET/PETE	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
R&D	Research and Development

RH	Relative humidity
WTR	Water vapor Transmission Rate

Symbol	**Description**	**Unit**
A	Area	m^2, cm^2
C_A	Concentration of component A	mol/m^3
D	Diffusion coefficient	m^2/s
D_0	Pre-factor, diffusion	m^2/s
dC_A/dx	Concentration gradient	
dn_A/dt	Molar consumption of component A	mol/s
dp_A/dt	Change in pressure of component A	atm/s
E_d	Activation energy of diffusion	kJ/mol
E_p	Activation energy of permeability	kJ/mol
J_A	Molar flux of component A	mol/m^{2}s
L	Thickness	µm, m
N_A	Flux of component A	m^3/m^{2}s
n_A	Mole of component A	mol
P	Permeability Coefficient	m^{3}m/m^{2}dayPa, molm/m^{2}sPa
p	Pressure	bar, mbar, atm
P_0	Pre-factor, permeability	m^{3}m/m^{2}dayPa
p_0	Standard pressure	1.01325 bar
p_A	Partial pressure of component A	bar, mbar, atm
R	Gas constant	8.3144 J/molK
S	Solubility	m^3/m^{3}Pa, mol/m^{3}Pa
S_0	Pre-factor, solubility	mol/m^{3}Pa
STP	Standard Temperature and Pressure	273.15 Kelvin and 1 atm
T	Temperature	K, °C
T_0	Standard temperature	273.15 K
T_g	Glass transition temperature	°C

T_m	Melting temperature	°C
V	Volume	m^3, dm^3
V_G	Molar volume at STP	0.022414 m^3/mol
α	Ideal separation factor	--
ΔH_s	Heat of solution	kJ/mol
Δp	Pressure difference	mbar
θ	time-lag	s

Contents

1 Introduction

Polymers are widely used in different branches in the industries like e.g. food packaging, medicine or cosmetics, which all require different properties of the polymer for their use.

In the food industry polymers are used for packaging and compared with other packaging materials like glass or metals, polymers have higher permeability. This means that low molecular weight compounds like gases, water-vapour, flavour, aromas etc. will penetrate into and diffuse through the walls of the packaging material. The permeability is the transfer rate of molecules through the barrier and is one of many factors that can reduce the shelf life [1]or damage the quality of the product inside the package.

An understanding of the barrier properties of the polymer is important for selecting the appropriate polymer material for food or beverage packaging. The polymeric material should prevent or control the diffusion of gases to maintain product quality and freshness during distribution and storage. Production and handling the packaging material are other factors that can affect the properties of the polymer. [1] [2]

1.1 Background

Norner AS is a global supplier of industrial research and development, R&D, services in polymers. They are located in Bamble, Norway. The company has over 40 years of experience exploring opportunities and sustainable solutions with polymers and is a world leading R&D centre. [3]

Norner AS has developed simulation models for the oxygen-(OTR) and the water vapour (WTR) transmission rate through different polymers and polymers layers. The models are a free online calculator which describes the transport of oxygen or water vapor through different objects like bottles, films, cups and boxes. This is a valuable tool for industries producing and using polymers as packaging material for food and beverage. Norner AS's futures plan is to expand this simulation model also including the carbon dioxide, CO_2, transmission rate (CO_2TR). [4]

In this report a suggestion of a mathematical model for the diffusion of CO_2 through different polymers will be given for the purpose to make a simulation model. The model will be based on experimental data and relevant values found in the literature or from the external company Innoform Testservice. A description of the empiric relation between the diffusion of CO_2 at different temperatures will be given with some of the material constants for the most common polymers.

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[1] Shelf life is "The period between the manufacture and the retail purchase of food product, during which time the product is of satisfactory quality in terms of nutritional value, flavour, texture, appearance and safety". [3]

1.2 Literature

The packaging material in the food and beverage industry has the function to protect the food to maintain its original quality against external undesirable effects, like gases, light and moisture which can harm the food. Another function is to give the consumers information about the product, like the ingredient and nutritional facts. Polymers are common packaging material used in the food and beverage industry. Polymers has several advantages as a packaging material being inexpensive and light weighted, easy to print, heat sealable and flexible, but polymers are permeable. [1] [5]

The degradation of food depends on time, temperature and the environment inside the packaging. Food like fruit and vegetables still respire after harvest and need different headspace conditions for their living to expand their shelf life. Such an environment can be seen in a modified atmosphere packaging, MAP, where the respiration conditions are dependent on the respiratory activity, the properties of the polymer and the micro perforations. CO_2 is used in the headspace of the packaging of both food and beverages. Undesirable levels of the CO_2 concentrations in the packages can harm the food and give a shorter shelf life. Therefore, a study of the properties of diffusion in different polymers is important. [6]

Each polymer has different properties and to select a proper polymer for the package these properties need to be studied. The barrier properties are ranged from high to low barrier where high barrier means polymers with a low permeability to gases and low barrier has a high permeability to gases. Depending on the properties of the food inside the package, this will determine in which side of the range the barrier is needed. The package can use one or more layers of polymer films to give the best barrier by combining two or more polymers with different barrier properties.

The permeation in polymers can be described as a relationship between Fick's law of diffusion and Henrys law of solubility seen in Eq. (1.1).

$$P = DS \tag{1.1}$$

Where P is the permeability [m^3m/m^2dayPa], D is the diffusion [m^2/day] and S is the solubility [$m^3(STP)/m^3Pa$]. The permeability coefficient varies with the morphology (structure) of the polymer and depends on many physical factors like the density, the degree of crystallinity, the glass transition temperature, humidity, temperature, orientation and crosslinking.

The density of the polymer can be described as the measure of free volume between the molecules and in general, the higher density, the lower is the permeability. The crystallinity of a polymer is related to the density, the higher degree of crystallinity in the polymer, the higher is the density and the lower is the permeability. The glass transition temperature is the temperature where a polymer transits from a rubbery state to a glassy state. Each polymer has different temperatures where the transition occurs and the properties of the polymer changes. Humidity and temperature from the surrounding environment increase the permeability. In crosslinked polymers, where the structure in the polymer is seen from connected side chains, and in orientated polymers, where the polymer chains are stretch and lined up, reduce the permeability.

The thickness of the film will in principle not affect the permeability, diffusion or solubility. Finding values experimentally using variable thicknesses, may give different values, this is due to the differences in drawing, orientation and crystallinity, not the thickness. Gases like carbon dioxide, CO_2, as the permeant does not interact with the polymer and the permeability coefficient is characteristic for the gas. [7] [8]

The food packaging industry need to follow rules on the composition of plastic Food Contact Materials, FCM, regulated from the Plastics Regulation (EU) No 10/20111. This regulation is a complete specific measure for the plastic FCM and includes a Union list, which consist of the substances authorized for use in manufacturing polymer materials. [9]

For testing and specify physical, mechanical and chemical properties for polymers different plastic standards are used. ASTM (American standards) have plastic standards based on instrumentally measures which ensure a safe quality of the result, both for the manufactures and end users of the plastics. [10]

1.3 Scope of the Work

The mathematical model can be obtained using a theoretical study of the transport of gases through polymers used for food packaging in a combination with experimental material constants needed for each polymer.

The model of diffusion of CO_2 through polymer membranes will be considered using a single polymer layer under steady state conditions. Different temperatures are used in an environment of 0 % humidity. The model does not consider what is inside the packaging, only the gas transport through polymers and the polymers studied in this thesis are:

- low-density polyethylene, LDPE
- high-density polyethylene, HDPE
- polypropylene, PP
- polyethylene terephthalate, PET
- polyvinylchloride, PVC
- polyamide, PA6
- polystyrene, PS
- ethylene vinyl alcohol, EVOH32 and EVOH44

Different methods can be used for finding the material constants for each polymer. A volumetric method is used for the experimental measures, determining the material constants used for the model. An alternative method used is finding the material constants in the literature or use an external test-centre for measuring the material constants.

2 Transport of a Gas in Polymeric Membranes

In this chapter, different properties for polymers and polymer membranes used in food packaging are explained. A theoretically study using physical laws for finding the gas transport through polymeric membranes is given, and methods that can be used for finding the material constants needed for determining the permeation.

2.1 Polymers

A polymer is a compound of high molecular weight, buildup from a simple monomer repeated throughout a chain. Polymerization is a polyreaction where the polymer chains are produced and due to the variation of monomers, polymers are further divided into different classes.

2.1.1 Classification of Polymers

The three main classes polymers can be divided into are; Thermosets, elastomers and thermoplastics. Thermosets are polymers that cannot be remolded and they are strong, durable and primarily used in automobiles and constructions. These types of polymers are not used in food packaging applications.

Elastomers are polymers that either is made from thermoplastic or thermoset, with the ability of frequently stretching to over twice its size with no permanent deformation and can be used in food packaging.

Thermoplastics are polymers that easily can be shaped and molded, and can be produced for food packaging as bottles, jugs and plastic films. These plastics are recyclable by melting and separation, then turn into a raw material for production of new products. [5] [11]

2.1.1.1 The Structure of Polymers

The structure of a polymer can either be linear, branched or crosslinked, seen in Figure 2-1.

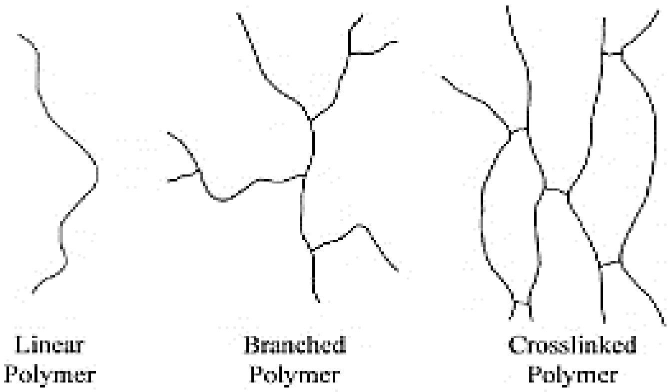

Figure 2-1: The different structures in linear-, branched- and crosslinked polymers. [11]

Linear polymers are a long chain of connected monomers. Branched polymer is a linear polymer as the main chain, with side chains of the same polymer attached to the main chain. The side chain is not connected to anything. Crosslinked polymers have a branched structure where the different side chains are connected. Crosslinking in polymers has large affections of the properties like the polymers becomes insoluble.

Polymers can either be homopolymers or co-polymers, where homopolymers are a polymer connected by the same monomer throughout its chain. Co-polymers are two or more different polymers connected in the same polymer chain. Based on the arrangement along the chain copolymers are classified into; alternating copolymer, random copolymer, block copolymer or graft copolymer. These structural differences impact the physical properties of the polymer.

In a polymer film the polymer chains is arranged in a random order and by stretching the film, the polymer chains will line up in the stretched direction and give the orientation of the polymer. The most common orientations in a polymer film are in one or two directions. The physical properties of the orientated polymer film are affected like the barrier properties are improved, the film will have higher resistance to break and tear and an increase of the stiffness. [11] [8]

2.1.1.2 Additives

To improve the processing and performance, additives are added to the polymer when pure polymers are not optimal for the production or for the end use. Additives are different materials which can be plasticizers[2], pigments or antioxidants. By adding additives, the properties in a polymer can be affected, like the permeability, diffusion and solubility. [11]

2.1.2 Polymers used in Food Packaging

In food-packaging where food is in contact with the packaging material, molecules can emigrate from the contact material and into the packed product. Additives in polymers used for packaging in plastic Food Contact Materials, FCM, are identified and regulated from the Plastics Regulation (EU) No 10/2011, to ensure food safety.

The most common polymer used as food packaging material is polyolefins and polyester. Other materials such as polyvinyl chloride, polystyrene, polyamide and ethylene vinyl alcohol are also used. The polymers used in this thesis are described in the following subchapters. [5] [9]

2.1.2.1 Polyolefins

Polyolefins is the term for both the polymers polyethylene, PE, and polypropylene, PP. These are the two most widely used polymers in food packaging because of their good combination of properties. These polymers are flexible, strong, light, stable, moisture and chemical resistant, easy to process and well suited for recycling and reuse.

PE, where its structure can be seen in Figure 2-2, is made by addition polymerization of ethylene and is the simplest and cheapest polymer.

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[2] Plasticizers are low-molecular weight materials which improves the melt flow properties and the flexibility in a polymer. [11]

$$-\!\!\left[CH_2-CH_2 \right]\!\!-_n$$

Figure 2-2: The chemical structure of PE. [12]

Because polyethylene can be produced with different structure and density, polyethylene is divided into smaller groups like: low-density polyethylene LDPE, linear-low-density polyethylene LLDPE and high-density polyethylene HDPE, seen in Figure 2-3. [5]

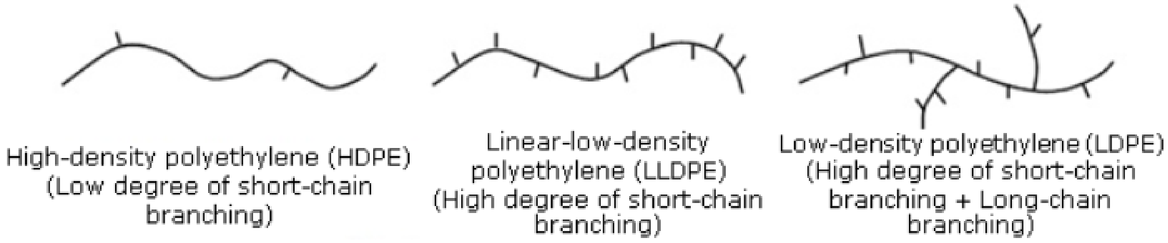


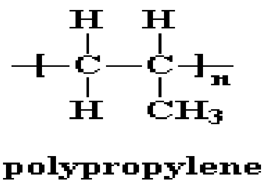
Figure 2-3: The structure of HDPE, LLDPE and LDPE. [13]

LDPE, is a polyethylene made in high pressure process by free radical polymerization and have branched structures. These polymers are characterized as flexible, strong and tough, easy to seal, resistant to moisture and are relative transparent. LDPE is most used as film applications, in applications where heat sealing is necessary, frozen food bags and squeezable food bottles.

LLDPE is a polyethylene made in low pressure process by Ziegler-Natta polymerization and have a linear structure. These polymers are characterized as soft, flexible and strong, and can be used in food packaging films.

HDPE, is a polyethylene characterized as a stiff, strong and tough polymer with resistance to chemicals and moisture, but is permeable to gasses. This polymer is made in a low-pressure process by Ziegler-Natta polymerization and have a linear structure. HDPE is easy to process and form, and mostly used in food packaging for bottles for milk, juice and water, cereal box liners, margarine tubes and grocery, thrash and retail bags.

Polypropylene, PP, is made in low pressure process by Ziegler-Natta polymerization and has a linear structure. The chemical structure of PP is seen in Figure 2-4.



$$-\!\!\left[\underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{H}{C}} \right]\!\!-_n$$

Figure 2-4: The chemical structure of PP. [12]

There are two main categories of polypropylene; the homopolymers and the copolymers. The copolymers can further be divided into block copolymers and random copolymers, where the polypropylene contains an amount of ethylene.

PP are characterized as harder, denser and more transparent than PE, with a good resistance to chemicals and an effective barrier to water vapor. PP has a high melting point, 160°C, and is suitable for applications where thermal resistance is required. In food packaging, polypropylene is used in applications like hot-filled packaging and microwavable packaging, yoghurt containers and margarine tubes. [5] [12]

2.1.2.2 Polyesters

Polyesters are condensation polymers formed from ester monomers which is a result from the reaction between carboxylic acid and alcohol. Polyester can be divided into polyethylene terephthalate (PET or PETE), which is the most common polyester used in food packing, polycarbonate and polyethylene naphtholate (PEN)

PET, see Figure 2-5, is formed when terephthalic acids reacts with ethylene glycol and is a good barrier to gases, like O_2 and CO_2, and moisture.

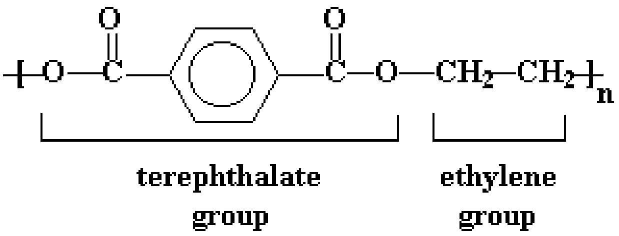


Figure 2-5: The chemical structure of PET. [12]

These polymers are characterized with their light weight and glass-like transparency and have a good resistance to heat, mineral oil, solvent and acids, but not bases. PET is used in packaging of beverages and mineral waters, containers like bottles, jars and tubs, thin films as bags and snack food wrappers and exists both as an amorphous (transparent) and a semicrystalline (opaque and white) thermoplastic material. [5]

2.1.2.3 Polyvinyl Chloride

Polyvinyl chloride, PVC, is made in free radical polymerization and is an addition polymer of vinyl chloride, seen in Figure 2-6.

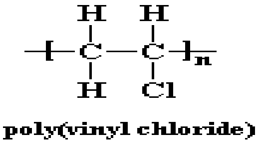
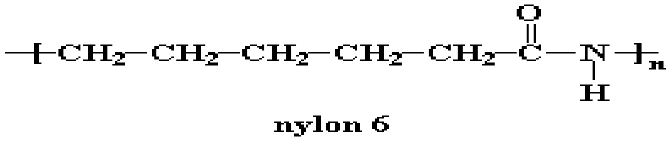


Figure 2-6: The chemical structure of PVC. [12]

This polymer is characterized to be a heavy, stiff, medium strong, amorphous, transparent material with an excellent resistance to chemicals, grease and oil. PVC are mostly used in medical and other nonfood applications, but also in food packaging applications like bottles and packaging films for meat products. [5]

2.1.2.4 Polyamide

Polyamide, PA, is formed by condensation reaction between diamine and diacid. PA6, also known as Nylon 6, is a polyamide containing 6 carbons in their chain with amide groups in their backbones chain. The chemical structure of PA6 is seen in Figure 2-7.



$$-\!\!\left[CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\right]_n$$

Figure 2-7: The chemical structure of PA6. [12]

These are semi-crystalline polymers, characterized as a material with low gas permeability, good chemical resistance and tough. Nylon 6 are typically used in packaging with mechanical and thermal properties like PET. [5]

2.1.2.5 Polystyrene

Polystyrene, PS, is made by free radical polymerization and is an addition polymer of styrene. A phenyl group is attached to every other carbon atom in the structure in Figure 2-8.

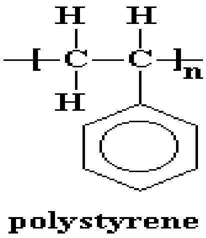
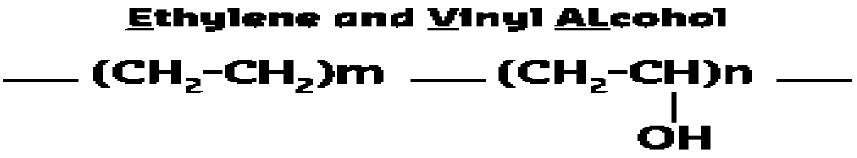


Figure 2-8: The chemical structure of PS. [12]

These polymers are characterized as clear, hard and brittle. PS is used in applications like egg cartons, containers, disposable plastic silverware, lids, cups, plates, bottles and food trays. [5]

2.1.2.6 Ethylene Vinyl Alcohol

Ethylene vinyl alcohol, EVOH, is a crystalline copolymer of ethylene and vinyl alcohol and the structure is seen in Figure 2-9.



$$-(CH_2-CH_2)m-(CH_2-\underset{\underset{OH}{|}}{CH})n-$$

Figure 2-9: The chemical structure of EVOH. [14]

EVOH is further divided into different grades named by the content of ethylene in the copolymer. EVOH 32 contains 32 mol% of ethylene and EVOH 44 contains 44 mol% of ethylene, the lower mol% of ethylene, the higher is the barrier properties to gases. These polymers are characterized to have an excellent barrier to oil, fat and oxygen, but are moisture sensitive. Mostly used in multilayers co-extruded films not in direct contact with liquids. [5]

2.2 Polymeric Membranes

A membrane can be described as an interface between two phases with selective barrier properties for different gasses. The nature of a membrane can either be classified as biologicalor synthetic membranes which is characterized by the variations in materials, structures and functions. A polymer is an organic synthetic material that can be used as a membrane. [8]

2.2.1 Structure of a Membrane

The structure (or morphology) of a membrane determines the separation mechanism and its application, and can be divided into two classes, symmetric- or asymmetric membranes, seen in Figure 2-10.

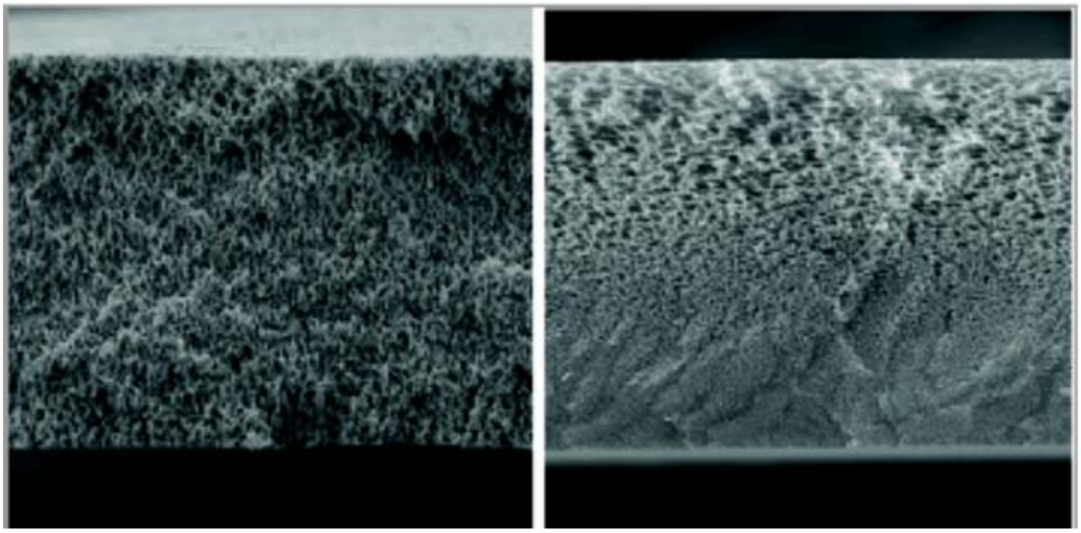


Figure 2-10: Micrographs of the cross section of a symmetric membrane to the left and an asymmetric membrane to the right. [15]

In symmetric membranes, the resistance of the gas transport is set by the total membrane thickness and can further be divided into nonporous or porous membranes, where porous membranes are most common. Asymmetric membranes consist of a thin nonporous top-layer supported on a thicker porous layer, where the resistance of the gas transport is set by the top layer.

Nonporous membranes can be described as membranes with molecular pores in terms of free volume. The nonporous membrane is a dense film where gases diffuse through by a pressure, concentration, temperature or electrical potential gradient. For understanding the gas transport in nonporous dense polymer membranes, two important parameters need to be discussed; the glass transition temperature, T_g, and the crystallinity of the polymer. [8]

2.2.1.1 The Glass Transition Phenomenon

Glass transition is a phenomenon where a polymer transits from a soft and rubbery state to a hard and brittle state. The temperature where this phenomenon occurs is different for each polymer and called the glass transition temperature. This phenomenon happens only to polymers and makes the polymer unique.

At the glass transition temperature, the physical properties of the polymer like the specific volume, specific heat and the permeability is changed. Figure 2-11 the specific volume is described as a function of the temperature.

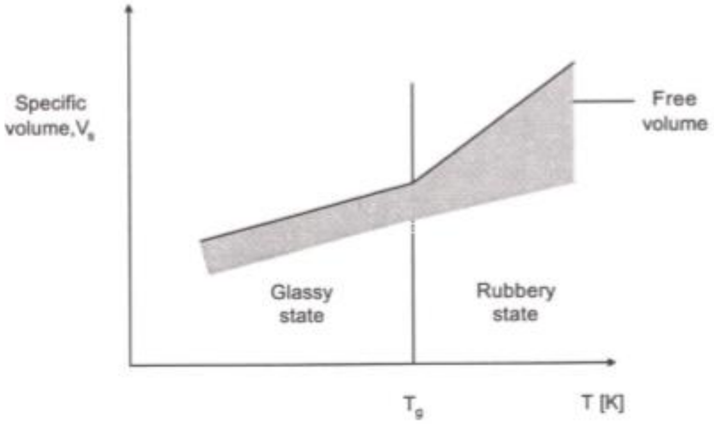


Figure 2-11: The specific volume in a polymer as a function of the temperature. [8]

From Figure 2-11 it is seen that above the glass transition temperature, the polymer has a rubbery state with free volume for the penetrant to be transported through. The transport of a gas in this state will increase with increasing temperature. Below the glass transition temperature, the polymer becomes glassy with a low degree of free volume where the penetrant is transported through small microvoids. [8] [16]

The glass transition is a change of the mobility of the molecules and happens at an exact temperature which depends on the characteristic of the polymer structure. A small change in the structure of a polymer can change the glass transition temperature a lot e.g. an increase in the molecular weight tends increase the glass transition temperature. In Table 2-1: the glass transition temperature for the polymers used in this report are listed where T_g are different for each polymer because of their different structure.

Table 2-1: The glass transition temperatures for the polymers used in this experiment.

Polymer		**Glass transition temperature, T_g, [°C]**
Low-density polyethylene	LDPE	-(95-130) [17]
High-density polyethylene	HDPE	-(120-140) [17]
Polypropylene	PP	-10 [17]
Polyethylene terephthalate	PET	81 [17]
Polyvinyl chloride	PVC	75-105 [17]
Polyamide	PA6	50 [17]
Polystyrene	PS	85-105 [17]
Ethylene vinyl alcohol	EVOH 32	60 [14]
Ethylene vinyl alcohol	EVOH 44	53 [14]

Due to its application, different polymers can be used either above or below their glass transition temperature. Polystyrene and polyamide are examples of polymers used in their glassy state below their glass transition temperature, and is called hard plastics used in room temperature. Polyethylene and polypropylene are examples of polymers used in their rubbery state above their glass transition temperature and is soft and flexible if they are used at room temperature. [12]

2.2.2 Amorphous and Crystalline Polymers

The chain structure of a polymer can either be amorphous or crystalline. Where in crystalline polymers the polymer chain has an ordered crystal structure and in amorphous polymers the polymer chain is not arranged in ordered crystals, but in a disorderly pattern.

The glass transition is a transition which happens to amorphous polymers and is not the same as melting. Melting is a transition which occurs in crystalline polymers, and happens for a temperature, T_m, when the polymer chains fall out of their crystal structure and become a liquid.

Semi-crystalline polymers are crystalline polymers with some amorphous portion, shown in Figure 2-12, where the degree of crystallinity is far less than 100%.

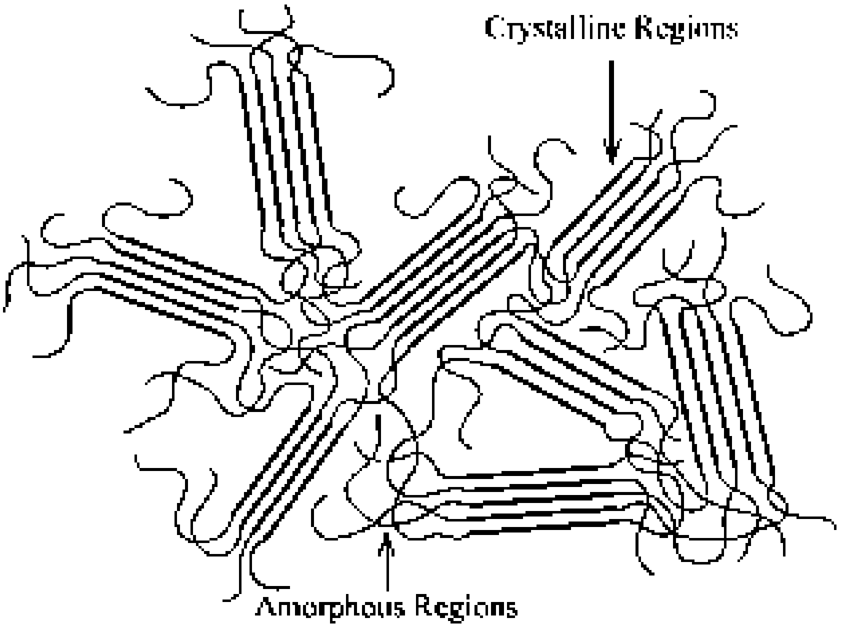


Figure 2-12: The structures of a semi-crystalline polymer. [11]

A semi-crystalline polymer has both the temperature for the glass transition and the melting. In Figure 2-13 the specific volume as a function of temperature illustrates a crystalline, a semi-crystalline and an amorphous polymer with their melting- and glass transition temperature.

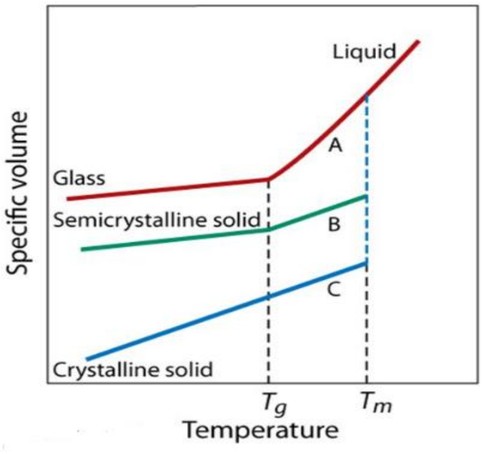


Figure 2-13: The specific volume as a function of the temperature for amorphous, semi-crystalline and crystalline polymers. [18]

Figure 2-13 shows that in an amorphous polymer, curve A, only the glass transition temperature takes place and after this transition there is a change in the slope for the specific volume. In a crystalline polymer, curve C, there is no change in the slope until the melting temperature, then the solid polymer appears as a liquid state. The semi-crystalline polymer, curve B, is in the midway of curve A and B where both melting and glass transition temperatures are observed. The transport rate is higher in the amorphous regions in a polymer and the degree of crystallinity influence the transport properties. [8] [18]

2.3 Flow Transport Through a Membrane

In year 1855 Adolf Fick derived Fick’s law of diffusion which describes that the diffusion corresponds to Fourier’s law for heat conduction and Ohms law for electrical conduction. The first theory of the permeation through polymers was done by Thomas Graham in 1866 where he presents the solution-diffusion process. Graham stated that a gas would absorb in one side of a polymer membrane, followed by diffusion through the membrane and adsorb out on the other side of the membrane. [11]

The transport through a membrane occurs when a driving force acting on the membrane in the feed side is higher than the driving force at the permeate side, seen in Figure 2-14.

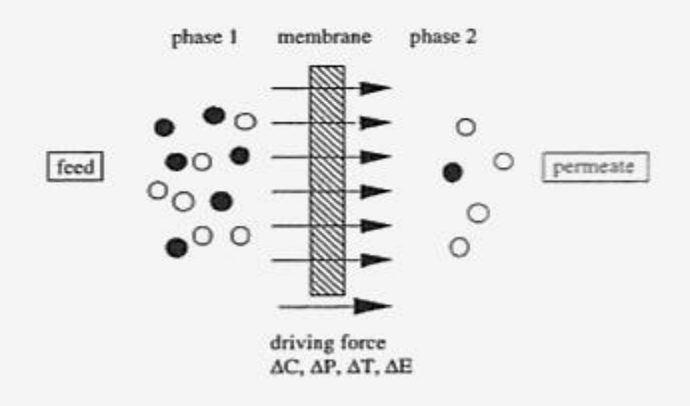


Figure 2-14: The transport of a gas from phase 1, through a membrane and into phase 2. [8]

The driving force is the chemical potential of the gas and can either be the concentration, pressure, temperature or electrical gradient. The simplest description of the gas transport through a nonporous membrane is by Fick's law of diffusion seen in Eq. (2.1).

$$J_A = D\frac{dC_A}{dx} \tag{2.1}$$

Where J_A, is the molar flow rate, or the flux of component A through the membrane, D, is the diffusion coefficient and dC_A/dx is the concentration gradient through the membrane. The diffusion describes the movement of the gas inside the membrane and is a measure of the (Area of the membrane/time) using the unit [m^2/day] in this report.

Under steady state conditions the integration of Fick's law across the membrane relates the molar flux to a concentration difference given in Eq. (2.2).

$$J_A = D\frac{C_{A2} - C_{A1}}{L} \tag{2.2}$$

Where L, [m], is the membrane thickness, C_A, [mol/m^3] is the concentration of component A, 1 and 2 is the different sides of the membrane. [8] [16] A schematic model of the gas transport under steady state conditions through a polymer membrane can be described by the solution-diffusion mechanism shown in Figure 2-15.

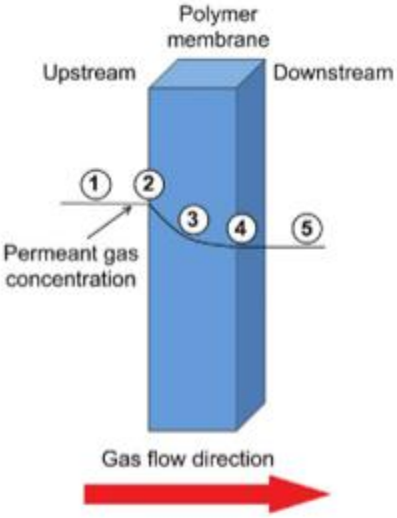


Figure 2-15: Schematic model of a steady state solution-diffusion mechanism of gas transport through a polymer. [11]

This model describes the gas transport which consists of the following processes:

1. Diffusion of the gas from the high concentrated bulk phase to the polymer membrane surface.
2. Absorption of the gas into the surface of the polymer membrane.
3. Diffusion of the gas through the polymer membrane material.
4. Desorption of the gas from the surface of the polymer membrane.
5. Diffusion of the gas away from the polymer surface into the low concentrated bulk phase.

From the model, the absorption and desorption steps are fast and the diffusion step which is slowest is the central step for determining the gas rate. In the solution-diffusion model, it is assumed:

- An ideal system, solubility and diffusivity are constant.
- Uniform thickness of the membrane.
- The pressure is uniform through the whole membrane thickness.

The solubility coefficient is a thermodynamic parameter which is a measure of a gas absorbed by the membrane under equilibrium conditions. For ideal systems where the concentrations are related to the partial pressures, Henrys law of solubility, from Eq. (2.3), can be used.

$$C_A = Sp_A \tag{2.3}$$

Where S [mol/m^{3}Pa] is the solubility coefficient and p_A [Pa] is the partial pressure of component A. The solubility, using the gas volumes, is measured by the (Amount of gas/ (Volume of the polymer*pressure)), using the unit [m^3(STP)/m^{3}Pa] in this report.

Combining Eq. (2.2), Fick's law of diffusion, and Eq. (2.3) ,Henrys law of solubility, the transport of a gas is described as a solution diffusion mechanism seen in Eq. (2.4).

$$J_A = D\frac{Sp_{A2} - Sp_{A1}}{L} \tag{2.4}$$

The permeation is the overall gas-rate through a nonporous dense membrane and can be described in terms of a solution-diffusion mechanism shown in Eq. (2.5) where the permeability is a relationship between Fick's law of diffusion and Henrys law of solubility.

$$P = DS \tag{2.5}$$

Where P, [molm/m^{2}sPa], is the permeability, D is the diffusion and S is the solubility. The permeability, is a measure of the [(Amount of gas*thickness of the membrane)/ (Area of membrane*time*pressure)] using the units [m^3(STP)m/m^{2}dayPa] in this report. From the literature, several units are used for the permeability coefficient.

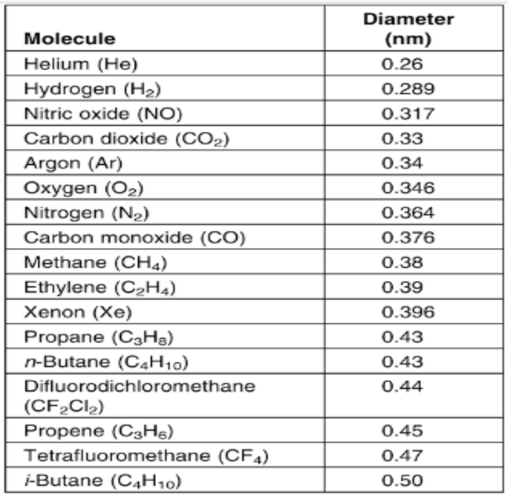
Combining Eq.(2.4) and Eq. (2.5) and changing the molar flux to a mass flux, the gas transport through a membrane is then related to the permeability coefficient seen in Eq. (2.6).

$$N_A = P\frac{p_{A2} - p_{A1}}{L} \tag{2.6}$$

N_A, [m^3/m^{3}s], is the mass flux where Eq. (2.6) describes the proportionality between the flux through the membrane and the difference in partial pressure. The flux is inversely proportional to the membrane thickness. [8] [11] [16]

2.3.1 Diffusivity

Diffusion is the kinetic part of the solution-diffusion model and occurs because of concentration difference on both sides of the membrane. The diffusivity in a polymer is dependent of the geometry and size of the penetrant and the free volume in the polymer matrix. In Figure 2-16 some kinetic diameters in various gases are shown.



Molecule	Diameter (nm)
Helium (He)	0.26
Hydrogen (H_2)	0.289
Nitric oxide (NO)	0.317
Carbon dioxide (CO_2)	0.33
Argon (Ar)	0.34
Oxygen (O_2)	0.346
Nitrogen (N_2)	0.364
Carbon monoxide (CO)	0.376
Methane (CH_4)	0.38
Ethylene (C_2H_4)	0.39
Xenon (Xe)	0.396
Propane (C_3H_8)	0.43
n-Butane (C_4H_{10})	0.43
Difluorodichloromethane (CF_2Cl_2)	0.44
Propene (C_3H_6)	0.45
Tetrafluoromethane (CF_4)	0.47
i-Butane (C_4H_{10})	0.50

Figure 2-16: Kinetic diameters of various gases. [11]

The kinetic diameter of a gas is the size of the molecule if the molecules are assumed spherical. The diffusion coefficient will decrease with increasing kinetic diameter, because the free volume in the polymer matrix available for the diffusion is limited. The solubility of a polymer and the ratio between the size of the molecule and the interstices in the polymer control the rate of passage of the gas through the polymer matrix. Generally, the diffusivity also depends on the temperature and in some cases on the solute concentration. [8] [11]

2.3.2 Solubility

Solubility is the highest amount of a gas to be dissolved in a solute area without phase separation at a given temperature and pressure. A measure of this is the solubility coefficient, S, which is a thermodynamic factor generally dependent on the temperature. From the solution-diffusion model the solubility of gases in polymers is low (< 0.2% by volume) and the model are considered as ideal.

Polymers considered as ideal systems are where the concentration of a component inside the polymer is proportional to the partial pressure of the component outside the membrane. This is seen in rubbery polymers and can be described using Henrys sorption isotherms where sorption is linear in ideal systems, seen in Figure 2-17.

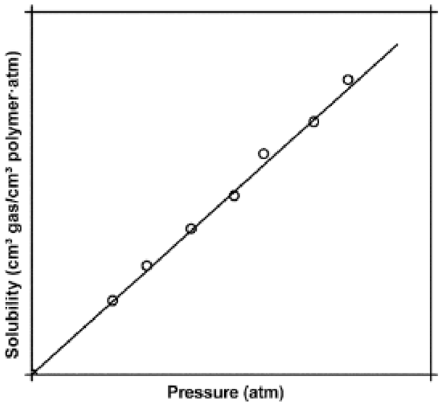


Figure 2-17: Ideal sorption from Henrys law. [11]

From Figure 2-17 the solubility is proportional to the pressure in ideal systems. If the system is not ideal, e.g. in glassy polymers, the sorption will act different from the ideal behaviour. The Langmuir sorption isotherm for a gas adsorbed on a polymer surface is described in Figure 2-18 where one part of the surface is covered by the adsorbed molecules and one is not.

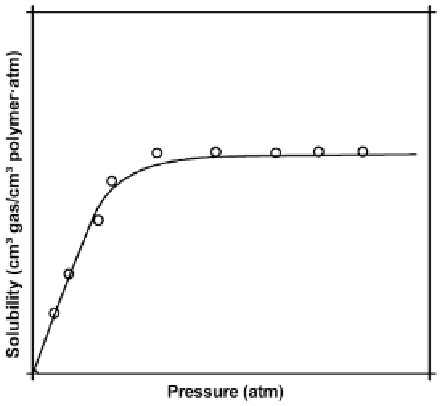


Figure 2-18: Langmuir sorption [11]

The Langmuir sorption describes a dynamic equilibrium between the adsorbed and desorbed molecules using one molecular layer. In glassy polymers, the sorption is highly non-linear where molecules also can be adsorbed on already adsorbed molecules. The Langmuir sorption is then not valid and the sorption in glassy polymers can be described using the dual mode sorption, in Figure 2-19, which is a combination of the sorption of Henrys and Langmuir.

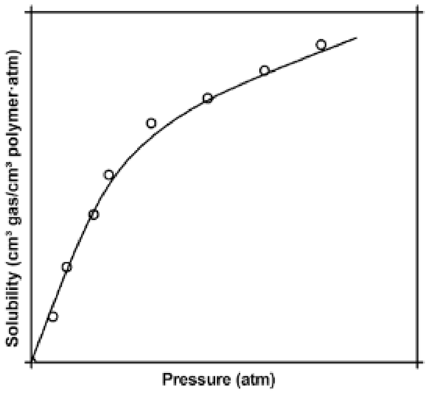


Figure 2-19: Dual sorption [11]

In dual sorption, one mode follows Henrys sorption and the one mode follows Langmuir sorption, where the microvoids present in glassy polymers are considered. This sorption model is useful for determining the permeation of gases like CO_2 through glassy polymers. [8] [11] [19]

2.3.3 Permeability

The permeability in polymers is dependent of both the diffusivity and the solubility in the polymer. Physical factors like temperature, humidity and the structure will affect the permeability coefficient and must be considered. [8] [11]

2.3.3.1 The Effect of the Temperature

The variations of the permeability, diffusivity and solubility coefficients with temperature can be described using the Arrhenius relationship in Eq. (2.7), Eq. (2.8) and Eq.(2.9). The Arrhenius relationship describes the temperature dependence of a chemical reaction rate.

$$P_A = P_0 e^{-\frac{E_p}{RT}} \tag{2.7}$$

$$D_A = D_0 e^{-\frac{E_d}{RT}} \tag{2.8}$$

$$S_A = S_0 e^{-\frac{\Delta H_s}{RT}} \tag{2.9}$$

Where P_0, D_0 and S_0 are temperature independent constants, E_p and E_d, [kJ/mol], is the activation energies for the permeability and diffusion, ΔH_s [kJ/mol] is the heat of solution of the gas in the polymer, R, [J/molK], is the gas-constant and T, [K], is the temperature. The permeability depends on both the diffusion and the solubility. An increased temperature, gives an increase in both the diffusion- and permeability coefficient and a decrease in the solubility coefficient. [11]

In the glass transition regions of a polymer there will have a deviation in the Arrhenius relation. The Arrhenius plot is a straight line where $\ln P_A$ is a function of 1/T seen in Figure 2-20.

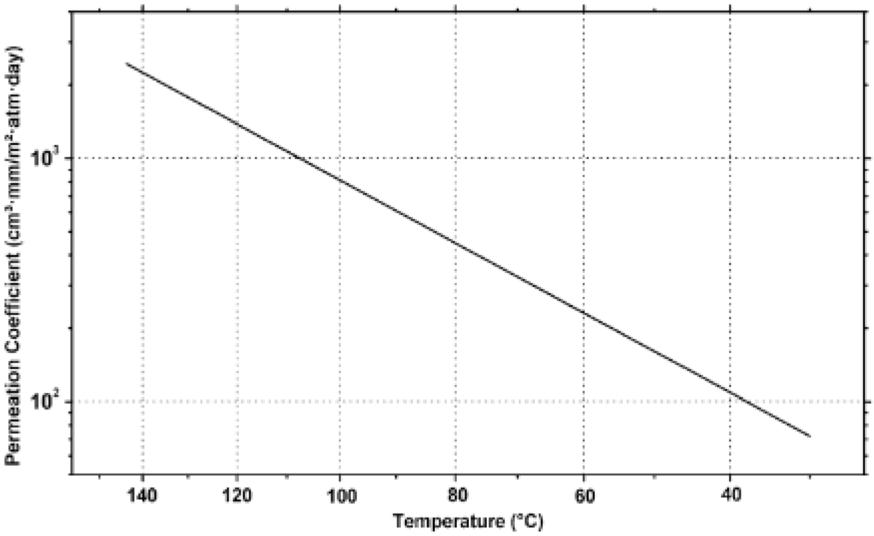


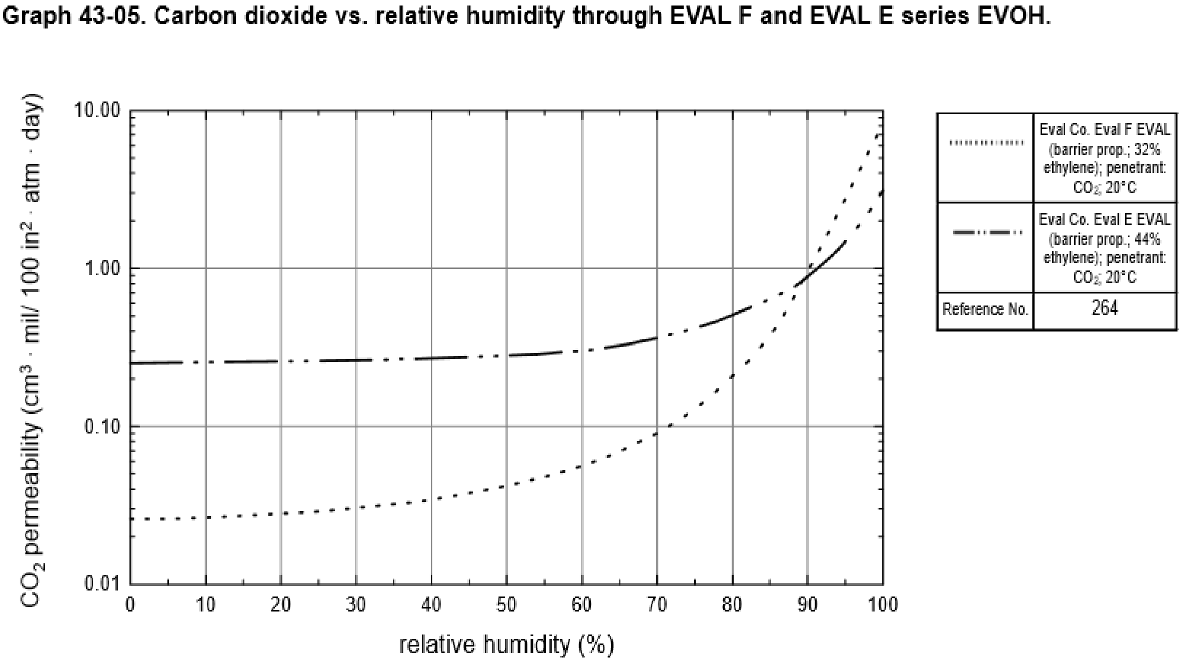
Figure 2-20: The Arrhenius plot of the permeability coefficient vs temperature. [11]

The straight line of the Arrhenius plot seen form Figure 2-20 will change in the transition region due to change in the physical properties of the polymer. For rubbery polymers, above the glass transition, the permeability and the activation energy is higher, and the selectivity is lower compared to polymers in the glassy state, below the transition. [20]

2.3.3.2 Humidity

In polymer used in food packaging the relative humidity of the environment are important to study because of the food quality preservation. Dried content in a humidity environment will absorb moisture, wet contents in a dry environment will lose moisture. The absorption of water in polymers can have a plasticizing effect and influence the permeability characteristic of the polymer.

The plasticizing effect leads to an increased permeability and the relative humidity can affect the permeability of gasses in polymers seen from Figure 2-21 where the CO_2 permeability as a function of the relative humidity in EVOH 32 and EVOH 44 are shown.



Graph 43-05. Carbon dioxide vs. relative humidity through EVAL F and EVAL E series EVOH.

Figure 2-21: The CO_2 permeability vs relative humidity in EVOH 32 and EVOH 44. [21]

The permeability coefficient of CO_2 in the polymer EVOH32 and EVOH44 increase with increasing humidity at 20°C. Also, the amount of ethylene in EVOH polymers affects the barrier properties. [1] [21]

2.3.3.3 The Structural Difference in Polymers

Crystallinity in a polymer is an important factor because the crystallites themselves are impermeable. The transport of a gas is higher in the amorphous regions of a polymer because the free volume between the molecules is larger in this region. The density in a polymer, which is a measure of this free volume, will increase with increasing degree of crystallinity. The permeability will decrease with increasing degree of crystallinity.

In a crosslinked polymer, different side chains are connected and the polymers becomes insoluble. The molecular orientation in a polymer will affect the permeability. An increased orientation decreases the permeability because the polymer chains will be lined up and make a difficult path for the transport of gases. [8] [19]

2.3.4 Selectivity

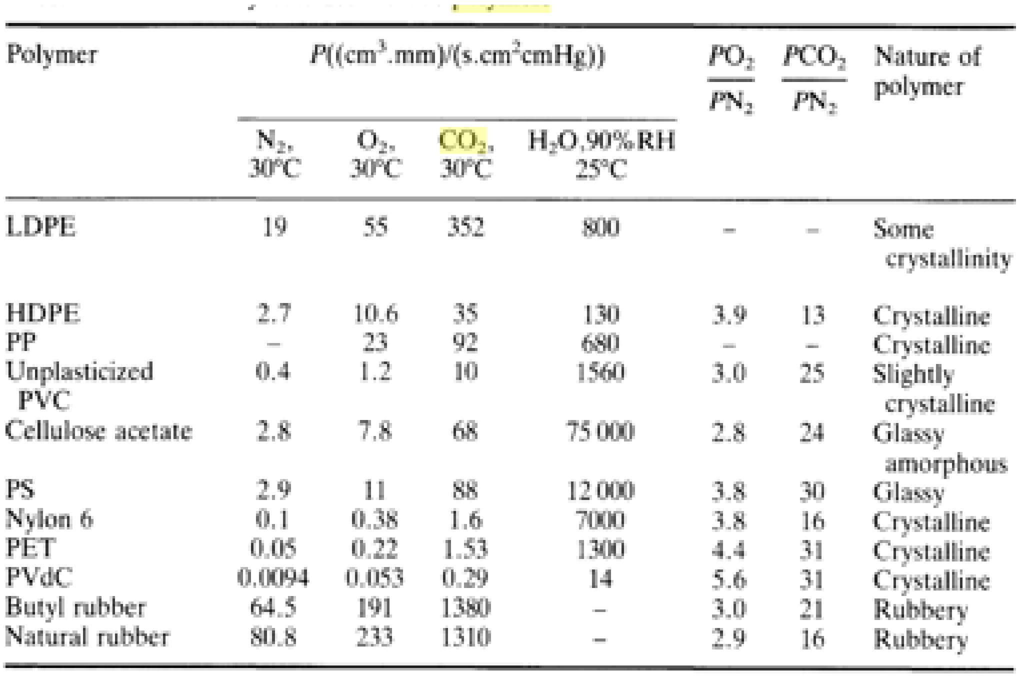
The selectivity of a membrane is used to compare the separating capacity of two species. The overall selectivity of permeability in membranes is expressed as an ideal separation factor, α, found in Eq. (2.10), along with the relation of the diffusion and solubility in Eq. (2.11) and Eq. (2.12).

$$\alpha = \frac{P_A}{P_B} \tag{2.10}$$

$$\alpha = \frac{D_A}{D_B} \tag{2.11}$$

$$\alpha = \frac{S_A}{S_B} \tag{2.12}$$

Where P, D and S is the permeability, diffusion and solubility of component A and B respectively. From these expressions, the membrane selectivity of 1 indicates no separation due to both gases will diffuse equally through the membrane. Figure 2-22 shows some examples the selectivity of CO_2 and N_2 through different polymers.



Polymer	$P((cm^3.mm)/(s.cm^2cmHg))$				$\frac{PO_2}{PN_2}$	$\frac{PCO_2}{PN_2}$	Nature of polymer
	N_2, 30°C	O_2, 30°C	CO_2, 30°C	H_2O,90%RH 25°C			
LDPE	19	55	352	800	–	–	Some crystallinity
HDPE	2.7	10.6	35	130	3.9	13	Crystalline
PP	–	23	92	680	–	–	Crystalline
Unplasticized PVC	0.4	1.2	10	1560	3.0	25	Slightly crystalline
Cellulose acetate	2.8	7.8	68	75 000	2.8	24	Glassy amorphous
PS	2.9	11	88	12 000	3.8	30	Glassy
Nylon 6	0.1	0.38	1.6	7000	3.8	16	Crystalline
PET	0.05	0.22	1.53	1300	4.4	31	Crystalline
PVdC	0.0094	0.053	0.29	14	5.6	31	Crystalline
Butyl rubber	64.5	191	1380	–	3.0	21	Rubbery
Natural rubber	80.8	233	1310	–	2.9	16	Rubbery

Figure 2-22 Permeation and their selectivity in different polymers [19]

The selectivity in polymers is affected by the nature of the polymer. The gas transport in nonporous dense membranes, based on the solution-diffusion model, the selectivity is high. [8] [16]

2.3.5 Multiple Film Layers

Plastic materials can be used as a single film or in layers with other plastic types in packaging to achieve the properties needed for the packaging. There are two ways of combining plastics, either with laminations or by co-extrusion.

In laminations two or more polymers are bonding together (or together with another material such as paper or aluminum) using adhesives in form of either water-, solvent-, or solid-based. The adhesives are applied on one film and the second film is passed between rollers to add pressure and bond them together.

Co-extrusion is a faster process than the lamination and during the film manufacture, two or more layers of molten polymers are combined using materials with thermal characteristics suitable for this process. [5]

The permeability of a multilayered packaging material is estimated using Eq. (2.13).

$$\frac{1}{P} = \sum_{i=1}^{n} \frac{L_i}{P_i} \tag{2.13}$$

Where L_i is the thickness of layer i and P_i is the permeability of layer i and P is total permeability of the film. [11]

2.4 Methods for the Permeability-, Diffusion- and Solubility Coefficient

There are different standards and methods for finding the permeability-, diffusion- and solubility coefficient of a polymer. Some experimentally methods are described in the following sections.

2.4.1 Standards for Measurement

Different standards for measuring the physical, chemical and mechanical properties for a polymer are used for ensure safe, reliable and good quality of materials and products made of plastic. Standards is a strategic tool allowing manufactures and end-users to evaluate the material and product of concern to reduce cost, by minimizing waste and errors, and ensure quality and safe utilization. Some important standards used is:

- ASTM International (American Society for Testing and Materials) deliver, among other different standards, technical standards for instrumental testing of material and products made of plastic.
- ISO (International Organization for Standardization) delivers international standards and technical requirements, specifications, guidelines for standard organizations.
- DIN Standards (Deutsches Institut für Normung) is a German national organization for standardization and a result of work at national, European and/or international level. [10] [22] [23]

2.4.2 Determination of the Diffusion Coefficient by the Time-lag Method

The time-lag is an experimental method measuring both the permeability coefficient, P, and the diffusion coefficient, D. This is a volumetric method based on using high pressure of the desired gas on one side of a membrane and vacuum on the other side. Initially the membrane is evacuated from any residual gas by applying vacuum on both sides of the membrane for several hours. Once the experiment is started the pressure on the vacuum side is measured all the time and a typically plot of this is shown in Figure 2-23.

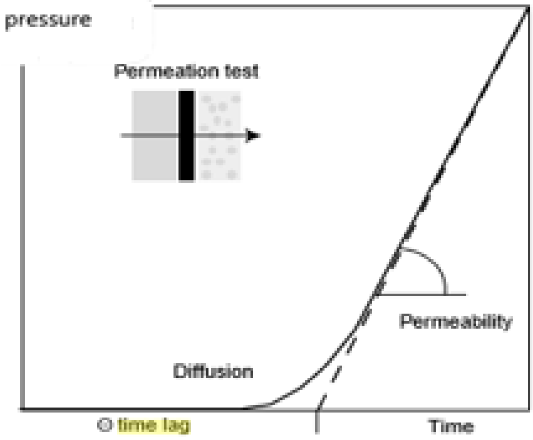


Figure 2-23: A plot of the time-lag, θ, for experimentally finding the diffusion coefficient where P is the pressure and t is time and θ time-lag. [24]

The plot shows initially a transient state before the system reach a steady state shown from the linear line in the plot. The interception for this steady state line is called the time-lag, θ. The diffusion coefficient can be calculated using Eq. (2.14).

$$D = \frac{L^2}{6\theta} \tag{2.14}$$

Where D is the diffusion, L is the thickness of the membrane and θ is the time-lag. This equation describes that there is a time lag ($\frac{L^2}{6D}$) for the system before reaching a desired steady state. [8] [11]

2.4.3 Determination of the Permeability Coefficient by the Time-lag Method

From the time-lag method the permeability coefficient, P, of the membrane can also be found experimentally. Using the same measuring as in determining the diffusivity, the permeability coefficient can be found by calculating the slope of the straight steady-state line using Eq. (2.15).

$$P = \frac{1}{p_1} \frac{VM_w L}{\rho RTA} \frac{dp_2}{dt} \tag{2.15}$$

Where p_1 is the applied pressure, V, is the volume on the vacuum side, M_w is the molecular weight of the penetrant at density, ρ, R is the gas constant, T is the temperature and A is the area of the membrane. Then the solubility coefficient, S, can be calculated from the diffusion and permeability coefficients. [8] [11]

2.4.4 Determination of the Solubility Coefficient by Absorption

Absorption can be used for finding the solubility coefficient. This is a pressure decay method where the exact weight and density of a membrane is measured before it is placed in a sample cell filled with high pressure of the absorbing gas. There is a pressure difference from the volume in the system (high pressure) and the cell volume before running. The pressure is measured from the start and until the pressure gradient (dp/dt) in the cell was zero. This is due to the sorption of the gas into the membrane and the solubility can be calculated from Eq.(2.16) using the pressure difference.

$$S = \frac{(p_{start} - p_{end})V_{Total}T_0}{V_{Polymer}Tp_{end}\,p_0} \tag{2.16}$$

Where T_0 and p_0 is the standard temperature and pressure, T is the temperature, V_{Total} is the total volume of the system, $V_{Polymer}$ is the volume of the polymer, p_{start} and p_{end} is the measured pressures. Pressure decay sorption can be used as a single-volume or dual-volume device. Initially the system was evacuated for several hours removing all the solvent inside the system and from the membrane. [16]

3 Experimental Method

To find a model of CO_2 diffusion through polymers, different methods can be used to obtain experimental values for the permeability, solubility and diffusion needed for the model. This chapter describes the method used in this experiment, which is a volumetric method finding the permeability coefficients, an alternative method for finding material constants and a suggestion of a model describing the diffusion through polymer membranes.

3.1 Permeability Cabinet

The system used in this experiment for finding the permeability coefficient of CO_2 and N_2 to different polymers, is shown in Figure 3-1. The principle for this system was to measure the pressure difference on each side of a membrane, using high pressure on one side and vacuum on the other side.

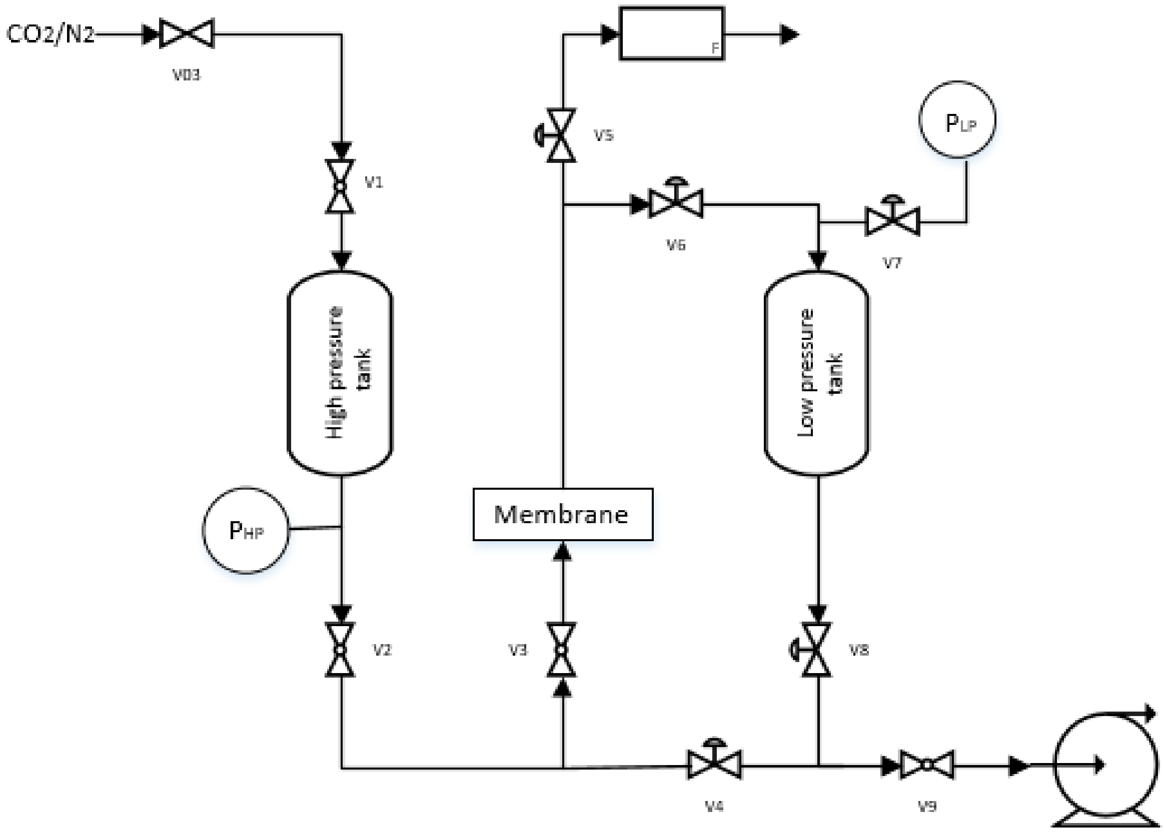


Figure 3-1: Flow sheet of the permeability cabinet.

The system consists of an insulated cabinet with two heaters inside for the regulation of, and to control the temperature using a temperature transducer. A temperature indicator was placed outside the cabinet together with fully automated pressure controllers and valve actuators. Inside the cabinet there was a high-pressure tank on the feed side and a low-pressure tank on the permeant side, both tanks had equal volume of 1 dm^3. The pressure controllers were MKS pressure transducers where data was logged in a computer using the program LabVIEW.

The membrane cell, shown in Figure 3-2 a) and b), was placed between both tanks and could easily be disconnected for changing the membrane.

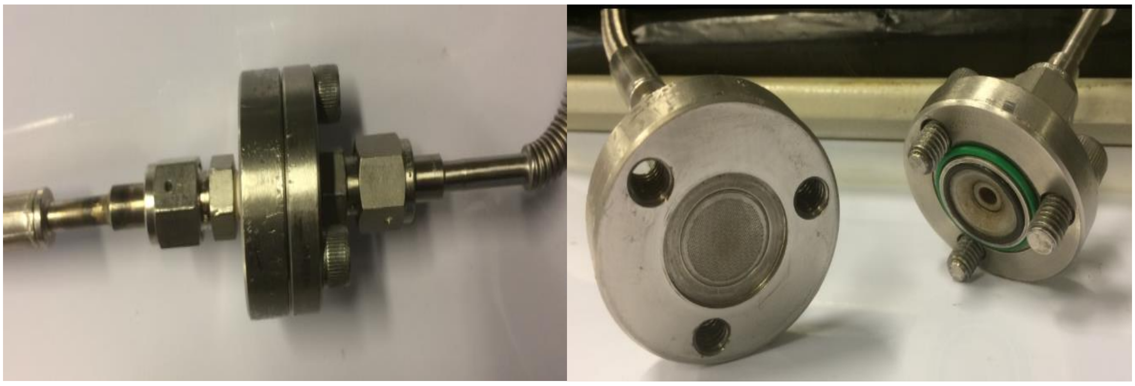


Figure 3-2: a) The membrane cell is connected. b) The membrane cell is disconnected.

The membranes had to be stamped out from a sample of a desired polymer film using a knockout puncher before it was placed inside the membrane cell in Figure 3-2 b).

3.1.1 Experimental Procedure

The membrane was stamped out and placed in the membrane cell before the system was evacuated to approximately 3mbar. The desired temperature was adjusted on the temperature transducer and the system was ready when it had reach a steady state.

A leakage test was performed for each membrane before every measure, where the purpose of this was to achieve a more accurate measurement. If the leakage in the system were too high, some actions was required to obtain the leakage and aluminum was used as a membrane for determining the size of the leakage in the system.

After the leakage test, the high-pressure side was first filled up with 5000 mbar of N_2 and the low-pressure side was evacuated to 3 mbar. When the process was running, the N_2-gas was released onto the membrane and the pressure increase on the low-pressure side was measured and logged using LabVIEW. The process was running for minimum 4 hours.

The whole system was then evacuated and the high-pressure side was filled with 5000 mbar of CO_2 for a new measurement. When the process was finished, a new membrane was placed in the membrane cell and the procedure was done over again. A more detailed procedure for running this system is found in Appendix B.

3.1.1.1 Calculating the Permeability Coefficient

The measures from the permeability cabinet was further used for determining the permeability coefficient of the membrane. The pressure at the low-pressure side was logged and used as a function of time, dp/dt. The specifications used in this experiment and calculations are listed in Table 3-1.

Table 3-1: Specifications used in this experiment.

Symbol	**Description**	**Value**	**Unit**
A	Area of the membrane	2.8339	cm^2
V	Volume of the low-pressure tank	1	dm^3
L	Thickness of the membrane	Varied with the membrane*	µm
p_1	Pressure on the high-pressure side	~5000	mbar
p_2	Pressure on the low-pressure side	~3	mbar
T	Temperature of the surroundings	Varied in the range [20,30,40,50]	°C
p_0	Standard pressure	1.01325	bar
T_0	Standard temperature	273.15	K

*see Table 3-2 Polymer films used in this experiment.

The gases used was N_2 and CO_2 and the polymer used for finding the permeability coefficients of N_2 and CO_2 are listed in Table 3-2.

Table 3-2: Polymer films used in this experiment

Sample	**Polyolefin film**	**Type**	**Density**	**Thickness [µm]**
Sample 3	Low Density Polyethylene*	LDPE	922	40
Sample 4	Low Density Polyethylene*	LDPE	923	125
Sample 5	Polypropylene**	PP		250

*LDPE used in the experimental tests contains no further additives.
**The polypropylene material used in the test are random propylene-ethylene copolymer with no additives. This polymer is intended for the manufacturing of un-oriented film on blown film processes.

The following assumption for the permeability calculations are:

- Neglecting the volume of the tubes between the pressure tanks and the volume of the membrane cell in the equation.
- Steady state gas transport if a constant gas pressure on each side of the membranes interfaces is achieved.
- Constant driving force, Δp, for the gas transport through the membrane.
- Constant temperature inside the cabinet and the membrane has the same temperature as the surroundings.
- The membrane is homogenous, with uniform thickness.
- 0% humidity inside the membrane cell during the analyses.

From the measurements and the specifications, the permeability was calculated in excel using Eq. (3.1) with a given gas, temperature and thickness.

$$P_A = \frac{L}{A\Delta p}\frac{VT_0}{Tp_0}\frac{dp_{A2}}{dt} \tag{3.1}$$

Where

- P_A [$m^3(STP)m/m^2dayPa$] is the permeability coefficient of component A.
- Δp (p_2-p_1) is the pressure difference and the driving force for the transport trough the membrane.
- dp_{A2}/dt is the pressure gradient on the low-pressure side of component A.

The mathematical background for Eq. (3.1) is given in Appendix C.

3.1.1.2 Calculating the Selectivity of the Membrane

The calculated permeability coefficient was used to determine selectivity of CO_2 an N_2 in the different polymer membranes. The selectivity of the polymer is found by using Eq. (3.2).

$$\alpha = \frac{P_{CO_2}}{P_{N_2}} \tag{3.2}$$

For valuable experimental measurements, the selectivity for each sample from the same polymer should be approximately equal.

3.1.2 Illustration test

An illustration test was performed using a membrane made of polydimethylsiloxane, PDMS, placed on a porous support layer of polyacrylnitrile. The test was performed in the same manner as the experimental tests using a temperature at 20°C and 5bar at the high-pressure side. From the producer, the nitrogen permeance in PDMS at 20°C is 0.53 [Nm^3/m^2hbar].

3.2 Alternative Method

An alternative method for determining material constants for obtaining a model was done by involving an external company for finding the experimental values and/or experimental values was found from the literature.

3.2.1 Innoform Testservice

Innoform Testservice is a laboratory for testing film packaging located in Oldenburg, Germany. This was the external company used for finding the CO_2 transmission rate on plane materials in LDPE and PP.

The required specification for finding the transmission rate was:

- using the gas CO_2
- Humidity of 0%
- Temperatures at:

  - LDPE: 23°C, 40°C and 60°C
  - PP: 23°C

Innoform uses ISO 15105-1 which is a standard using differential pressure for determining the gas transmission rate. This standard specifies two methods, one using a pressure sensor and one a gas chromatograph. Innoform use the Brugger-method which is a GDP-C Gas Permeability Tester designed for testing the permeability of dry gases on films. And the standard DIN 53380 T2 which is a volumetrically method for determination of the gas transmission rate in plastic films. [23] [22] [25] [26]

3.2.2 Literature Values

From the literature, several experimental tests have been performed and can be used for developing a mathematical model. Literature values was found for:

- the permeability coefficient:
  - in different polymers
  - with different temperatures
- material constants:
  - pre-factor
  - activation energy

Using values from the literature will have some uncertainties for the validation because of the leak in specification like method and property of the polymer from the source.

4 Mathematical Model

A mathematical model was developed by using the theoretically study combined with empirical material constants. In this case a single component diffusion are considered in a steady state homogeneous polymeric barrier.

4.1.1 Consumption of CO_2 Inside a Packaging

The flux of CO_2 through a polymer packaging, e.g. a film, chamber, bottle or a box, was considered from environment 1 and out to environment 2, illustrated in Figure 4-1, in the model.

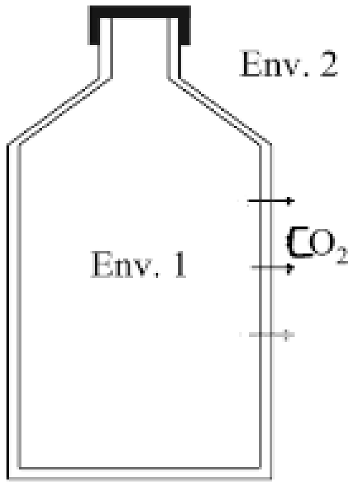


Figure 4-1: The diffusion of CO_2 out from a polymerically packaging. [27]

Environment 1 represents the CO_2 content inside the package and environment 2 represents the CO_2 content in the atmosphere. In the atmosphere, the partial pressure of CO_2 is $3.75*10^{-4}$ atm and assumed constant. [28]

Other assumptions used for the model:

- The polymeric barrier is homogeneous
- Steady state conditions
- Only diffusion of CO_2 through the membrane, neglecting emerging of CO_2 into the product inside the packaging
- The solubility and diffusion are constant
- Temperature of the membrane is equal as the surroundings
- All mass transport occurs only across the membrane thickness

The model was found by using the solution-diffusion model, in Eq. (4.1) described by Fick's law of diffusion and Henrys law of solubility using fixed boundary conditions. The model considers only the diffusion of CO_2 through the membrane, not if some of the CO_2 emerge into the product inside the packaging.

$$N_{CO_2} = -\frac{D_{CO_2} S_{CO_2}}{L}\left(p_{CO_2 1} - p_{CO_2 2}\right) \tag{4.1}$$

Where:

- N_{CO2} = flux of CO_2 [m^3/m^2s]
- D_{CO2} = diffusion of CO_2 [m^2/s]
- S_{CO2} = the solubility coefficient of CO_2 [m^3/m^3Pa]
- L = thickness of the membrane [m]
- p_{CO2} = the partial pressure of CO_2 [atm]

Using the steady state flux from Fick's first law, the flux is constant and uniform through the whole membrane where the pressure difference is the driving force. The permeability coefficient is a function of the solubility and diffusion of the membrane and described in Eq. (4.2), assuming the solubility and diffusion are constant.

$$P_{CO_2} = D_{CO_2} S_{CO_2} \tag{4.2}$$

Where

- P_{CO2} = permeability coefficient of CO_2 [m^3m/m^2dayPa]

Combining Eq. (4.1) and Eq. (4.2) the permeability coefficient can be used to find the mass transfer through a membrane in Eq. (4.3).

$$N_{CO_2} = \frac{P_{CO_2}}{L}\left(p_{CO_2 2} - p_{CO_2 1}\right) \tag{4.3}$$

Eq. (4.3) describes the flux through a membrane using the partial pressure difference of CO_2 from environment 1 and environment 2 as the driving force. The pressure dynamic in the membrane is seen in Figure 4-2.

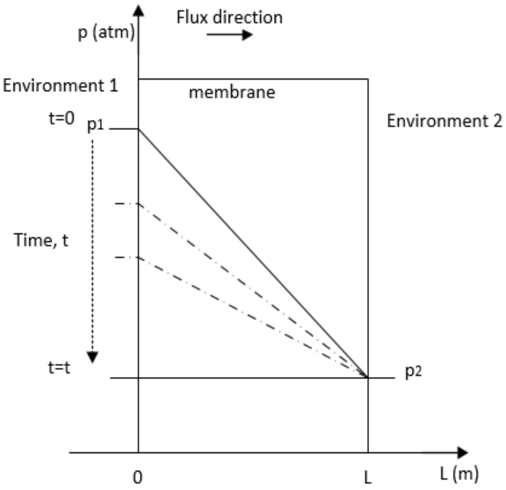


Figure 4-2: The pressure dynamic in a membrane. [27]

The steady state situation for Henrys linear sorption isotherm is used for this model. The continuity of the pressure across the membrane seen in Figure 4-2 is accepted for other sorption isotherms (unsteady diffusion) if the interfacial sorption is rapid enough compared to the diffusion in the membrane.

The Ideal gas law, seen in Eq. (4.4), can be used describing the environment inside the package due to using relative low pressures and simple non-polar gases as CO_2 and N_2 used in the model.

$$p_{CO_2} V = n_{CO_2} RT \tag{4.4}$$

Where

- V = gaseous headspace volume inside the package [m^3]
- R = gas constant [8.3144 J/molK]
- T = temperature [K]
- n_{CO2} = mole of CO_2 inside the package [mol]

The sorption of the gas into the boundary is fast due to the slow diffusion through the membrane thereby the central step for determining the flux. The change in moles per time, dn_{CO2}/dt, inside the package can therefore be found from Eq. (4.5) knowing the gaseous headspace volume.

$$\frac{dn_{CO_2}}{dt} = \frac{V}{RT} \frac{dp_{CO_2 1}}{dt} \tag{4.5}$$

Where

- dn_{CO2}/dt = mole consumption of CO_2 [mol/s]
- dp_{CO21}/dt = change in pressure per time [atm/s]

The molar flux of CO_2 through a package, if the occupied surface area of CO_2 in the package is known, can be described by the mole consumption of CO_2, seen in Eq. (4.6).

$$J_{CO_2} A = \frac{dn_{CO_2}}{dt} \tag{4.6}$$

Where

- J_{CO2} = molar flux of CO_2 [mol/m^2s]
- A = occupied surface area of component A [m^2]

The conversion from a mass flux to a molar flux is seen in Eq.(4.7).

$$N_{CO_2} = J_{CO_2} V_G \tag{4.7}$$

Where

- V_G = Molar volume at STP [0.022414 m^3/mol]. [8]

Combining Eq. (4.3), Eq. (4.5), Eq. (4.6) and Eq. (4.7) and rearranging gives an ordinary differential equation for the change of partial pressure inside the package in Eq. (4.8).

$$\frac{dp_{CO_2 1}}{dt} = \frac{P_{CO_2}}{V_G L} \frac{ART}{V} \left(p_{CO_2 2} - p_{CO_2 1} \right) \tag{4.8}$$

Rearranging the variables and integrating both side of the Eq. (4.8) with the initial condition for p_{CO21} (t =0) gives the solution in Eq.(4.9).

$$p_{CO_2 1(t=t)} = p_{CO_2 2} - \left(p_{CO_2 2} - p_{CO_2 1(t=0)}\right)e^{kt} \tag{4.9}$$

Where k is seen in Eq.(4.10).

$$k = -\frac{P_{CO_2} ART}{LVV_G} t \tag{4.10}$$

The model describes the decrease in concentration of CO_2 inside the packaging over time because there is a pressure difference of CO_2 inside and outside a packaging and the polymer used are permeable. This model can also be used for other gases.

4.1.2 The Temperature Dependency of the Permeability Coefficient

Polymers used for packaging of food are exposed to different temperatures during storing and transporting. The permeability coefficient for a polymer is depended of the temperature, and a model describing the temperature dependence related to the permeability coefficient was found from the Arrhenius relation in Eq. (4.11).

$$P_{CO_2} = P_0 e^{-\frac{Ep}{RT}} \tag{4.11}$$

Where:

- P = permeability coefficient [m^3m/m^2dayPa]
- P_0 = pre-factor [m^3m/m^2dayPa]
- E_p = activation energy [kJ/mol]
- R = gas constant gas [8.3144 J/molK]
- T = temperature [K]

The activation energy, E_p, and the pre-factor, P_0, for a polymer is given for a specific temperature range. The activation energy and pre-factor can be found plotting the natural logarithm for the permeability as a function of the inverse temperature from the Arrhenius relation. There is also a relation for two permeability coefficients seen in Eq. (4.12).

$$P_{CO_2 2} - P_{CO_2 1} = P_0 e^{-\frac{Ep}{RT_2}} - P_0 e^{-\frac{Ep}{RT_1}} \tag{4.12}$$

Rearranging and integrating Eq. (4.12) gives the model in Eq. (4.13), used for finding a permeability coefficient at specific temperature, if one permeability coefficient for a different temperature are known, and the activation energy for a given temperature range is known.

$$P_{CO_2 2} = P_{CO_2 1} e^{\frac{E_P}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \tag{4.13}$$

This model can be used for finding the permeability coefficient used in the model for the consumption of CO_2 inside a package at any desired temperature. The glass transition temperature must be considered using this model, because the gas transport will act differently on each side of the transition and affect the permeability coefficient.

5 Experimental Result

This chapter represent the results of the material constants from different polymers found either from experimental measurements, the literature or by the external company Innoform Testservice. Microsoft Excel was used for the calculations.

5.1 Permeability Coefficients found Experimentally

A permeability cabinet was used for finding the permeability coefficients experimentally for different polymers used in food packaging. The results from the experimental test gives the slope, dp/dt, measured on the low-pressure side of the system and the result of a test using aluminium as membrane is seen in Table 5-1.

Table 5-1: Shows the slopes for different samples from the experiment.

			Leak	**N_2**	**CO_2**
Sample	**L [µm]**	**Temp. [°C]**	**dp/dt**	**dp/dt**	**dp/dt**
LDPE	40	20	0.00006	0.00006	0.0002
LDPE	125	20	0.00008	0.00007	0.00009
LDPE	125	30	0.00009	0.00008	0.0001
LDPE	125	40	0.0001	0.0001	0.0001
LDPE	125	50	0.0004	----------	0.0003
PP	250	20	0.00007	0.00005	0.00006
Aluminum	----	20	0.00005		

From Table 5-1 the slopes in all measures for both N_2 and CO_2 are almost equal to the slope of the leakage measured in the same system. An example for illustrating the measured slopes was done by plotting the measured pressure on the low-pressure side as a function of time can be seen in Figure 5-1.

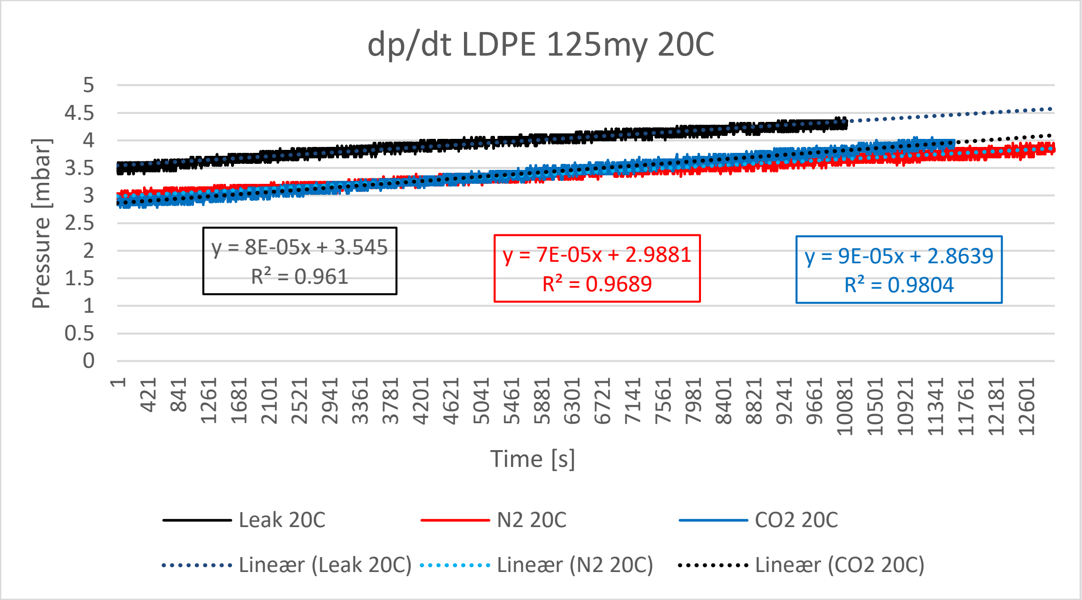


Figure 5-1: The slopes of the pressure increase using N_2, CO_2 through a membrane of 125 µm LDPE at 20°C compared with the slope of the leakage in the system.

Figure 5-1 shows the slopes for both the N_2, in red, and CO_2, in blue, and the leakage, in black. These slopes were used for calculating the permeability coefficient and the selectivity for CO_2 and N_2 shown in Table 5-2.

Table 5-2: The experimentally results of the permeability coefficient and the selectivity of the polymer.

Gas:			**N_2**		**CO_2**		
Sample	**L [µm]**	**Temp. [°C]**	**dp/dt**	**P * 10^{-13} [m^3m/m^2dayPa]**	**dp/dt**	**P * 10^{-13} [m^3m/m^2dayPa]**	**α** $\frac{P_{CO_2}}{P_{N_2}}$
LDPE	40	20	0.00006	13.8	0.0002	44.1	3.2
LDPE	125	20	0.00007	49.8	0.00009	62.2	1.25
LDPE	125	30	0.00008	57.2	0.0001	67.2	1.17
LDPE	125	40	0.0001	65.1	0.0001	63.8	0.97
LDPE	125	50	----------	------	0.0003	172.4	-----
PP	250	20	0.00005	68.9	0.00006	92.5	1.34

The selectivity for all sample are calculated for further comparisons of the validation of the permeability coefficient. The measures used for the calculation can be found in Appendix D.

5.1.1 Result from the Illustration Test

The results of calculated permeability coefficients and selectivity from the illustration test using PDMS as membrane for the gas transport of CO_2 and N_2 are shown in Table 5-3.

Table 5-3: The permeability coefficient for both CO_2 and N_2 and their selectivity using PDMS as membrane.

Gas:			**N_2**		**CO_2**		
Sample	**L [μm]**	**Temp. [°C]**	**dp/dt**	**P/L * 10^{-7} [m^3/m^2dayPa]**	**dp/dt**	**P/L * 10^{-7} [m^3/m^2dayPa]**	**α** $\frac{P_{CO_2}}{P_{N_2}}$
PDMS	---	20	0.0912	5.4	0.8884	51.7	9.6

The thickness of the membrane is unknown; therefore, the permeation, P/L, is calculated in Table 5-3. An illustration of the slopes can be seen in Figure 5-2.

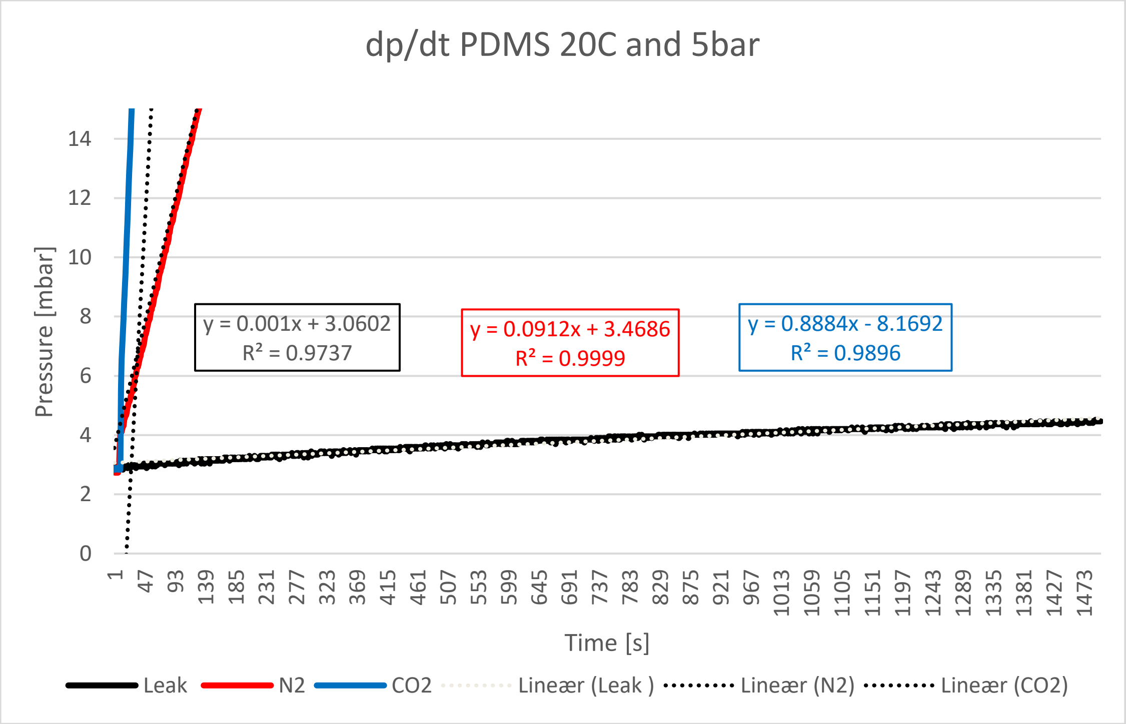


Figure 5-2: The slopes of the pressure increase using N_2, CO_2 through a membrane of PDMS at 20°C compared with the slope of the leakage in the system

In Figure 5-2 red colour is used for the slope for N_2, blue colour slope for CO_2 and black colour on the slope for the leakage. The measures used for the calculations can be found in Appendix D.

5.2 Results from the Alternative Method

The alternative method was using an external company performing experimental measures of the permeability coefficient and search for material factors from the literature.

5.2.1 Results from Innoform Testservice

The results of the permeability coefficients for CO_2 in LDPE and PP from Innoform Testservice can be found in Table 5-4. The permeability coefficients were converted because Innoform Testservice used different units.

Table 5-4: Test result from Innoform Testservice converted to the unit used in this thesis.

		Test 1		**Test 2**	
Film	**Temperature [°C]**	**Thickness [µm] (average)**	**P*10^{-13} [m^3m/m^2dPa]**	**Thickness [µm] (average)**	**P*10^{-13} [m^3m/m^2dPa]**
LDPE	23	124	55.3	113	57.3
PP	23	250	20.5	252	20.2
LDPE	40	124	119	113	124.3
LDPE	60	124	235.6	113	237.3

Each sample in Table 5-4 was tested twice using an average thickness of the membrane. The permeability coefficients were further used for finding the pre-factor and activation energy for LDPE. The test result from Innoform Testservice can be found in Appendix E.

5.2.2 Material Constants found from the Literature

The presented material constants collected from different sources from the literature including any detail available from the source document are shown in tables below.

5.2.2.1 Permeability Coefficients for LDPE

Table 5-5 shows the permeability coefficients for N_2 and CO_2 in LDPE found in the literature.

Table 5-5: Experimental literature values for the permeability of N_2 and CO_2 in LDPE.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted *10^{-13} [m^3m/m^2dayPa]**	**P_{CO2} Converted *10^{-13} [m^3m/m^2dayPa]**	**α** $\frac{P_{CO_2}}{P_{N_2}}$
LDPE [29]	25	-(95-130) [17]	6.1	86.4	14
LDPE4 [7]	25		6.3	82.1	13
LDPE1 [21]	25		7	94.6	13
LDPE2 [21]	25		7	104.6	15
LDPE3 [30]	30		12.3	228.1	19

References from permeability coefficients in Table 5-5 was specified with:

- [1] - measured at 0% RH
- [2] - measured at STP
- [3] - some crystallinity
- [4] - density of 0.914g/cm^3

5.2.2.2 Permeability Coefficients for HDPE

Table 5-6 shows the permeability coefficients for N_2 and CO_2 in HDPE found in the literature.

Table 5-6: Experimental literature values for the permeability of N_2 and CO_2 in HDPE.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^{3}m/m^{2}dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^{3}m/m^{2}dayPa]**	$\alpha = \frac{P_{CO_2}}{P_{N_2}}$
HDPE [21]	23	-(120-140) [17]	2.07	13.4	6
HDPE [21]	24		1.5-2.3	23.3-27.1	12-15
HDPE [29]	25		0.86	2.6	3
HDPE[3] [7]	25		0.95	2.3	2
HDPE[1] [21]	25		1.68	22.5	13
HDPE[2] [30]	30		1.75	22.7	13

References from permeability coefficients in Table 5-6 was specified with:

- [1] - measured at STP
- [2] - crystalline
- [3] - density of 0.964g/cm^3

5.2.2.3 Permeability Coefficients for PP

Table 5-7 shows the permeability coefficients for N_2 and CO_2 in PP found in the literature.

Table 5-7: Experimental literature values for the permeability of N_2 and CO_2 in PP.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^{3}m/m^{2}dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^{3}m/m^{2}dayPa]**	$\alpha = \frac{P_{CO_2}}{P_{N_2}}$
PP [29]	30	-10 [17]	2.6	51.8	20
PP[2] [7]	30		2.9	59.6	21
PP[1] [30]	30		-----	59.6	-----

References from permeability coefficients in Table 5-7 was specified with:

- [1] - crystalline
- [2] - density of 0.907g/cm^3, 50% crystallinity

5.2.2.4 Permeability Coefficients for PET

Table 5-8 shows the permeability coefficients for N_2 and CO_2 in PET found in the literature.

Table 5-8: Experimental literature values for the permeability of N_2 and CO_2 in PET.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	$\alpha = \frac{P_{CO_2}}{P_{N_2}}$
PET [29]	25	81 [17]	0.035	1.7	49
PET^2 [21]	25		0.038	0.6	16
PET^1 [21]	25		0.03-0.04	0.6-1.0	19-24
PET^3 [30]	30		0.032	1	31

References from permeability coefficients in Table 5-8 was specified with:

- ^{1} - measured at STP
- ^{2} - using ASTM D1434-72
- ^{3} - crystalline

5.2.2.5 Permeability Coefficients for PVC

Table 5-9 shows the permeability coefficients for N_2 and CO_2 in PVC found in the literature.

Table 5-9: Experimental literature values for the permeability of N_2 and CO_2 in PVC.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	$\alpha = \frac{P_{CO_2}}{P_{N_2}}$
PVC [21]	24	75-105 [17]	----	0.78-1.94	----
PVC [29]	25		0.078	1.04	13
PVC^2 [7]	25		0.077	1.04	13
PVC^1 [30]	30		0.26	6.48	25

References from permeability coefficients in Table 5-9 was specified with:

- ^{1} - unplasticized, slightly crystalline
- ^{2} - unplasticized

5.2.2.6 Permeability Coefficients for PA 6

Table 5-10 shows the permeability coefficients for N_2 and CO_2 in PA6 found in the literature.

Table 5-10: Experimental literature values for the permeability of N_2 and CO_2 in PA6.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**$\alpha = \frac{P_{CO_2}}{P_{N_2}}$**
PA6[2] [21]	0	40-87 [17]	0.0079	0.024	3
PA6[2] [21]	23		0.035	0.18	5
PA6[1-3] [21]	23		0.049	0.32	6
PA6 [29]	25		0.06	0.52	9
PA6[4] [30]	30		0.065	1.04	16
PA6[2] [21]	50		0.46	1.71	4

References from permeability coefficients in Table 5-10 was specified with:

- [1] - measures at 0% RH
- [2] - measured at STP and 0% RH
- [3] - for finding P_{CO2} DIN53380 are used and for finding P_{N2} DIN53122 are used, the thickness of the membrane is 0.05mm.
- [4] - crystalline

5.2.2.7 Permeability Coefficients for PS

Table 5-11 shows the permeability coefficients for N_2 and CO_2 in PS found in the literature.

Table 5-11: Experimental literature values for the permeability of N_2 and CO_2 in PS.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**$\alpha = \frac{P_{CO_2}}{P_{N_2}}$**
PS [21]	24	85-105 [17]	1.56-1.94	38.9-58.2	25-30
PS [29]	25		5.18	69.12	13
PS [7]	25		5.1	68.3	13
PS[1] [30]	30		1.88	57.03	30

References from permeability coefficients in Table 5-11 was specified with:

- [1] - glassy

5.2.2.8 Permeability Coefficients for EVOH

Table 5-12 shows the permeability coefficients for N_2 and CO_2 in EVOH 32 and EVOH 44 found in the literature.

Table 5-12: Experimental literature values for the permeability of N_2 and CO_2 in EVOH.

Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**$\alpha = \frac{P_{CO_2}}{P_{N_2}}$**
EVOH 32 [21]	5	60 [14]	-----	0.00038	-----
EVOH 32 [21]	23		0.000039	0.0001	3
EVOH[1] 32 [14]	25		0.000034	0.0016	47
EVOH 32 [21]	35		0.000079	0.003	38
Type Polymer	**T [C]**	**T_g [C]**	**P_{N2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**P_{CO2} Converted $*10^{-13}$ [m^3m/m^2dayPa]**	**$\alpha = \frac{P_{CO_2}}{P_{N_2}}$**
EVOH 44 [21]	5	53 [14]	----	0.002	----
EVOH 44 [21]	23		0.00031	0.008	25
EVOH[1] 44 [14]	25		0.00026	0.014	54
EVOH 44 [21]	35		0.00099	0.02	20

References from permeability coefficients in Table 5-12 was specified with:

- [1] - measured at 0% RH

The conversion of the permeability's from all tables can be found in Appendix F.

5.2.2.9 Pre-factor and Activation Energies for Different Polymers

Table 5-13 shows the pre-factor and activation energies for some polymers found in the literature.

Table 5-13: The pre-factors and activation energies for some polymers found in the literature.

Polymer	**Permeant**	**Temperature range[°C]**	**P_0 *10^{-13} [m^3m/m^2day Pa]**	**E_p [kJ/mol]**
LDPE 0.914g/cm^3 [7]				
	CO_2	5-60	535.7	38.9
	N_2	5-60	2842.6	49.4
HDPE 0.964g/cm^3 [7]				
	CO_2	5-60	0.437	30.1
	N_2	5-60	8.56	39.7
PP 0.907g/cm^3, 50% crystallinity [7]				
	CO_2	20-70	207.4	38.1
	N_2	20-70	11059.2	55.7
Polyvinyl chloride unplasticized [7]				
	CO_2	25-90	8035.2	56.8
	N_2	25-80	81043.2	69
Poly(imino-1-oxohexamethylene) Nylon 6 [7]				
	CO_2	0-90	10.4	40.6
	N_2	0-90	9.1	46.9

Specifications from the source for the material constants in Table 5-13 are listed along with the material constants. The conversion of the pre-factors can be found in Appendix F.

6 Simulations using the Mathematical Model

The result of the mathematical models was simulated using MATLAB. The simulations use the permeability coefficients found either from Innoform Testservice or from the literature.

6.1 Specification and Variables for the Models

MATLAB was used for simulating some examples of the mathematical model which describes the diffusion of CO_2 through different polymers by finding the CO_2 consumption inside a packaging using Eq. (6.1) and Eq. (6.2).

$$p_{CO_2-1(t=t)} = p_{CO_2-2} - \left(p_{CO_2-2} - p_{CO_2-1(t=0)}\right)e^{kt} \tag{6.1}$$

$$k = -\frac{P_{CO_2} ART}{LVV_G}t \tag{6.2}$$

This model shows the consumption of CO_2 inside a packaging. The permeability Coefficient is temperature dependent and the model in Eq. (6.3) was used for finding the permeability coefficient at different temperatures.

$$P_{CO_2 2} = P_{CO_2 1} e^{\frac{E_p}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \tag{6.3}$$

Rearranging Eq. (6.3) the activation energy was found by using permeability coefficients at different temperatures. Combining Eq. (6.1), Eq. (6.2) and Eq. (6.3) the consumption for a specific polymer can be found at different temperatures. The constants used for the model can be found in Table 6-1.

Table 6-1: Constants used in the model.

Symbol	Description	Value	Unit
p_{CO2} [28]	Partial pressure of CO_2 in the atmosphere	$3.75*10^{-4}$	Atm
V_G	Molar volume at STP	0.022414	m^3/mol
R	Gas constant	$8.31444 *10^{-3}$	kJ/molK

The partial pressure of CO_2 in the atmosphere is assumed constant. The variable constants used for the model are found in Table 6-2. These values can be varied depending on the specifications for the desired packaging.

Table 6-2: Variable constants for the model.

Symbol	Description	Value	Unit
$p_{CO2-1(t=0)}$	Initial partial pressure of CO_2	Variable	atm
A	Occupied surface area	Variable	m^2
V	Volume of the headspace inside a package	Variable	m^3
L	Thickness of the polymer	Variable	m
T	Temperature of the surroundings	Variable	K
E_p	Activation energy	Variable	kJ/mol

The activation energy can either be calculated or found in the literature. The permeability coefficients can be variable when using the temperature dependency model from Eq. (6.3) or constant for an experimental measure at a given temperature. The variables from the models is seen in Table 6-3.

Table 6-3: Variables from the models.

Symbol	Description	Value	Unit
P_{CO2}	Permeability coefficient of CO_2	Variable/experimental	m^3m/m^2dayPa
$p_{CO2-1(t=t)}$	Partial pressure of CO_2 after time, t	-----	atm
t	Time	-----	days

The permeability coefficients used for simulating is either from Innoform Testservice or the literature.

6.2 Example of Simulations using the Models

The different simulations of the models are done by using an empty bottle as packaging with the given specification:

- $p_{CO2\ 1(t=0)} = 4.0$ atm, the partial pressure of CO_2 inside the bottle
- $A = 0.05\ m^2$, the occupied surface area
- $L = 0.0008$ m, the thickness of the packaging material
- $V = 0.0005\ m^3$, volume of the bottle.

6.2.1 Simulation of the Consumption of CO_2

For simulating the consumption of CO_2 through different polymers the permeability coefficients, P_{CO2}, used in this example was found in the literature, shown in Table 6-4.

Table 6-4: Permeability coefficients used for simulating

Polymer	**Temperature [°C]**	**P_{CO_2} *10^{-13} [m^{3}m/m^{2}dayPa]**
LDPE [7]	25	82.1
HDPE [7]	25	2.33
PET [21]	25	0.62
PVC [7]	25	1.04
PA6 [29]	25	0.52
PS [7]	25	68.3
EVOH32 [14]	25	0.0016
EVOH44 [14]	25	0.014

The permeability coefficient of polypropylene at 25ºC was not found in the literature, therefore this polymer is missing in the simulation. The permeability coefficients found in Table 6-4 are further used in the simulations of the partial-pressure of CO_2 per time in different polymers at 25ºC, seen in Figure 6-1, using the model from Eq. (6.1) and Eq. (6.2).

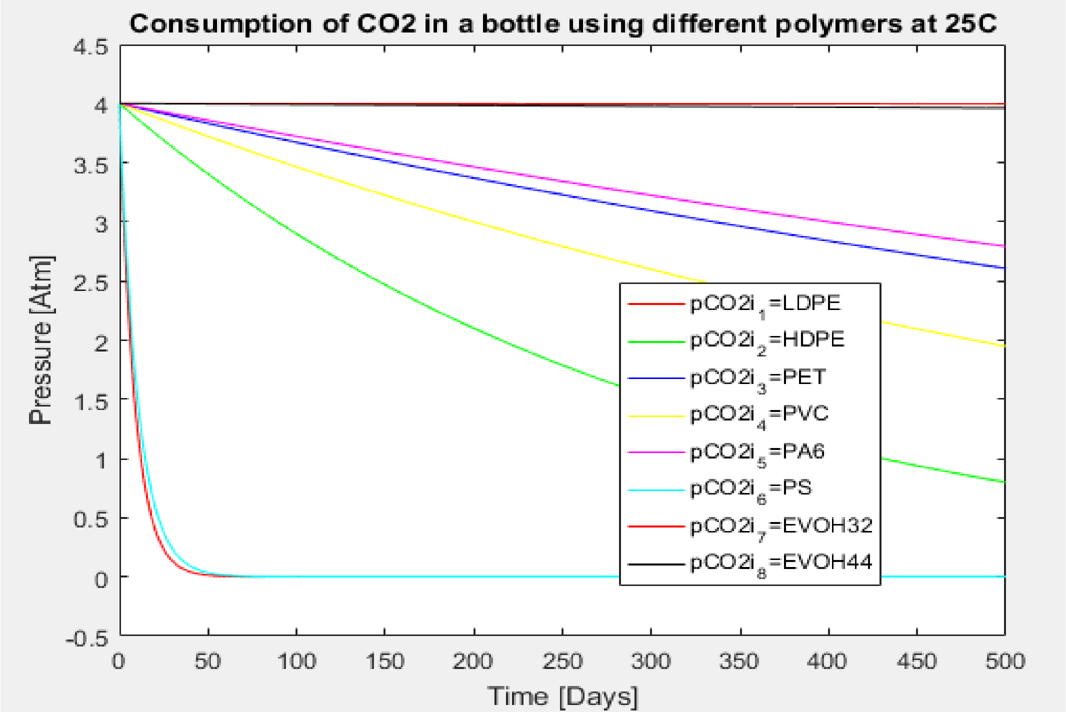


Figure 6-1: The consumption of CO_2 in a bottle using different polymers.

The simulation in Figure 6-1 shows a higher gas barrier for CO_2 through polymers EVOH32 and EVOH44 compared to the polymers LDPE and PS. From the model, it will take approximately fifty days for the CO_2 concentration inside the bottle made of LDPE and PS to be in equilibrium with the concentration in the atmosphere.

6.2.2 Simulating the Temperature Dependency Model

For simulating the temperature dependency of the permeability coefficients in a polymer, the activation energy must be known from the model in Eq. (6.3). The rearranged equation in Eq. (6.4) are used to find the activation energy

$$E_p = \frac{R\ln\left(\frac{P_{CO_2 2}}{P_{CO_2 1}}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} \tag{6.4}$$

Eq. (6.4) are further used in the simulations for finding the activation energy in a temperature range of the polymer.

6.2.2.1 Using Permeability Coefficients from the Literature

In this example, the permeability coefficients used for finding the activation energy to PA6 are found in the literature, shown in Table 6-5. The glass transition temperature for PA6 I 50°C.

Table 6-5: Permeability coefficients for CO_2 in PA6 at different temperatures.

Polymer	Temperature [°C]	P_{CO_2} *10^{-13} [m^3m/m^2dayPa]
PA6 [21]	0	0.024
PA6 [21]	23	0.18
PA6 [21]	50	1.71

From this the activation energy is calculated to be 62.6kJ/mol, and used for simulating the temperature dependence for the permeability coefficients of PA6 the temperature range of 0-50°C seen in Figure 6-2.

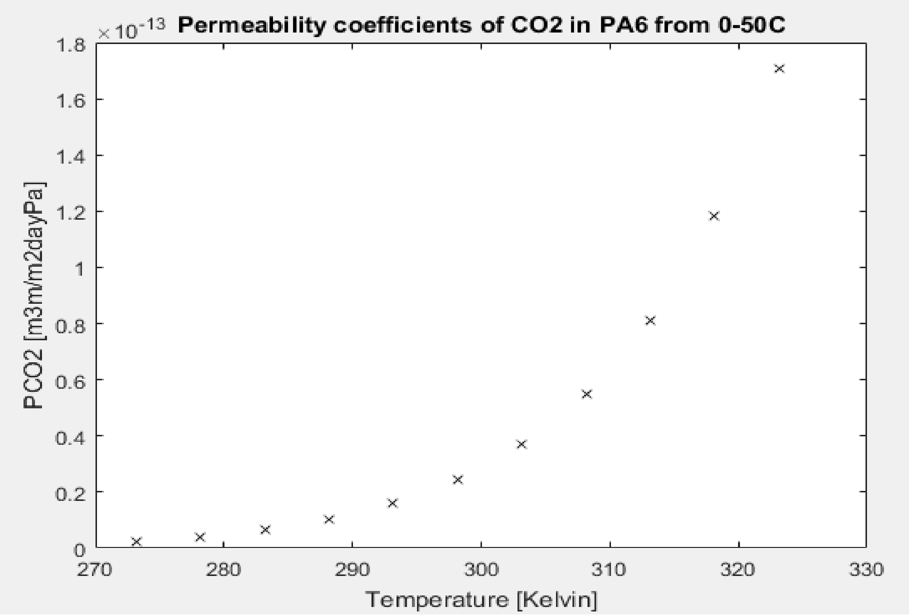


Figure 6-2: The permeability coefficients of CO_2 in PA6 from 0-50 ºC.

The simulation in Figure 6-2 indicates as expected, an increase in permeability coefficient of CO_2 when increasing the temperature in a range of 0 - 50ºC for PA6. The permeability coefficient found from the model in Figure 6-2 are listed in Table 6-6 together with permeability coefficients of CO_2 in PA6 found in the literature.

Table 6-6: Permeability coefficients of CO_2 in PA6 from the model compared with permeability coefficients of CO_2 in PA6 from the literature.

Temperature [°C]	**Temperature [K]**	**Permeability $*10^{-13}$ model [m^3m/m^2dayPa]**	**Permeability$*10^{-13}$ literature [m^3m/m^2dayPa]**
0	273.15	0.024	0.024 [7]
23	296.15	0.204	0.18 [7], 0.32 [7]
25	298.15	0.242	0.52 [1]
30	303.15	0.367	1.04 [6]
50	323.15	1.71	1.71 [7]

In Table 6-6 the permeability coefficients of CO_2 in PA6 from the model are compared with literature values. The permeability coefficients in the model are some lower than from the literature, this can be due to the structure and properties of the measured polymer, or the method used for estimating the permeability factor.

6.2.2.2 Using Permeability Coefficients from Innoform Testservice

In this example, the permeability coefficient used to find the activation energy for LDPE is the experimental measure from Innoform Testservice found in Table 6-7.

Table 6-7: Permeability coefficients CO_2 through LDPE measure by Innoform Testservice.

		Test 1 Thickness [124µm]	**Test 2 Thickness [113µm]**
Polymer	**Temperature [°C]**	**P_{CO_2} $*10^{-13}$ [m^3m/m^2dayPa]**	**P_{CO_2} $*10^{-13}$ [m^3m/m^2dayPa]**
LDPE	23	55.3	57.3
LDPE	40	119	124.3
LDPE	60	235.6	237.3

The activation energy was calculated to be 32.1kJ/mol for test 1 and 31.5 kJ/mol for test 2. The activation energies were further used for simulating the temperature dependence for the permeability coefficients of LDPE seen in Figure 6-3.

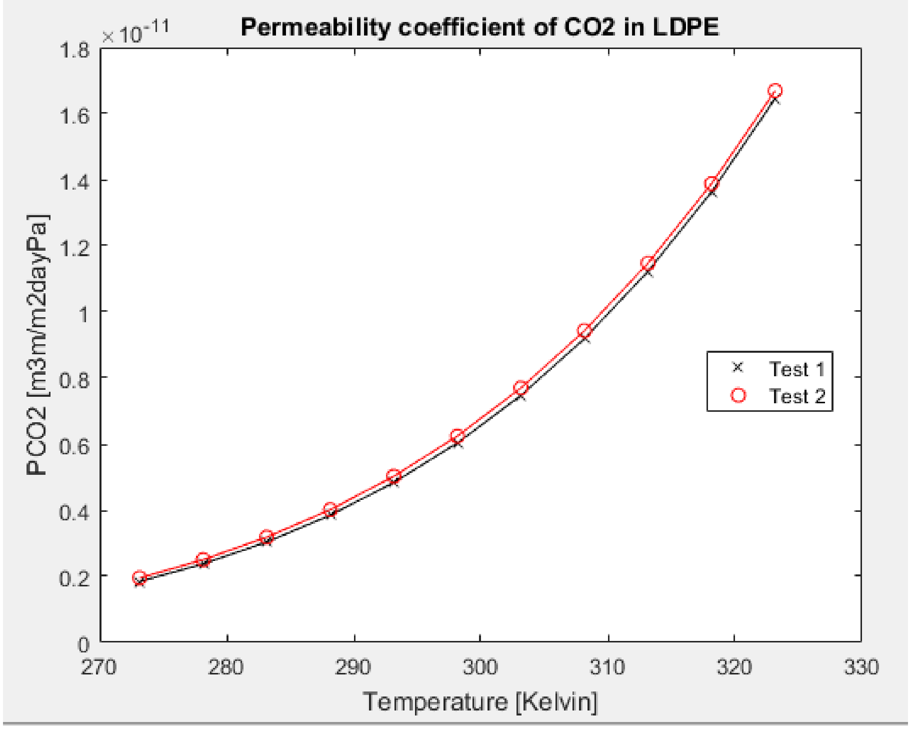


Figure 6-3: The permeability coefficient of CO_2 through LDPE.

Figure 6-3 simulates the permeability coefficients for LDPE, in both Test 1 and Test 2, from Innoform Testservice using a temperature range from 0-50 °C. From Test 1, the polymer film is some thicker than for the polymer film in Test 2, which results in a higher activation energy and a decrease in the permeability coefficients.

6.2.2.3 Comparison of the Activation Energies

The calculated activation energies for CO_2 in PA6 using the model in Eq. (6.3) are listed in Table 6-8 together with the activation energies for LDPE and PA6 from Innoform Testservice and the literature.

Table 6-8: The pre-factors and activation energies for CO_2 in different polymers.

			Model	**Innoform**	**Literature**
Type polymer	**Temperature range [°C]**	**T_g [°C]**	**E_p [kJ/mol]**		
PA6 [21]	0-50	50	62.6		
PA6 [7]	0-90	50			40.6
LDPE Test 1	23-50	(-95) - (-130)		32.1	
LDPE Test 2	23-50	(-95) - (-130)		31.5	
LDPE [7]	5-60				38.9

From Table 6-8 the activation energies from the model, for both PA6 and LDPE, is compared with activation energies from the literature. The glass transition temperature for PA6 is 50°C and the activation energy for PA6 from the literature found in the temperature range of 0-90°C. which can be one of the reason for the deviation in activation energies. Other reasons can be the structure and properties of the measured polymer. The calculated activations energies can be further used for determining the diffusion of CO_2 through different polymers.

6.2.3 Simulating the Combination of the Models

The permeability coefficient of CO_2 used in the model of CO_2 consumption through a polymer is found by using the temperature dependency model in Eq.(6.3). The activation energy, $E_{p,}$ for the polymer PA6 was in the temperature range from 0 to 50°C. The permeability coefficient at each 10th degree in the temperature range, combined with the model of CO_2 consumption vs time is seen in Figure 6-4.

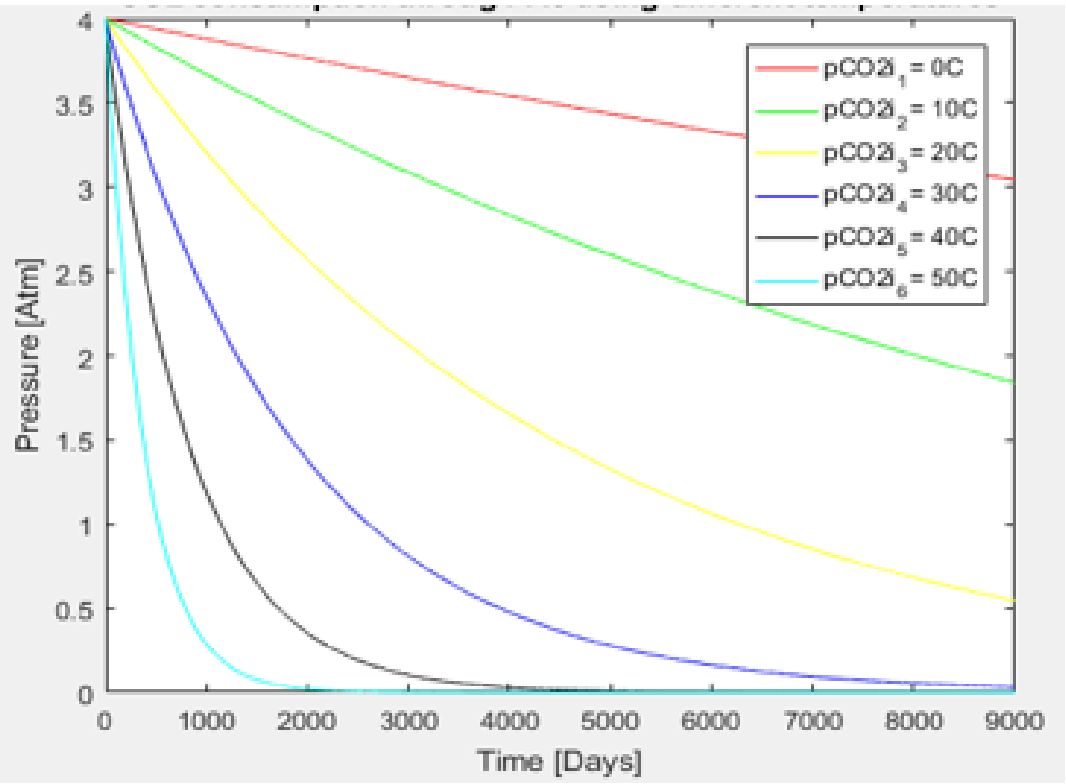


Figure 6-4: The consumption of CO_2 through PA6 at different temperatures.

Figure 6-4 shows the time estimated for the consumption of CO_2 through PA6 increase with increasing temperature.

6.2.4 Comparison of Permeability Coefficient using the Models

The permeability coefficients found in the literature and measured by Innoform Testservice used for comparing and validation are listed in Table 6-9.

Table 6-9: Permability coefficients used for simulating.

		Literature	**Innoform Test 1**	**Innoform Test 1**
Polymer	**T [°C]**	**P_{CO2} *10^{-13} [m3m/m2dayPa]**		
LDPE	23		55.3	57.3
LDPE [29]	25	86.4		
LDPE [7]	25	82.1		
LDPE [21]	25	94.6		
LDPE [30]	30	228.1		
LDPE	40		119	124.3
LDPE	60		235.6	237.3
PP	23		20.5	20.2
PP [29]	30	51.8		
PP [7]	30	59.6		

The permeability coefficient in Table 6-9 are used for simulating the model.

6.2.4.1 Consumption of CO_2 through LDPE using Different Temperatures

The consumption of CO_2 through LDPE for different temperatures is seen in Figure 6-5, were both results, Test 1 and Test, from Innoform Testservice was used.

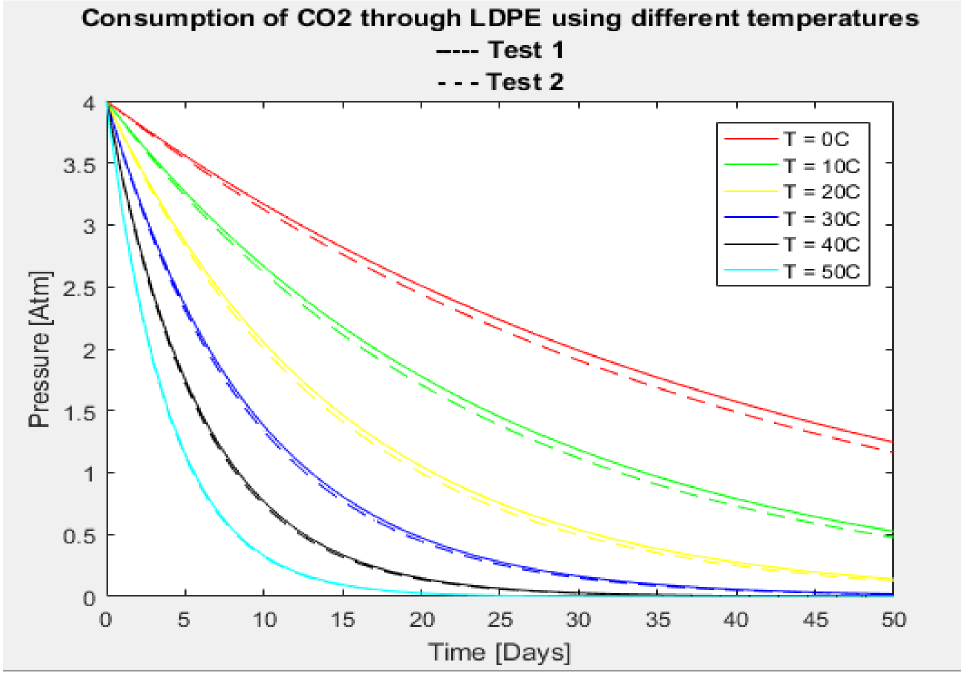


Figure 6-5: The consumption of CO_2 through LDPE at different temperatures.

Figure 6-5 describes the temperature effect on how fast the partial pressure of CO_2 decreases inside the bottle for both Test 1 and Test 2. An increased temperature and permeability coefficient gives an increased consumption of CO_2.

6.2.4.2 Comparison of the Consumption of CO_2 through PP at 23°C and 30°C

The permeability coefficient of CO_2 in PP from Innoform Testservice was measured at 23°C. Using the model of CO_2 consumption through PP, a comparison with permeability coefficients found in the literature at 30°C is seen in Figure 6-6.

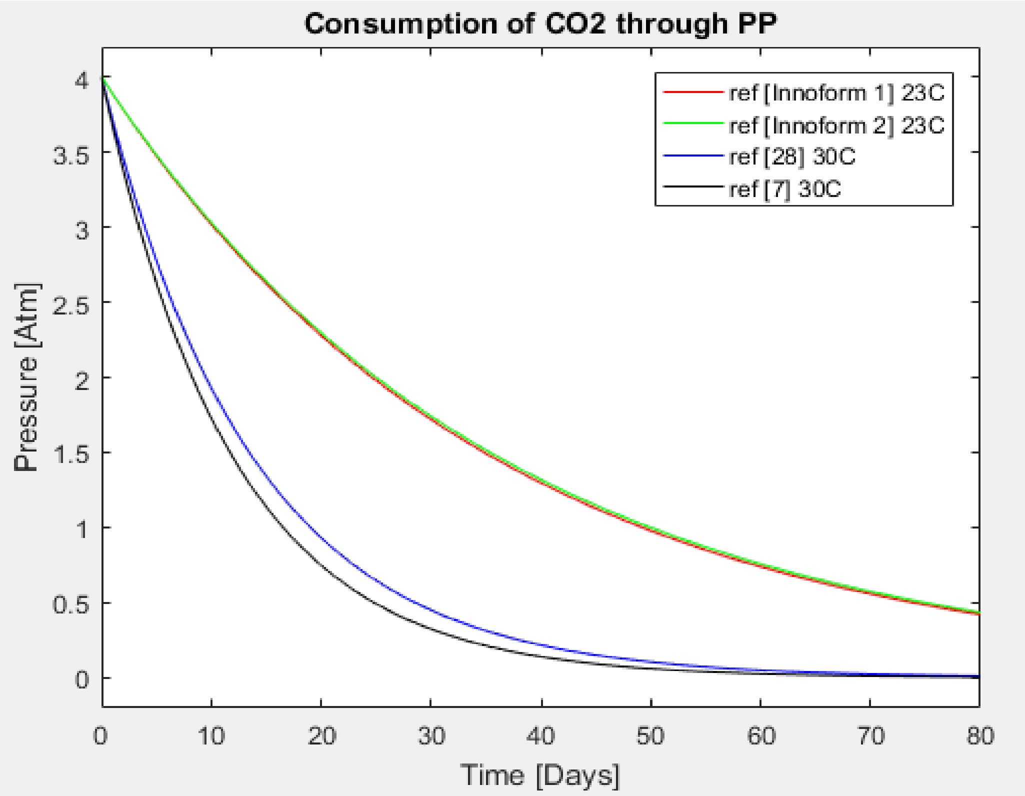


Figure 6-6: The consumption of CO_2 through PP at 23°C and 30°C.

Figure 6-6 simulates the consumption of CO_2 in PP at 23°C and 30°C, were the consumption is higher with increased temperature. It is difficult to compare the accuracy of both the permeability coefficient used from Innoform and the accuracy of the model, due to the different temperatures for the permeability coefficients.

6.2.4.3 Comparison of the Consumption of CO_2 through LDPE at 25°C and 30°C

The permeability coefficients of CO_2 in LDPE were used from the literature and for both tests from Innoform Testservice at 25°C and 30°C. The permeability coefficients were further compared using the model of CO_2 consumption. Different plots for each temperature was used seen in Figure 6-7.

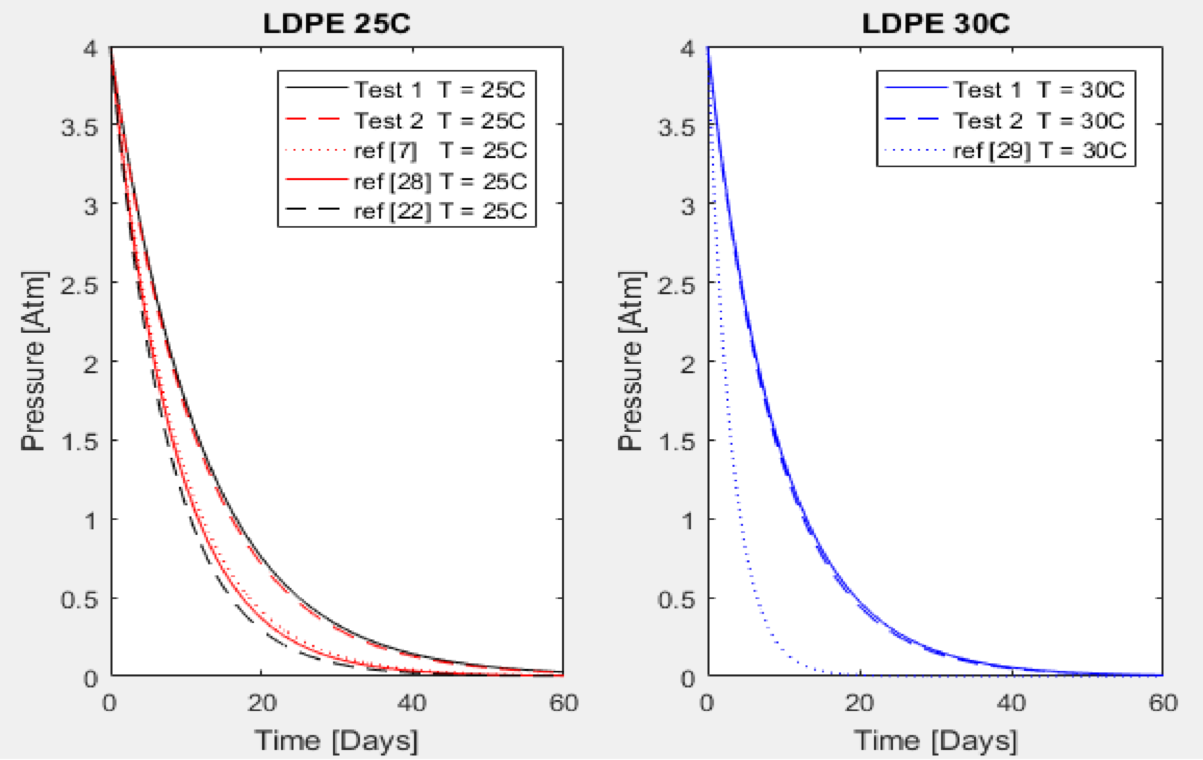


Figure 6-7: A comparison of the consumption of CO_2 through LDPE at 25°C and 30°C, using the permeability coefficients from Innoform and from the literature.

Figure 6-7 shows a comparison of the models using the permeability coefficients of CO_2, at 25°C and 30°C in LDPE, from Innoform Testservice and found in the literature. The permeability constants found in the literature is higher which results in a slower consumption of CO_2, than the measured coefficients from Innoform for both temperatures. The simulated curves for the consumption of CO_2 follows the same trends using the model. The MATLAB-script used for these simulations can be found in Appendix G.

7 Discussion

This report presents a suggestion for a model of the diffusion of CO_2 through different polymers used in food packaging. Material constants used for the model was either found by experimental measuring, from the literature or from the external company, Innoform Testservice. In this chapter a discussion of the accuracy of the experimental measurements together with a comparison of material constant from other sources are done for the validation. A suggestion of a model based on the validation of the material constants discussed in this chapter will be presented in the conclusion.

7.1 The Validation of the Material Coefficients

Material factors from experimental measures, literature and the external company Innoform Testservice are found for suggest a model for the diffusion of CO_2 through different polymers. The model is based on mathematical relations and empiric values which defines the model more accurate and valuable. There will always be sources of errors during experimentally testing, both from assumptions and uncertainties which are discussed in this chapter.

7.1.1 Validation of the Results from the Experimental Measures

The accuracy of the experimental measures from the permeability cabinet and the assumption used in the equation will affect the result of the calculated permeability coefficient.

7.1.1.1 Accuracy of the Experimental Measurement

From the permeability cabinet, two pressure transmitters from MKS Instruments, type 121AA, was used. One, on the low-pressure side, with the pressure range from 0-100 mbar and another, on the high-pressure side, with the pressure range from 0-15000 mbar. The error of both transmitters is 0.5% of measured value. The error in temperature variation in the system is approximately 0.3 % based on the accuracy of the temperature controller.

Due to the high accuracy of the transducers the result of the measurements will not be affected too much compared to the assumptions discussed below.

7.1.1.2 Assumption for the Experimental Measures and Calculation

The assumption used for calculating the permeability coefficient of CO_2, will give some errors for the result. By assuming the membrane as homogeneous with a uniform thickness through the whole membrane area will affect the permeation rate, P/L, but not the separation properties of the polymer. The thicker the membrane is the slower is the gas transport through the membrane. This can be solved by measuring each membrane thickness using e.g. a digital micrometer or by electron microscope images to give a more accurate thickness, and permeability coefficient.

The assumption of constant temperature affects the gas transport through a membrane and the partial pressure inside the cabinet. An increased temperature will result in an increase in the permeability coefficient. To achieve a better control of the temperature, a temperature transducer controlled from the program should be used instead of an indicator. A transducer would also lead to a better safety during experiment using high temperatures.

Assuming 0% humidity using vacuum in the system is an approximately good assumption. But polymers response to humidity in the air and whenever there is a difference in relative humidity between the inside and outside of a film the permeability coefficient is affected. By doing a study of how the humidity influence the material constant for the diffusion of CO_2 through polymers used in food packaging the consideration of the humidity could be evaluated.

All assumption used for calculation combined with the accuracy of the measurements leads to small errors for the calculated permeability coefficient. Thus, the main error in calculated permeability coefficients is caused by leakage in the system.

7.1.1.3 Leakage in the Permeability Cabinet

Polymers used for food packaging has a high CO_2 barrier, which means that the permeability coefficient and gas transport through these polymers are low compared with polymers used in membrane separation. A measure of the leakage in the permeability cabinet was done for each sample where the slope of the leakage in the system should be neglectable compared with the slope of the real measures. The slopes in all experimental measurements done was equal or close to the slope of the leakage seen in Figure 7-1.

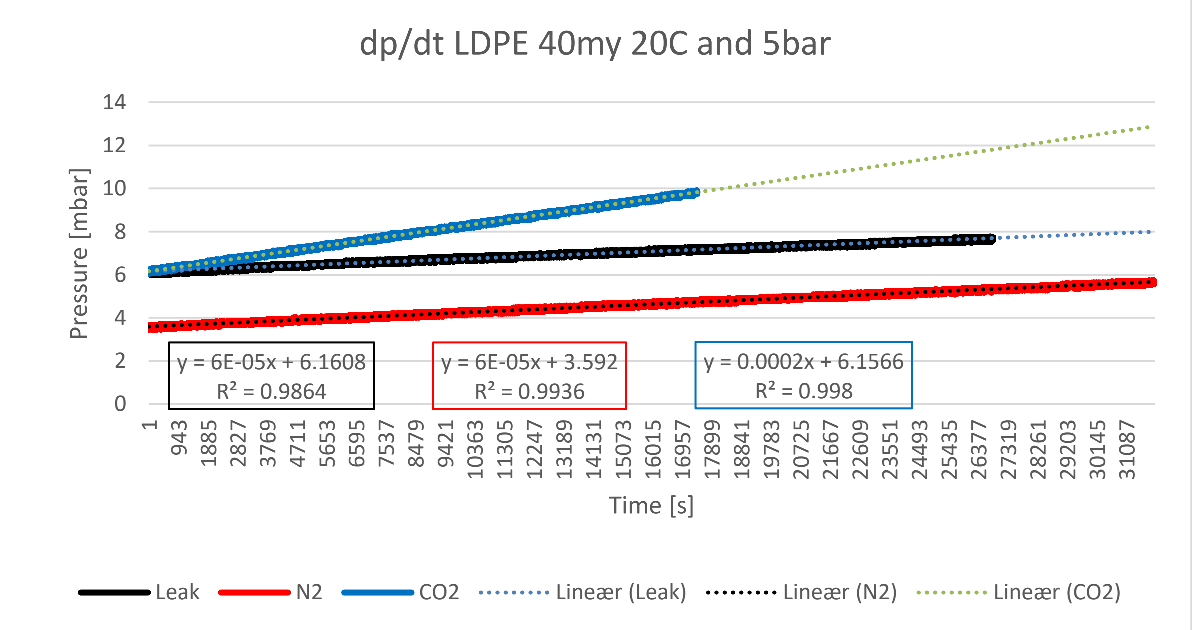


Figure 7-1: The slopes of the pressure increase using N_2, CO_2 through a membrane of 40 µm LDPE at 20°C compared with the slope of the leakage in the system.

Figure 7-1 shows an example of one result measuring the pressure increase through a 40µm membrane of LDPE at 20ºC using N_2 and CO_2 compared with the leakage in the system. The slopes for both the measures and the slope for the leakage in the system are nearly equal, and difficult to evaluate if the measuring was only the leakage in the system or the gas transport through the polymer membrane. An illustration test was performed using PDMS, which is an open membrane, where the gas transport is higher than for barrier membranes, seen in Figure 7-2.

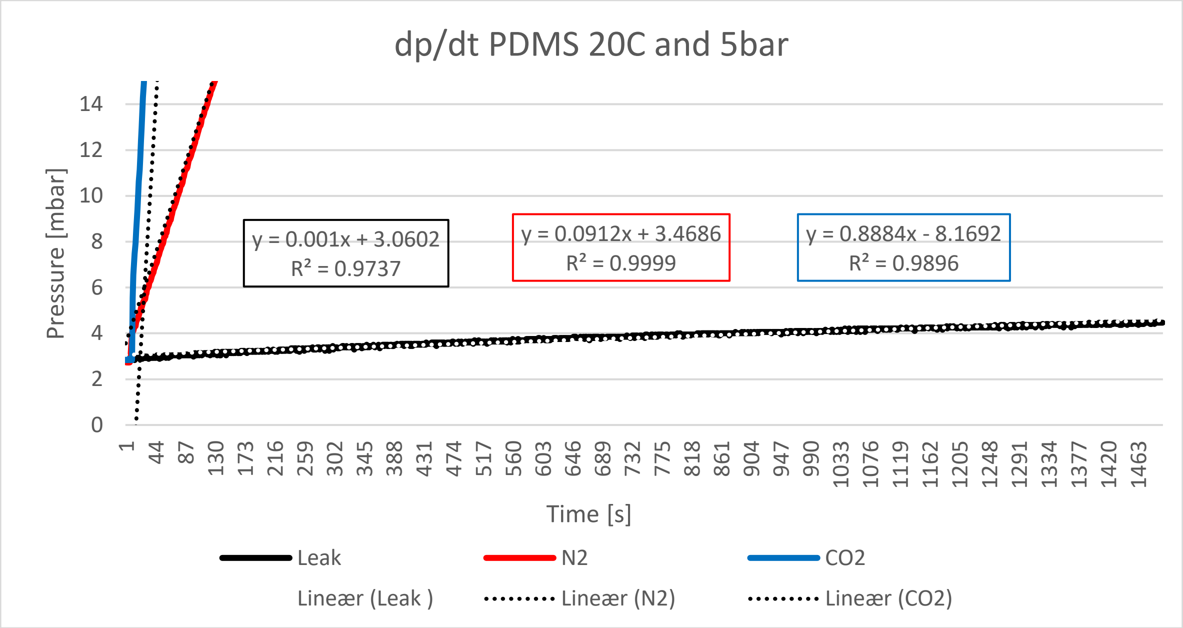


Figure 7-2: The slopes of the pressure increase using N_2, CO_2 through a membrane of PDMS at 20°C compared with the slope of the leakage in the system.

Figure 7-2 shows the slopes for the real measures, of both N_2 and CO_2, is steeper than the slope of the leakage in the system and illustrates the expected function for the measures in system where the leakage in the system is neglectable.

7.1.1.4 Comparing of the Illustration Test and Experimental measures

Calculating the % leakage for measuring the pressure increase of both N_2 and CO_2 in different polymers is shown in Table 7-1.

Table 7-1: The % leakage for the illustration test and the measured values.

Polymer	**Thickness [µm]**	**T [°C]**	**dp/dt Leak**	**dp/dt N_2**	**% leakage N_2**	**dp/dt CO_2**	**% leakage CO_2**
PDMS	-----	20	0.001	0.0912	1.1	0.8884	0.11
LDPE	40	20	0.00006	0.00006	100	0.0002	30
LDPE	125	20	0.00008	0.00007	not valid	0.00009	89
LDPE	125	30	0.00009	0.00008	not valid	0.0001	90
LDPE	125	40	0.0001	0.0001	100	0.0001	100
LDPE	125	50	0.0004	-----	----	0.0003	not valid
PP	250	20	0.00007	0.00005	not valid	0.00006	not valid

Table 7-1 shows the %leakage for the illustration test was between 0.11-1.1% compared with the %leakage for the experimental test was between 30-100%. This indicates a high leakage in the system when measuring polymer used as a barrier and gives the measures low accuracy.

A comparison of the calculated permeability coefficient measured in LDPE and in PDMS from the illustration test are listed in Table 7-2, together with the calculated selectivity.

Table 7-2: The permeability coefficient from the experimental measures and the illustration test.

Polymer	**N_2**		**CO_2**		**α**
T = 20°C	**P/L** **[m^3/m^2dayPa]**	**P $*10^{-13}$** **[m^3m/m^2dayPa]**	**P/L [m^3/m^2dayPa]**	**P $*10^{-13}$** **[m^3m/m^2dayPa]**	$\frac{P_{CO2}}{P_{N2}}$
PDMS	$5.4 * 10^{-07}$	----	$51.7 * 10^{-07}$	----	9.6
LDPE 40µm	$3.35 * 10^{-10}$	13.8	$10.7 * 10^{-10}$	44.1	3.2

The permeability (P/L) for PDMS using N_2 is lower than expected from the producer, which can be due to the leakage in the system. The calculated selectivity for CO_2/N_2 in LDPE are lower than for PDMS. From the theoretical study the selectivity for CO_2/N_2 in polymers are higher than 10, which also indicates a high leakage in the system.

To detect the leakage in the system, high pressure of helium combined with soap bubbles and a gas sniffer was used. This results in replacing the pipes, valves and some of the couplings. O-rings was replaced couplings and the membrane-cell was cleaned.

The test using aluminium, which is a close material, as membrane indicates high leakage in the system after replacing and fixing. The experimental measures were stopped and the model was found using material constants from the alternative method.

For using the permeability cabinet for measuring the gas transportation through barrier membranes, some suggestions for optimisation of the existing system is:

- Reconstruct the system using less couplings to decrease possible leakage.
- Changes the low-pressure transmitter using a higher-pressure range where atmospheric pressure can be used instead of vacuum on the low-pressure side.
- Implement a temperature controller into the LabVIEW program for more accuracy of the temperature measurement and for safety reason.
- Make the membrane-cell larger for using lager membranes which increase the area for the diffusion.

Another consideration of the leakage problems can be if the CO_2 is absorbed into the pipes because of the porous walls caused by corrosion, this can also affect the gas transport through the membrane.

7.1.2 Validation of the Results from the Alternative Method

The accuracy for the material factors found from the alternative method for develop a model for the diffusion of CO_2, is discussed because of the leak of information from the source.

7.1.2.1 Innoform Testservice

Innoform Testservice used the standards ISO 15105-1 and DIN 53380T2 for measuring four samples, where the samples were conditioned for at least two days in the specified testing climate. The accuracy of the measured material constant is not specified but due to the standards used for the measures these coefficients are considered valuable.

From simulating the measured permeability coefficients and comparing the result with literature values in Chapter 6.2.4, the measured coefficients are smaller than the values from literature. This can be due to the difference in structure and properties of the polymer, and the method used for estimating the permeability coefficients.

Using an external test-centre for finding the necessary material constants is expensive, therefore only four samples was measured.

7.1.2.2 Literature Values

The material coefficients found from the literature was gathered from different sources, where the specified details used for the measures was given. The specified detail for each value differed from each source, were the specified conditions could be e.g. method, relative humidity, film thickness, temperature, material structure or standards used.

The material constants for a polymer is not constant because polymers can be processed differently which will affect the properties and the gas transport of the polymers. The leak of information gives a high uncertainty for material coefficient found in the literature, but these material coefficients was used for comparing and simulating trends in the model.

7.2 Validation of the Mathematical Model

For developing a mathematical model of the diffusion of CO_2 through a polymeric membrane based on empiric relations different assumption was used. The model of the consumption of CO_2 through polymer membranes are considered for a single polymer layer, under steady state conditions in an environment of 0% humidity using different temperatures.

7.2.1 Accuracy of the Assumptions

The system was considered as an ideal system where the solubility and diffusivity are constant due to low concentrations of the gas. Polymers films can vary in thickness which can affect the permeation rate of CO_2, therefore in this model the thickness is considered as uniform.

The ideal model is highly valid for polymers in their rubbery state because of the assumed henrys sorption isotherm used in the solubility equation. In the glass transition the accuracy of the model is not considered. In glassy polymers, a non-ideal behavior is observed where the dual mode sorption is used for the solubility. Due to the low pressure used in system, the ideal situation can be used for glassy polymers.

The polymeric barrier is considered as homogeneous, which means the pressure is uniform through the whole membrane thickness and all mass transport occurs only in the x-direction across the membrane thickness. Mass transport occurs in other directions, e.g. along the membrane, is low compared with the transport across a thin polymer film.

This model considers only the diffusion of CO_2 through the membrane, and neglecting emerging of CO_2 into the product inside the packaging. CO_2 can react with water and form carbon acid which can harm the product and affect the properties of the polymeric packaging.

The mass transport through a polymer depends on different properties of the membrane and the material constants should be found experimentally due to the leak of information from external measures to obtain a good validation of the model.

7.2.2 Evaluation of the Simulations

The temperature dependency model based on Arrhenius relation shows a good trend, but should be further studied using experimental material coefficients for all polymers studied. The activation energies can achieve a higher accuracy plotting the Arrhenius relation of lnP vs 1/T for each polymer.

The simulated model of the consumption of CO_2 inside a polymeric packaging gives a good description of the gas diffusion. The model does not consider what is inside the packaging, only the gas transport through polymers.

From the simulations of the model using the material coefficients found in the literature compared with the measured material constants from Innoform Testservice, it was observed curves following the same trends. Using more experimental values, and studies of other properties will do the model more accurate and complete.

7.3 Further work

For a more accurate and complete model of the diffusion of CO_2 through different polymers used in food packaging different studies can be done.

- Experimental measures of the material constants by either fix and replace equipment on the already exiting permeability cabinet or use another method for finding the empirical material constants.
- A study of how the humidity influence the material constant for the diffusion of CO_2 through polymers used in food packaging.
- A study of the diffusion of CO_2 through polymers used in food packaging using different film layers.
- Experimental measures of the solubility of CO_2 in the polymers used in food packaging.
- A study of the diffusion of CO_2 through different polymers used in food packaging in a non-ideal environment.

8 Conclusion

The model of diffusion of CO_2 through different polymers was found from a theoretical study of the gas transport in polymeric membranes. Relevant material factors were found either experimentally, from the literature or from the external test-center Innoform Testservice.

From the theoretical study of the gas transport through polymer membranes the permeability coefficient depends on many properties; High temperatures and relative humidity increases the permeability coefficient of CO_2 in polymers, while high density and degree of crystallinity decreases the permeability coefficient. Crosslinking and orientation in polymers will also have a decreasing effect on the permeability.

Rubbery polymers have higher permeation rate than glassy polymers, and the thickness of the polymer membrane affects the permeation rate.

The measured values from the experiment cannot be used in the model because of the high uncertainty due to the leakage in the system. The result from Innoform Testservice is reliable and can be used for simulating and an evaluation of the model. Material factors found in the literature can be used for comparing trends simulated in the model with measured material constants.

The temperature dependency of the permeability coefficient of CO_2 is modeled using the relations from Arrhenius seen in Eq. (8.1).

$$P_{CO_2 2} = P_{CO_2 1} e^{\frac{E_p}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \tag{8.1}$$

The temperature dependency model shows a good trend from simulations, but should be further studied using experimental material coefficients. The suggested model for diffusion of CO_2 through different polymers used in food packaging is seen in Eq. (8.2) and Eq. (8.3).

$$p_{CO_2-1(t=t)} = p_{CO_2-2} - \left(p_{CO_2-2} - p_{CO_2-1(t=0)}\right)e^{kt} \tag{8.2}$$

$$k = -\frac{P_{CO_2} ART}{LVV_G} t \tag{8.3}$$

This model describes the consumption of CO_2 through polymeric barriers using a single polymer layer, under steady state conditions and in an environment of 0% relative humidity for different temperatures. This model can be used for estimating and simulations of the diffusion of CO_2 through polymer membranes validated with material factors found experimentally.

To achieve a higher accuracy of the model, experimental values should be used towards with other studies affecting the diffusion of CO_2 through polymers, like the humidity and different polymer layers is recommended.

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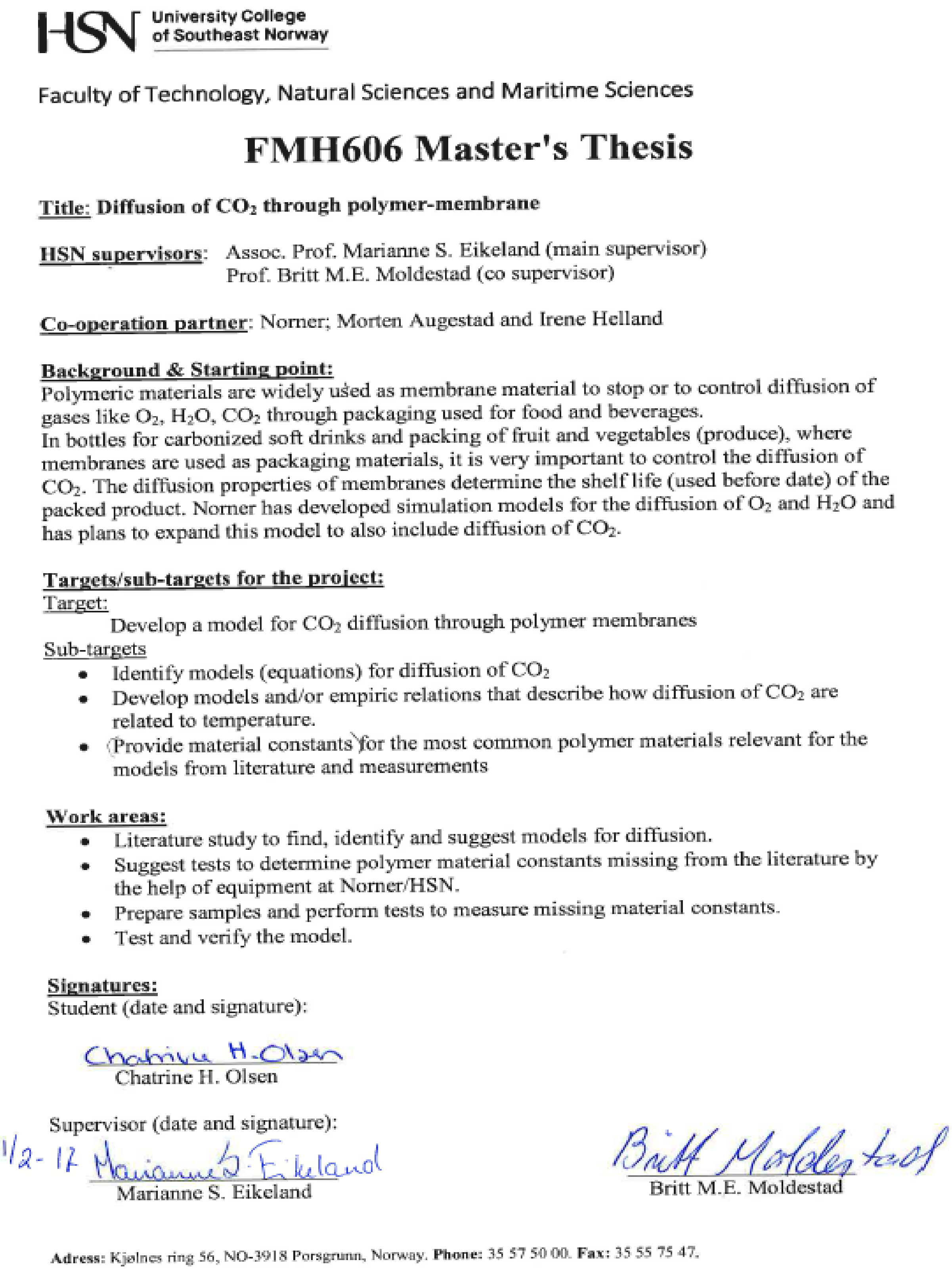
Appendices

Appendix A: Task Description



HSN University College of Southeast Norway

Faculty of Technology, Natural Sciences and Maritime Sciences

FMH606 Master's Thesis

Title: Diffusion of CO_2 through polymer-membrane

HSN supervisors: Assoc. Prof. Marianne S. Eikeland (main supervisor)
Prof. Britt M.E. Moldestad (co supervisor)

Co-operation partner: Norner; Morten Augestad and Irene Helland

Background & Starting point:
Polymeric materials are widely used as membrane material to stop or to control diffusion of gases like O_2, H_2O, CO_2 through packaging used for food and beverages.
In bottles for carbonized soft drinks and packing of fruit and vegetables (produce), where membranes are used as packaging materials, it is very important to control the diffusion of CO_2. The diffusion properties of membranes determine the shelf life (used before date) of the packed product. Norner has developed simulation models for the diffusion of O_2 and H_2O and has plans to expand this model to also include diffusion of CO_2.

Targets/sub-targets for the project:
Target:
Develop a model for CO_2 diffusion through polymer membranes
Sub-targets
- Identify models (equations) for diffusion of CO_2
- Develop models and/or empiric relations that describe how diffusion of CO_2 are related to temperature.
- Provide material constants for the most common polymer materials relevant for the models from literature and measurements

Work areas:
- Literature study to find, identify and suggest models for diffusion.
- Suggest tests to determine polymer material constants missing from the literature by the help of equipment at Norner/HSN.
- Prepare samples and perform tests to measure missing material constants.
- Test and verify the model.

Signatures:
Student (date and signature):

Chatrine H. Olsen
Chatrine H. Olsen

Supervisor (date and signature):

1/2-17 Marianne S. Eikeland
Marianne S. Eikeland

Britt Moldestad
Britt M.E. Moldestad

Adress: Kjølnes ring 56, NO-3918 Porsgrunn, Norway. **Phone:** 35 57 50 00. **Fax:** 35 55 75 47.

Appendix B: Procedure of running the Permeability Cabinet

Figure 8-1 shows the system for finding the permeability constant for the different polymers in this experiment, with equipment and equipment-number used in the procedure.

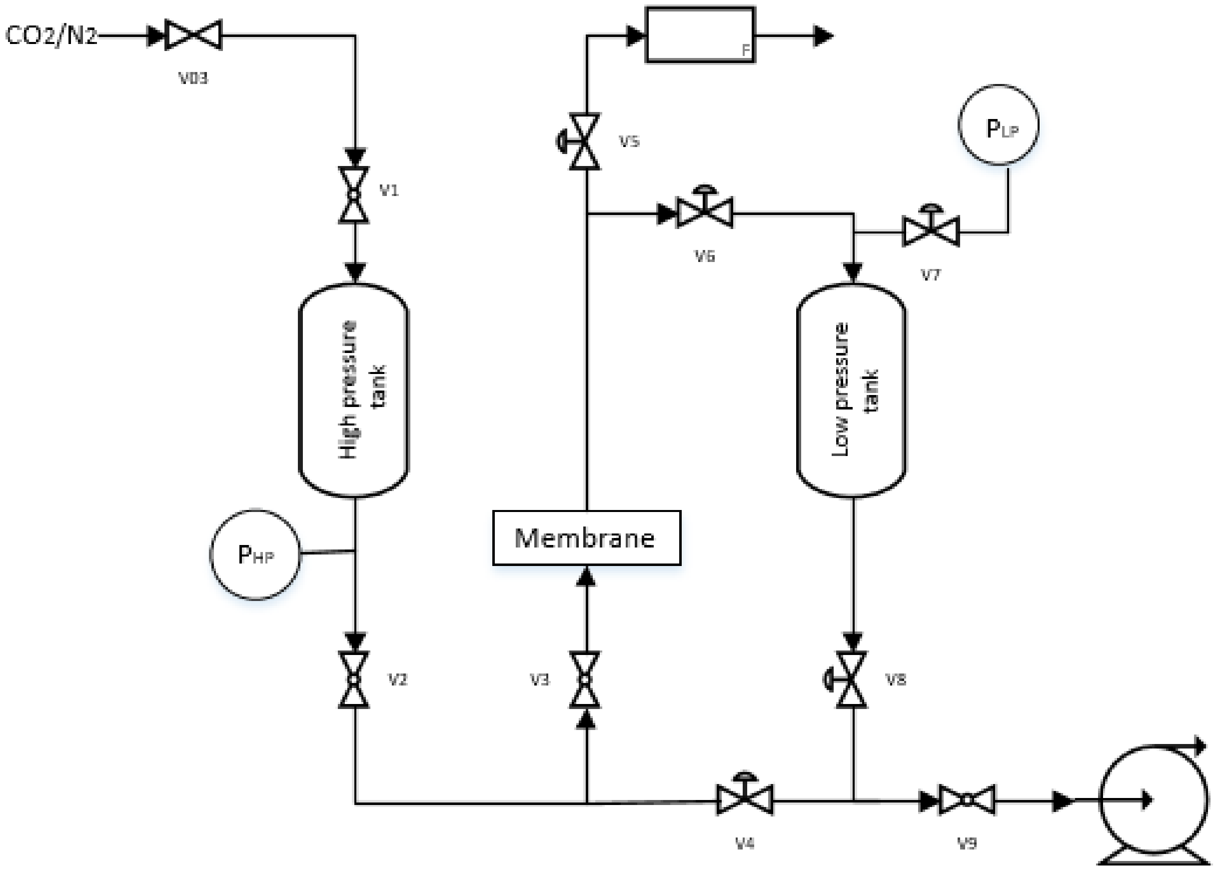


Figure 8-1: Flow sheet of the system.

Procedure for running the permeability system:

I. Membrane:
1) Make the membrane by stamping it out from the polymer film and place it in the membrane cell.

II. Starting the system:
2) Set all valves to their closed position and get to know the system before starting up using the switch behind the cabinet (make sure the system is connected to power).
3) Start the program Pressure_Logger.vi in LabVIEW at the computer and create a filename for storing the measurements.
4) Run the program using the white arrow up at the left corner.

III. Prepare the system for measuring by evacuation:

  5) Evacuate the system by:
    a. Valve V5 is always closed.
    b. Open the valves V6 and V7.
    c. Turn on the vacuum pump and open the valves: V9, V8, V2, V3, V4 and V1 respectively.
    d. Look at the high-pressure measures in LabVIEW and evacuate until the pressure is below 30 mbar.
    e. Close the valves: V1, V2, V3 and V4.
    f. Look at the low-pressure measures in LabVIEW and evacuate until the pressure is 3 mbar.
    g. Close the valves V8 and V9 and turn off the vacuum pump.

IV. Leaking test before replacing membranes.

  6) Make sure the system is in vacuum after evacuation.
  7) Press the “Start logging data” button in the LabVIEW program. A green light will turn on in the screen.
  8) Let the system run for 3-4 hours.
  9) Stop logging by pressing the “Stop logging data” in the LabVIEW program.
  10) Press the “Stop program” button in the LabVIEW program and create a new filename for storing new measurements.
  11) Run the program using the white arrow up at the left corner.
  12) Repeat the evacuating procedure in point III.

Figure 8-2 shows a drawing of the pressurized gas bottle for filling the permeability system, with the equipment-numbers used in the procedure.

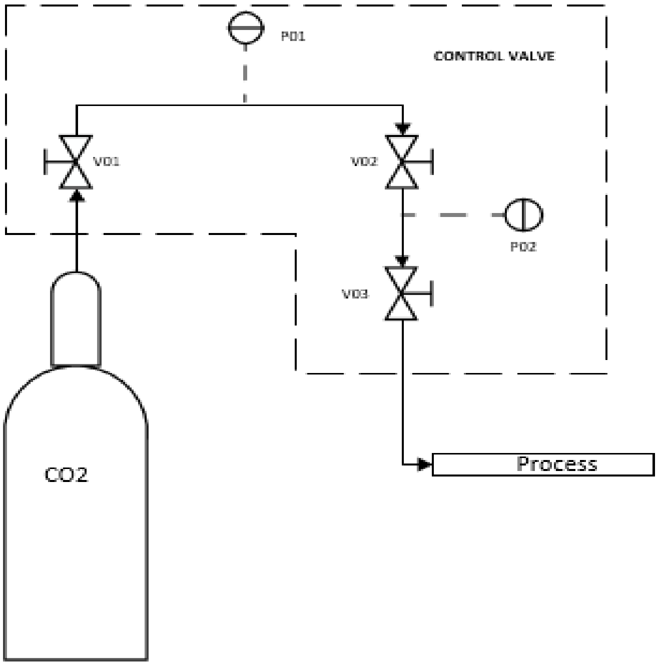


Figure 8-2: A pressurized gas bottle with the control valve.

V. Filling the system with gas

13) Connect the pressurized bottle with the right gas for the measurement (CO_2 or N_2).
14) Start filling by:
    a. Open valve V03.
    b. Adjust the pressure gauge, P02, using the control valve, V02, until 6 bar.
    c. Open valve V01.
    d. Open V1 in the process and fill the high-pressure tank with gas until the pressure has reached 5000 mbar (5 bar) by watching the measures of the high-pressure in LabVIEW.
    e. Close valve V1.
15) Close the control valve by:
    a. First close valve V01, then valve V03.
    b. Release valve V02

VI. Running the experimental test:

16) Press the “Start logging data” button in the LabVIEW program. A green light will turn on in the screen.
17) Open valve V2 and V3.
18) Let the process run for at least 4 hours.
19) Stop logging using the “stop logging” button in LabVIEW. The data is logged and stored in a file.
20) The saved measurements can now be analyzed.

VII. Changing the gas:

21) Press the “Stop program” button in the LabVIEW program and create a new filename for storing new measurements.
22) Run the program using the white arrow up at the left corner.
23) Repeat the evacuation procedure in point 4. OBS! Under point 4b, also open V03 for releasing the pressure on the control valve, V02. The pressure gauge shall be 0 bar before closing V03. Continue the evacuation until the low pressure shows 5 mbar.
24) Close all valves.
25) Repeat procedure V, Filling the system with gas.
26) Repeat procedure VI, Running the experimental test.

VIII. Stop the process:

27) Repeat the evacuation procedure in point 4. Under point 4b, also open V03 for releasing the pressure on the control valve, V02. The pressure gauge shall be 0 bar before closing V03. Continue the evacuation until the low pressure shows 5 mbar.
28) Close all valves.
29) Turn off the switch behind the cabinet.

Appendix C: Mathematical Background for the Permeability Cabinet.

Using relative low pressures and simple non-polar gases when operating the system, this system can be described using the ideal gas law from Eq. (8.4).

$$pV = nRT \tag{8.4}$$

Where p is the pressure [Pa] of a gas, V is the volume [m^3] occupied, n is the number of mole [mol] of a gas, R is the gas constant [J/(K mol)] and T is the temperature [K] of the gas.

Using the ideal gas law on the low-pressure side, further referred as 2, with a constant volume and temperature, the change of mole per time on this side is given from Eq. (8.5).

$$\frac{dn_2}{dt} = \frac{V}{RT}\frac{dp_2}{dt} \tag{8.5}$$

The mole change is further converted to a gas volume by Eq. (8.6) at standard pressure, p_0, and temperature, T_0.

$$\frac{dV_{0.2}(n_2)}{dt} = \frac{T_0 R}{P_0}\frac{dn_2}{dt} \tag{8.6}$$

The molar volume, V_0, for gases at STP is 0.022414 m^3/mol. The flux of a gas given over a permeation area A of the membrane is described in Eq. (8.7) combined with Eq. (8.5) and Eq. (8.6).

$$N_A = \frac{dV_{0.2}(n)}{dt}\frac{1}{A} \Rightarrow \frac{1}{A}\frac{T_0 R}{P_0}\frac{V}{RT}\frac{dp_2}{dt} \Rightarrow \frac{1}{A}\frac{T_0}{P_0}\frac{V}{T}\frac{dp_2}{dt} \tag{8.7}$$

Where the area of the membrane is found by using Eq. (8.8).

$$A = \frac{\pi D^2}{4 \cdot 10^{-4}} \tag{8.8}$$

Where D is the diameter [m] of the membrane. The flux of a gas through a membrane using the relation of Fick's law of diffusion and Henrys law of solubility is given in Eq. (8.9).

$$N_A = \frac{P_A \cdot (p_{A2} - p_{Al})}{L} = \frac{P_A}{L}\Delta p \tag{8.9}$$

Combining Eq. (8.7) and Eq. (8.9) the relation for the pressure change, dp/dt, and the permeability coefficient, P/L, is found in Eq. (8.10).

$$\frac{P}{L} = \frac{1}{A}\frac{VT_0}{Tp_0(p_1 - p_2)}\frac{dp_2}{dt} \tag{8.10}$$

This relation is used in this experiment for finding experimental values for the model.

Appendix D: Measures and Calculation for the Experimental Tests

Measures used for the calculations from the experimental test are plotted in graphs and can be seen in Figure 8-3, Figure 8-4, Figure 8-5, Figure 8-6, Figure 8-7, Figure 8-8 and Figure 8-9.

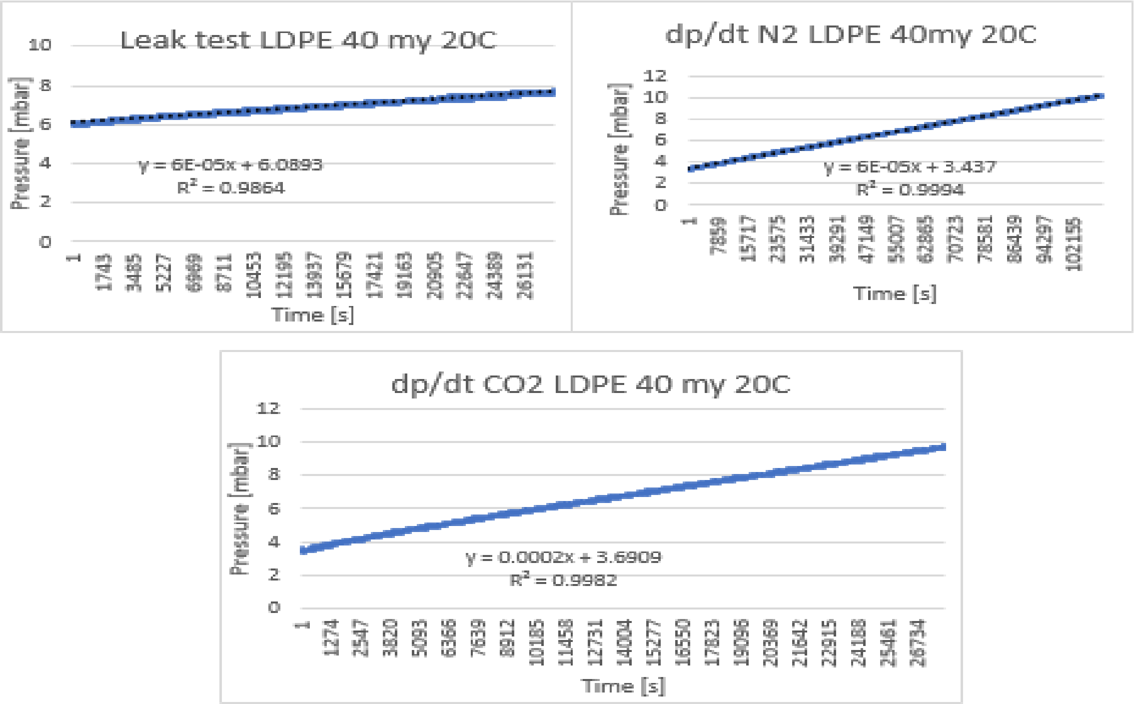


Figure 8-3: The measures used from LDPE 40µm at 20°C.

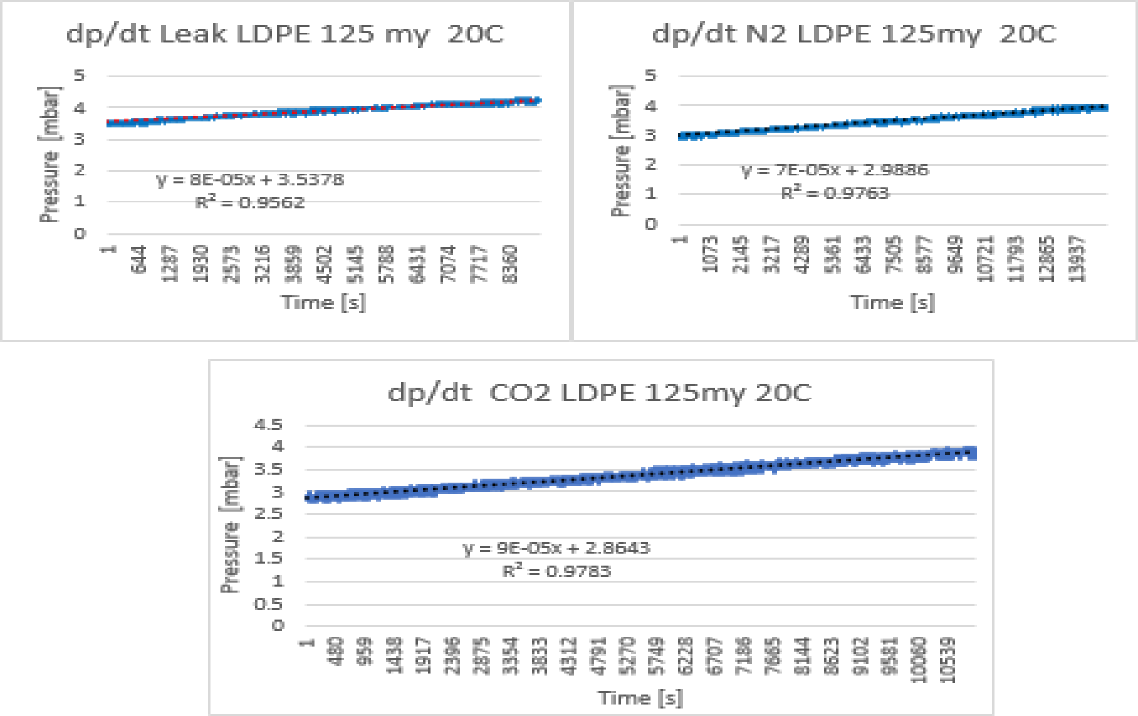


Figure 8-4: The measures used from LDPE 125µm at 20°C.

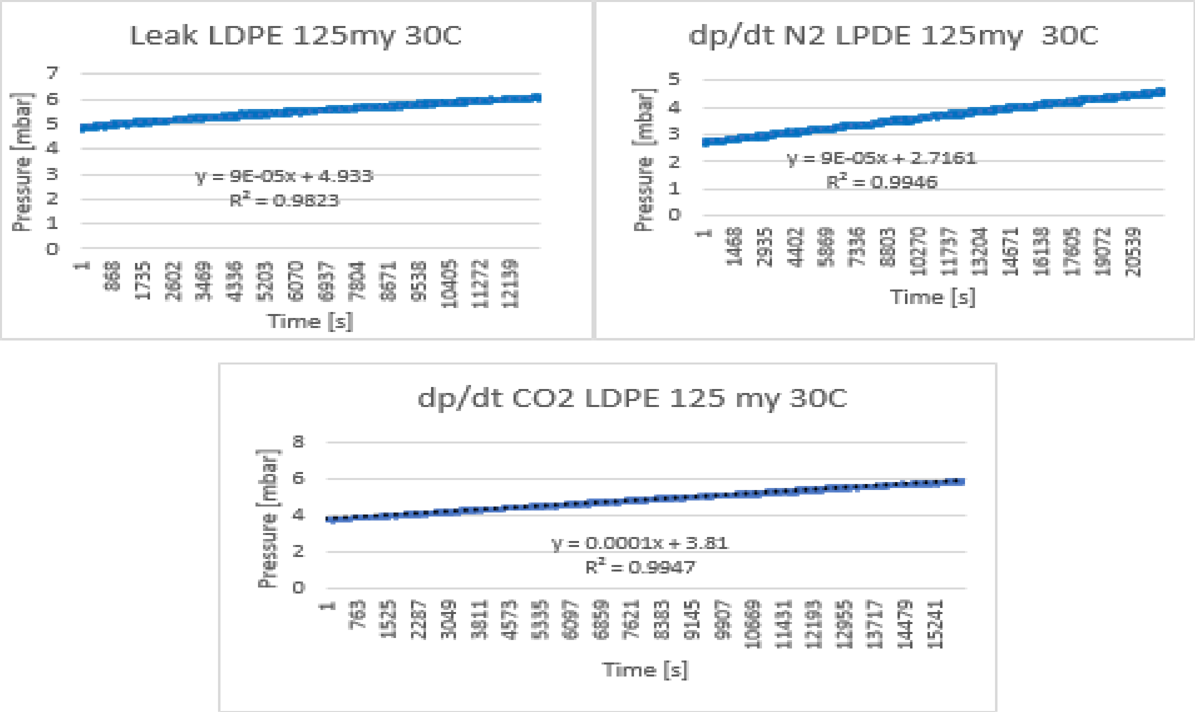


Figure 8-5: The measures used from LDPE 125µm at 30°C.

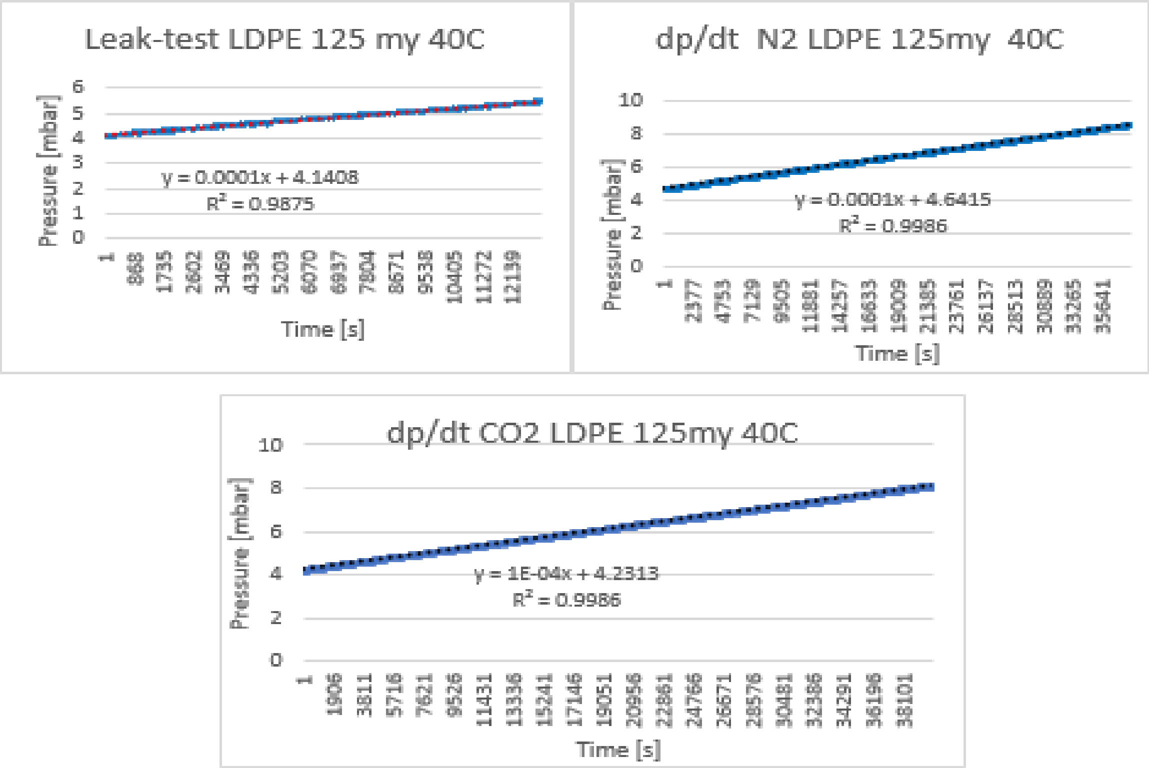


Figure 8-6: The measures used from LDPE 125µm at 40°C.

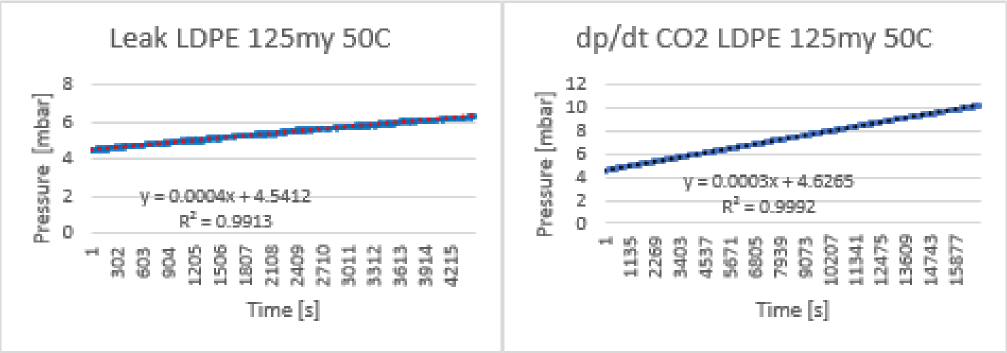


Figure 8-7: The measures used from LDPE 125µm at 50°C.

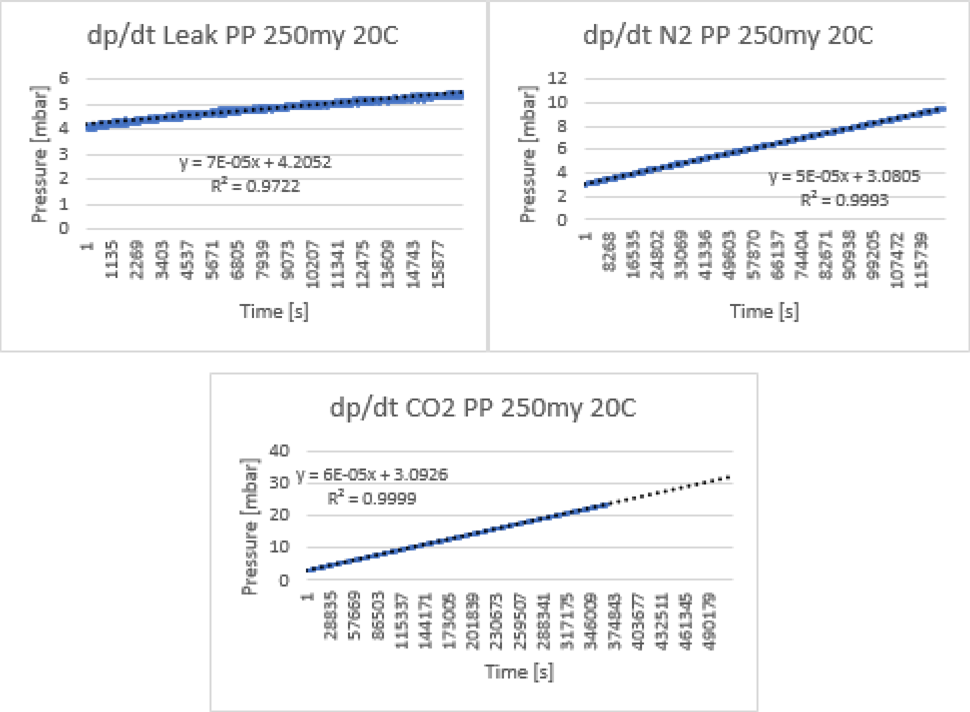


Figure 8-8: The measures used from PP 250µm at 20°C.

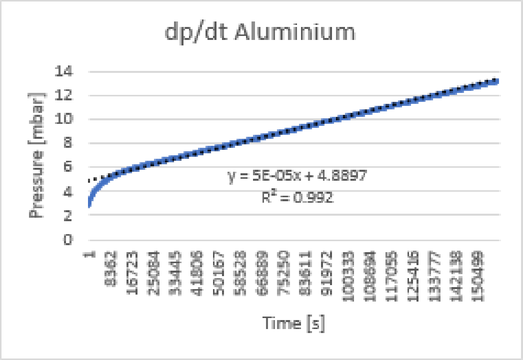


Figure 8-9: The measures used from aluminium test.

The measures were used for the calculations using Eq.(8.11)

$$P = \frac{L}{A} \frac{VT_0}{Tp_0(p_1 - p_2)} \frac{dp_2}{dt} \tag{8.11}$$

Where:

- $\Delta p \approx 5$bar
- A = 2.8339 cm^2
- V = 1dm^3
- T_0 = 273.15 K
- p_0 = 1.01325 bar

The result from the calculations are listed in Table 8-1.

Table 8-1: The results from calculations from the experiment.

		N_2		**CO_2**	
Polymer	**T [C]**	**dp/dt**	**P_{N2} *10^{-13} [m^3m/m^2dayPa]**	**dp/dt**	**P_{CO2}*10^{-13} [m^3m/m^2dayPa]**
LDPE 40 µm	20	6*10^{-5}	13.8	0.0002	44.1
LDPE 125 µm	20	7*10^{-5}	49.8	9*10^{-5}	62.2
LDPE 125 µm	30	9*10^{-5}	57.2	0.0001	67.2
LDPE 125 µm	40	0.0001	65.2	0.0001	63.8
LDPE 125 µm	50			0.0003	172.4
PP 250 µm	20	5*10^{-5}	68.9	6*10^{-5}	92.5
Aluminium		5*10^{-5}			

Illustration Test:

Measures used for the calculations from the experimental test are plotted in graphs and can be seen in Figure 8-10.

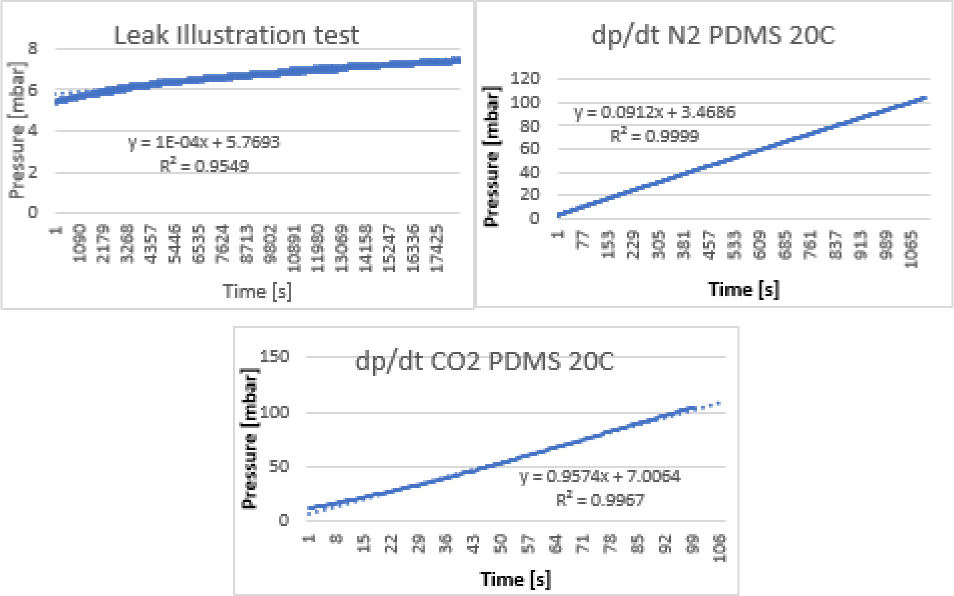


Figure 8-10: The measures used from the illustration test, PDMS, at 20°C.

The measures were used for the calculations using Eq. (8.12)

$$\frac{P}{L} = \frac{1}{A}\frac{VT_0}{Tp_0(p_1 - p_2)}\frac{dp_2}{dt} \tag{8.12}$$

Where:

- $\Delta p \approx 5$bar
- A = 2.8339 cm^2
- V = 1dm^3
- T_0 = 273.15 K
- p_0 = 1.01325 bar

The result from the calculations can be seen in Table 8-2.

Table 8-2: The result from the calculations of P/L from the illustration test.

		N$_2$		**CO$_2$**	
Polymer	**T [C]**	**dp/dt**	**P7L$_{N2}$ *10^{-7} [m^3/m^{2}dayPa]**	**dp/dt**	**P/L$_{CO2}$*10^{-13} [m^3/m^{2}dayPa]**
PDMS	20	0.0912	5.4	0.9574	51.7

Appendix E: Test results from Innoform Testservice

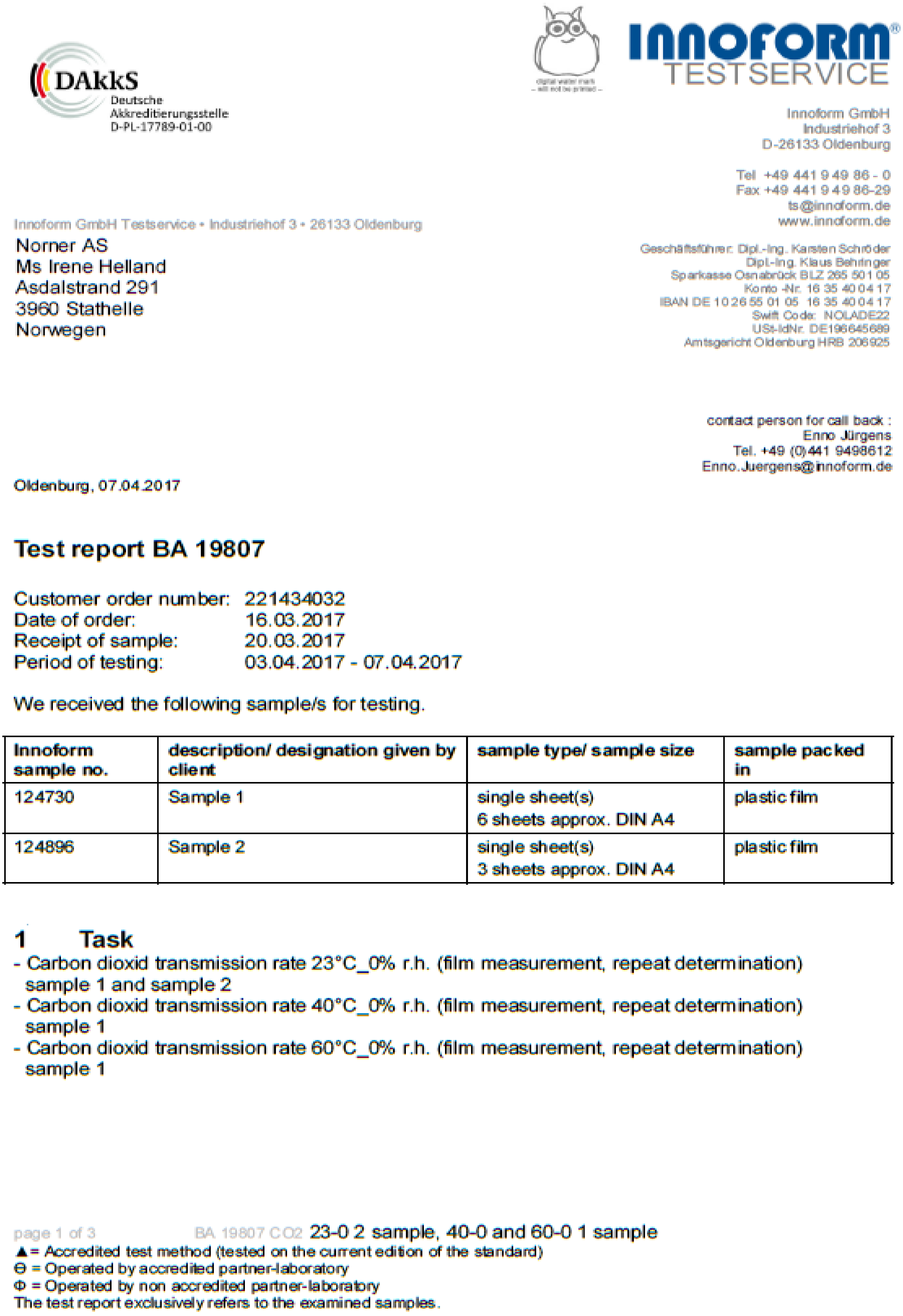
The test results from Innoform are listed in Table 8-3.

Table 8-3: Test results from Innoform Testservice.

		Test 1		**Test 2**	
Film	**Temperature [°C]**	**Thickness [µm] (average)**	**P/L [cm^3/m^{2}dbar]**	**Thickness [µm] (average)**	**P/L [cm^3/m^{2}dbar]**
LDPE	23	124	4460	113	5070
PP	23	250	820	252	800
LDPE	40	124	9600	113	11000
LDPE	60	124	19000	113	21000

Eq. (8.13) is used to convert the results of the permeation rates to the units used in this thesis.

$$\frac{cm^3 \mu m}{m^2 day bar} = \frac{\left(cm \frac{m}{100 cm}\right)^3 \left(\mu m \frac{m}{10^6 \mu m}\right)}{m^2 day \left(bar \frac{10^5 Pa}{bar}\right)} = 1*10^{-17} \frac{m^3 m}{m^2 day Pa} \tag{8.13}$$



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Oldenburg, 07.04.2017

Test report BA 19807

Customer order number:	221434032
Date of order:	16.03.2017
Receipt of sample:	20.03.2017
Period of testing:	03.04.2017 - 07.04.2017

We received the following sample/s for testing.

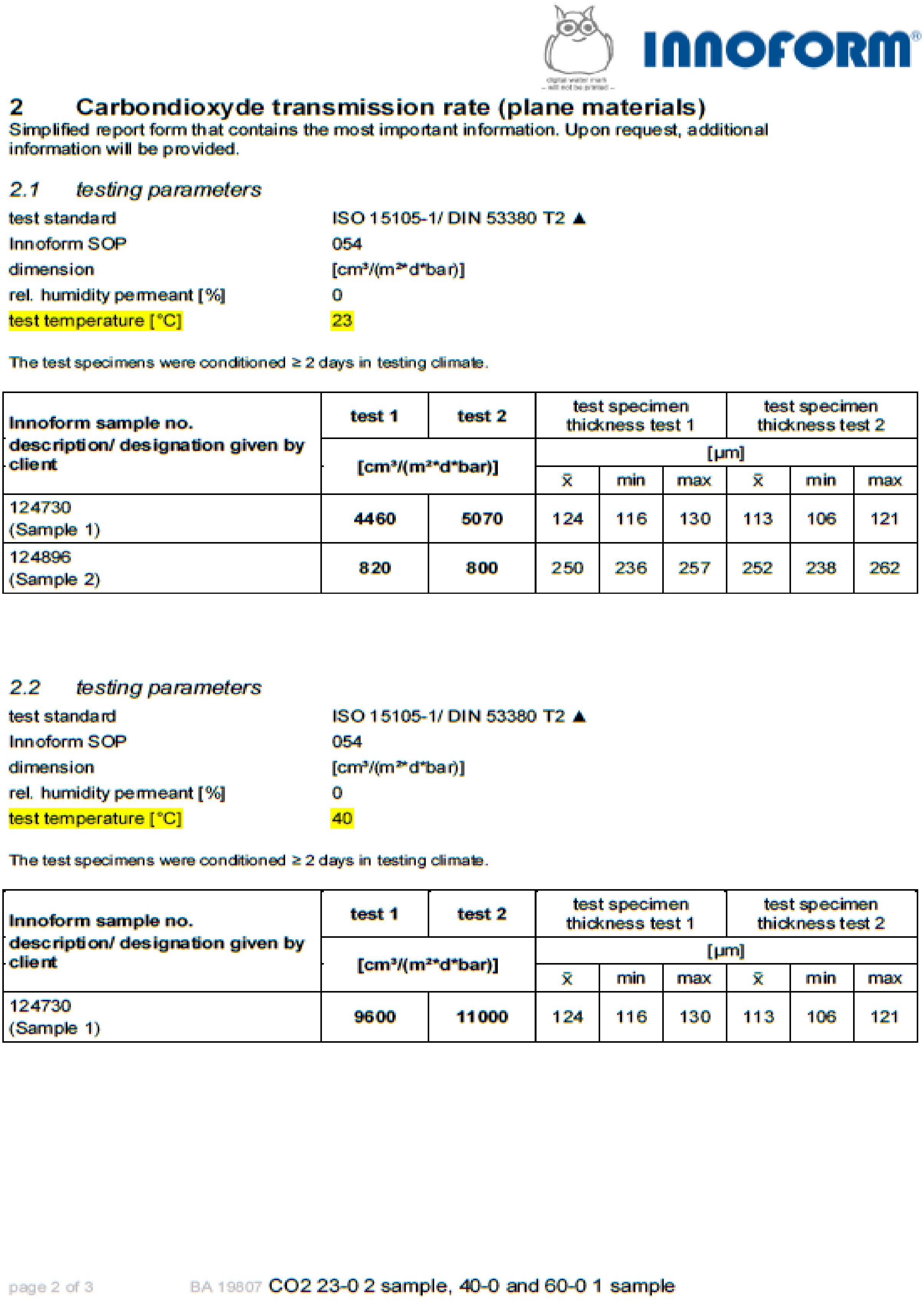
Innoform sample no.	description/ designation given by client	sample type/ sample size	sample packed in
124730	Sample 1	single sheet(s) 6 sheets approx. DIN A4	plastic film
124896	Sample 2	single sheet(s) 3 sheets approx. DIN A4	plastic film

1 Task

- Carbon dioxid transmission rate 23°C_0% r.h. (film measurement, repeat determination) sample 1 and sample 2
- Carbon dioxid transmission rate 40°C_0% r.h. (film measurement, repeat determination) sample 1
- Carbon dioxid transmission rate 60°C_0% r.h. (film measurement, repeat determination) sample 1

page 1 of 3 BA 19807 CO2 23-0 2 sample, 40-0 and 60-0 1 sample

▲ = Accredited test method (tested on the current edition of the standard)
ϴ = Operated by accredited partner-laboratory
Φ = Operated by non accredited partner-laboratory
The test report exclusively refers to the examined samples.



2 Carbondioxyde transmission rate (plane materials)

Simplified report form that contains the most important information. Upon request, additional information will be provided.

2.1 *testing parameters*

test standard	ISO 15105-1/ DIN 53380 T2 ▲
Innoform SOP	054
dimension	[cm^3/(m^2*d*bar)]
rel. humidity permeant [%]	0
test temperature [°C]	23

The test specimens were conditioned ≥ 2 days in testing climate.

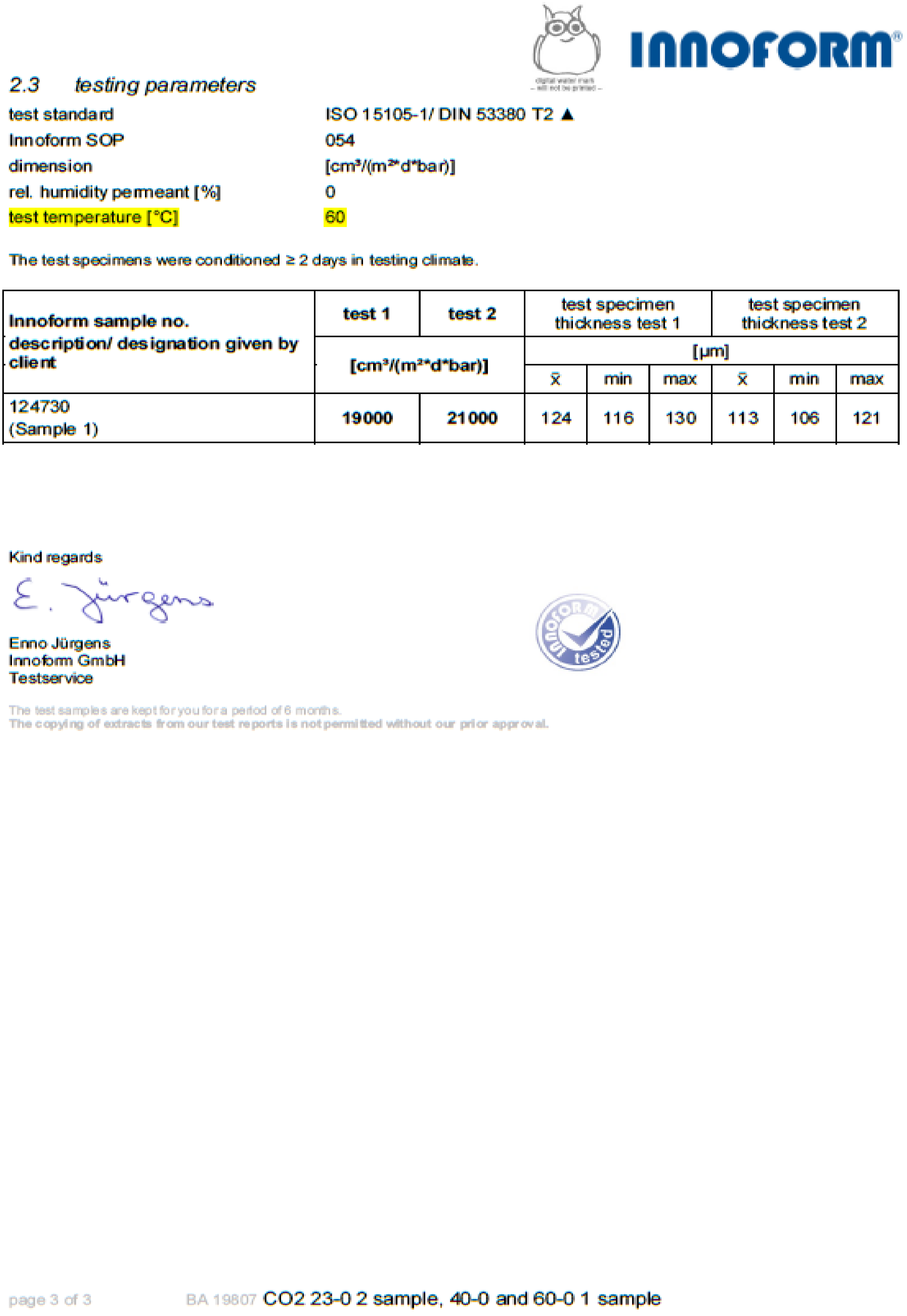
Innoform sample no. description/ designation given by client	**test 1**	**test 2**	test specimen thickness test 1			test specimen thickness test 2		
	[cm^3/(m^2*d*bar)]		[µm]					
			$\bar{x}$	min	max	$\bar{x}$	min	max
124730 (Sample 1)	**4460**	**5070**	124	116	130	113	106	121
124896 (Sample 2)	**820**	**800**	250	236	257	252	238	262

2.2 *testing parameters*

test standard	ISO 15105-1/ DIN 53380 T2 ▲
Innoform SOP	054
dimension	[cm^3/(m^2*d*bar)]
rel. humidity permeant [%]	0
test temperature [°C]	40

The test specimens were conditioned ≥ 2 days in testing climate.

Innoform sample no. description/ designation given by client	**test 1**	**test 2**	test specimen thickness test 1			test specimen thickness test 2		
	[cm^3/(m^2*d*bar)]		[µm]					
			$\bar{x}$	min	max	$\bar{x}$	min	max
124730 (Sample 1)	**9600**	**11000**	124	116	130	113	106	121



INNOFORM®

2.3 *testing parameters*

test standard	ISO 15105-1/ DIN 53380 T2 ▲
Innoform SOP	054
dimension	[cm³/(m²*d*bar)]
rel. humidity permeant [%]	0
test temperature [°C]	60

The test specimens were conditioned ≥ 2 days in testing climate.

Innoform sample no. **description/ designation given by client**	**test 1**	**test 2**	test specimen thickness test 1			test specimen thickness test 2		
	[cm³/(m²*d*bar)]		[µm]					
			x̄	min	max	x̄	min	max
124730 (Sample 1)	**19000**	**21000**	124	116	130	113	106	121

Kind regards

E. Jürgens

Enno Jürgens
Innoform GmbH
Testservice

innoform tested

Appendix F: Permeability Coefficients from the Literature, their Converting and References.

The permeability coefficient used in this project are found in the literature and is given in Table 8-4 below. The coefficient found has a temperature-range from 0 ºC to 50 ºC in different polymers. The gas used is CO_2 and N_2 and the selectivity of these gases are also calculated.

Table 8-4: Permeability coefficients from literature and their converted values.

Type Polymer	T [C]	Tg [C]	P_{N2}	P_{N2} Converted	P_{CO2}	P_{CO2} Converted	$\frac{P_{CO_2}}{P_{N_2}}$
LDPE [29]	25	-(95-130) [17]	0.7 [29]	6.05	10 [29]	86.4	14
LDPE [7]	25		0.73 [7]	6.3	9.5 [7]	82.1	13
LDPE [21]*	25		71 [21]	7	959 [21]	94.6	13
LDPE [21] **	25		71 [21]	7	1060 [21]	104.6	15
LDPE [30]	30		19 [30]	12.3	352 [30]	228.1	19
HDPE [21]	23		21 [21]	2.07	136 [21]	13.4	6
HDPE [21]	24		15-23 [21]	1.5-2.3	236-275 [21]	23.3-27.1	12-15
HDPE [29]	25	-(120-140) [17]	0.1 [29]	0.86	0.3 [29]	2.6	3
HDPE [7]	25		0.11 [7]	0.95	0.27 [7]	2.33	2
HDPE [21]**	25		17 [21]	1.68	228 [21]	22.5	13
HDPE [30]	30		2.7 [30]	1.75	35 [30]	22.68	13
PP [29]	30	-10 [17]	0.3 [29]	2.59	6 [29]	51.84	20
PP [7]	30		0.33 [7]	2.85	6.9 [7]	59.62	21
PP [30]	30		-----	-----	92 [30]	59.62	-----
PET [29]	25	81 [17]	0.004 [29]	0.035	0.2 [29]	1.73	49
PET [21]#	25		0.39 [21]	0.038	6.3 [21]	0.62	16
PET [21]**	25		0.28-0.39 [21]	0.03-0.04	5.9-9.8 [21]	0.58-0.97	19-24
PET [30]	30		0.05 [30]	0.032	1.53 [30]	0.992	31
PVC [21]	24		----	----	7.9-19.7 [21]	0.78-1.94	----
PVC [29]	25	75-105 [17]	0.009 [29]	0.078	0.12 [29]	1.04	13
PVC [7]	25		0.0089 [7]	0.077	0.12 [7]	1.04	13

PVC [30]	30		0.4 [30]	0.26	10 [30]	6.48	25
PA 6 [21]* **	0		0.08 [21]	0.0079	0.24 [21]	0.024	3
PA 6 [21]* **	23		0.35 [21]	0.035	1.8 [21]	0.18	5
PA 6 [21]* ##	23		0.5 [21]	0.049	3.28 [21]	0.32	6
PA 6 [29]	25	310-365 [17]	0.007 [29]	0.06	0.06 [29]	0.52	9
PA 6 [30]	30		0.1 [30]	0.065	1.6 [30]	1.04	16
PA 6 [21]* **	50		4.7 [21]	0.46	17.3 [21]	1.71	4
PS [21]	24		15.8-19.7 [21]	1.56-1.94	394-590 [21]	38.9-58.2	25-30
PS [29]	25	85-105 [17]	0.6 [29]	5.18	8 [29]	69.12	13
PS [7]	25		0.59 [7]	5.1	7.9 [7]	68.3	13
PS [30]	30		2.9 [30]	1.88	88 [30]	57.03	30
EVOH 32 [21]	5		-----	-----	0.0039 [21]	0.00038	-----
EVOH 32 [21]	23		0.0004 [21]	0.000039	0.01 [21]	0.0001	3
EVOH 32 [14]	25	60 [14]	0.017 [14]	0.000034	0.81 [14]	0.0016	47
EVOH 32 [21]	35		0.0008 [21]	0.000079	0.03 [21]	0.003	38
EVOH 44 [21]	5		----	----	0.02 [21]	0.002	----
EVOH 44 [21]	23		0.0031 [21]	0.00031	0.08 [21]	0.008	25
EVOH 44 [14]	25	53 [14]	0.13 [14]	0.00026	7.1 [14]	0.014	54
EVOH 44 [21]	35		0.01 [21]	0.00099	0.2 [21]	0.02	20

Where the units from the source and conversion is:

- Converted P =[m^3m/m^2dayPa] x 10^{-13}
- [28] P (at 25ºC) = [cm^3cm]/[cm^2sPa] x 10^{-13}
- [14] P (at 25ºC) = [$cm^3$20my/m^2dayatm]

- [7] P (at 25ºC) = [cm^3(STP)cm/cm^2sPa] x10^{-13}
- [29] P (at 30ºC) =[mlmm/cm^2s(cmHg)] x10^{-10}
- [22] P = [cm^3mm/m^2dayatm]

And the specified information from the source is

- *0% RH
- **STP
- #ASTM D1434-72
- ## P_{CO2} DIN 53380, P_{N2} DIN 53122, thickness 0.05mm

Pre-factors and activation energies for different polymers are listed in Table 8-5.

Table 8-5: Pre-factors and activation energies for different polymers found in the literature.

Polymer	**Permeant**	**T-range [C]**	**P_0 *10^{-7} [cm^3cm/cm^2sPa]**	**P_0*10^{-13} [m^3m/m^2dayPa]**	**E_P [kJ/mol]**
LDPE 0.914g/cm3	CO_2	5-60	62	535.7	38.9
[7]	N_2	5-60	329	2842.6	49.4
HDPE 0.964g/cm3	CO_2	5-60	0.0506	0.437	30.1
[7]	N_2	5-60	0.991	8.56	39.7
PP 0.907 50% crystallinity	CO_2	20-70	24	207.4	38.1
[7]	N_2	20-70	1280	11059.2	55.7
Polyvinyl chloride un-plasticized	Co_2	25-90	930	8035.2	56.8
[7]	N_2	25-80	9380	81043.2	69
Poly(imino-1-oxohexamethylene) Nylon 6	CO_2	0-90	1.2	10.4	40.6
[7]	N_2	0-90	1.05	9.1	46.9

Table 8-5 shows the pre-factors and activation energies from different polymers found in the literature, with the specified information from the source. These coefficients are converted to the dimensions used in this report. The conversion of the permeability coefficient P and P_0 from [x] to $\frac{m^3 m}{m^2 dayPa}$, are used by Eq. (8.14), Eq. (8.15), Eq. (8.16) and Eq. (8.17).

$$\frac{cm^3 cm}{cm^2 sPa} = \frac{\left(cm\frac{m}{100cm}\right)^3\left(cm\frac{m}{100cm}\right)}{\left(cm\frac{m}{100cm}\right)^2\left(s\frac{h}{3600s}\frac{day}{24h}\right)Pa}10^{-13} = 8.64*10^{-13}\frac{m^3 m}{m^2 dayPa} \tag{8.14}$$

$$\frac{cm^3\,20\mu m}{m^2 day Atm} = \frac{\left(cm\frac{m}{100cm}\right)^3\left(20\mu m\frac{m}{10^6\,\mu m}\right)}{m^2 day\left(Atm\frac{101325Pa}{Atm}\right)} = 1.974*10^{-16}\,\frac{m^3 m}{m^2 day Pa} \tag{8.15}$$

$$\frac{mlmm}{cm^2 scmHg} = \frac{\left(ml\frac{m}{100ml}\right)^3\left(mm\frac{m}{1000mm}\right)}{\left(cm\frac{m}{100cm}\right)^2\left(s\frac{h}{3600s}\frac{day}{24h}\right)\left(cmHg\frac{1333.2239Pa}{cmHg}\right)}10^{-10} = 6.4805*10^{-14}\,\frac{m^3 m}{m^2 day Pa} \tag{8.16}$$

$$\frac{cm^3 mm}{m^2 day Atm} = \frac{\left(cm\frac{m}{100cm}\right)^3\left(mm\frac{m}{1000mm}\right)}{m^2 day\left(Atm\frac{101325Pa}{Atm}\right)} = 9.869*10^{-15}\,\frac{m^3 m}{m^2 day Pa} \tag{8.17}$$

Appendix G: MATLAB-Script used for the Models.

Consumption of CO_2 through a polymer

This script is used for the consumption of CO_2 using the permeability-coefficient from different polymers at 25°C.

```
PCO2_1 = (82.1*10^(-13)); %permeability constant [m3m/m2dayPa] LDPE[7]
PCO2_2 = (2.33*10^(-13)); %permeability constant [m3m/m2dayPa] HDPE[7]
PCO2_3 = (0.62*10^(-13)); %permeability constant [m3m/m2dayPa] PET[22]
PCO2_4 = (1.04*10^(-13)); %permeability constant [m3m/m2dayPa] PVC[7]
PCO2_5 = (0.52*10^(-13)); %permeability constant [m3m/m2dayPa] PA 6[28]
PCO2_6 = (68.3*10^(-13)); %permeability constant [m3m/m2dayPa] PS[7]
PCO2_7 = (0.0016*10^(-13));%permeability constant[m3m/m2dayPa] EVOH 32%[14]
PCO2_8 = (0.014*10^(-13)); %permeability constant[m3m/m2dayPa] EVOH 44%[14]
Vn = 0.022414; %Molar volume [m3/mol]
A = 0.05; %Area of the film [m2]
V = 0.0005; %Volume of the packaging element [m3]
L = 0.0008; % Thickness of the film [m]
R = 8.3144; %Gas constant [J/K*mol]
T = 298.15; %Temperature [K]

pCO2out = 3.75*10^(-4); %Partial pressure of CO2 in the air, constant [Atm]
pCO2i0 = 4.0; % Pressure of CO2 inside the headspace in a soda bottle [Atm]
t = [0:0.5:500]; %time in days
%LDPE
k1 = ((PCO2_1/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_1 = pCO2out - (pCO2out - pCO2i0)*exp(-k1*t);
%HDPE
k2 = ((PCO2_2/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_2 = pCO2out - (pCO2out - pCO2i0)*exp(-k2*t);
% PET
k3 = ((PCO2_3/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_3 = pCO2out - (pCO2out - pCO2i0)*exp(-k3*t);
% PVC
k4 = ((PCO2_4/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_4 = pCO2out - (pCO2out - pCO2i0)*exp(-k4*t);
% PA6
k5 = ((PCO2_5/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_5 = pCO2out - (pCO2out - pCO2i0)*exp(-k5*t);
% PS
k6 = ((PCO2_6/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_6 = pCO2out - (pCO2out - pCO2i0)*exp(-k6*t);
% EVOH 32
k7 = ((PCO2_7/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_7 = pCO2out - (pCO2out - pCO2i0)*exp(-k7*t);
% EVOH 44
k8 = ((PCO2_8/Vn)*A*R*T)/(L*V); % [1/day]
pCO2i_8 = pCO2out - (pCO2out - pCO2i0)*exp(-k8*t);

plot(t,pCO2i_1,'r');
xlabel('Time [Days]')
ylabel('Pressure [Atm]')
ylim([-0.5 4.5])
hold on
plot(t,pCO2i_2,'g')
hold on
```

```
plot(t,pCO2i_3,'b')
hold on
plot(t,pCO2i_4,'y')
hold on
plot(t,pCO2i_5,'m')
hold on
plot(t,pCO2i_6,'c')
hold on
plot(t,pCO2i_7,'r')
hold on
plot(t,pCO2i_8,'k')
legend('pCO2i_1=LDPE','pCO2i_2=HDPE','pCO2i_3=PET','pCO2i_4=PVC', ...
'pCO2i_5=PA6','pCO2i_6=PS','pCO2i_7=EVOH32','pCO2i_8=EVOH44')
```

Activation energy in a polymer:
This script was used to find the activation energy for PA6.

```
T_1 = 0.0 + 273.15; % Temperature 1 for the polymer PA 6 [K]
Pco2_1 = 0.024*10^(-13); % Permeability coefficient [m3m/m2dayPa]
T_2 = 50.0 + 273.15; % Temperature 2 for the polymer PA 6 [K]
Pco2_2 = 1.71*10^(-13); % Permeability coefficient [m3m/m2dayPa]
R = 8.3144*10^(-3); %Gas constant [kJ/K*mol]
Ep = (R*(log(Pco2_2)-log(Pco2_1)))/((1/T_1)-(1/T_2)); % [kJ/mol]
```

Temperature dependency:
This script was used to find the permeability coefficients for CO_2 at different temperatures.

```
T_1 = 0.0 + 273.15; % Temperature 1 for the polymer PA 6 [K]
Pco2_1 = 0.024*10^(-13); % Permeability coefficient [m3m/m2dayPa]
R = 8.3144*10^(-3); %Gas constant [kJ/K*mol]
Ep = 62.6191; % Activation energy range [0-50C] [kJ/mol]
T_2 = (273.15:5:323.15);
Pco2_2 = Pco2_1* exp((Ep/R)*((1./T_1)-(1./T_2)));

plot(T_2,Pco2_2,'k x');
xlabel('Temperature [Kelvin]')
ylabel('PCO2 [m3m/m2dayPa]')
```

The Combination of all three script:
This script was used for finding the consumption of CO_2 through PA6 at different temperatures.

```
% constants
A = 0.05; %Area of the film [m2]
V = 0.0005; %Volume of the packaging element [m3]
L = 0.0008; % Thickness of the film [m]
T_1 = 0.0 + 273.15; %Temperature [K]
T_2 = 10.0+ 273.5;
T_3 = 20.0+ 273.5;
T_4 = 30.0+ 273.5;
T_5 = 40.0+ 273.5;
T_6 = 50.0+ 273.5;
pCO2i0 = 4.0; %Pressure of CO2 inside the headspace in a soda bottle [Atm]
% Constants
Vn = 0.022414; %Molar volume [m3/mol]
R = 8.3144; %Gas constant [J/K*mol]
```

```
pCO2out = 3.75*10^(-4); %Partial pressure of CO2 in the air, constant [Atm]
%Finding Ep
T_0 = 0.0 + 273.15; % Temperature 1 for the polymer PA 6 [K]
Pco2_1 = 0.024*10^(-13); % Permeability coefficient PA 6 [m3m/m2dayPa]
T_ = 50.0 + 273.15; % Temperature 2 for the polymer PA 6 [K]
Pco2_2 = 1.71*10^(-13); % Permeability coefficient [m3m/m2dayPa]
Ep = ((R*10^(-3))*(log(Pco2_2)-log(Pco2_1)))/((1./T_0)-(1./T_)); % [kJ/mol]
% Finding PCO2
PCO2_1 = Pco2_1* exp((Ep/(R*10^(-3)))*((1./T_0)-(1./T_1)));% permeability
constant CO2[m3m/m2dayPa]PA6
% Finding the concentration loss per time for a given temperature
t = [0:9000]; %time in days
k1 = -((PCO2_1/Vn)*A*R*T_1)/(L*V); % [1/day]
pCO2i_1 = pCO2out - (pCO2out - pCO2i0)*exp(k1*t);

PCO2_2 = Pco2_1* exp((Ep/(R*10^(-3)))*((1./T_0)-(1./T_2)));% permeability
constant CO2[m3m/m2dayPa]PA6
k2 = -((PCO2_2/Vn)*A*R*T_2)/(L*V); % [1/day]
pCO2i_2 = pCO2out - (pCO2out - pCO2i0)*exp(k2*t);

PCO2_3 = Pco2_1* exp((Ep/(R*10^(-3)))*((1./T_0)-(1./T_3)));% permeability
constant CO2[m3m/m2dayPa]PA6
k3 = -((PCO2_3/Vn)*A*R*T_3)/(L*V); % [1/day]
pCO2i_3 = pCO2out - (pCO2out - pCO2i0)*exp(k3*t);

PCO2_4 = Pco2_1* exp((Ep/(R*10^(-3)))*((1./T_0)-(1./T_4)));% permeability
constant CO2[m3m/m2dayPa]PA6
k4 = -((PCO2_4/Vn)*A*R*T_4)/(L*V); % [1/day]
pCO2i_4 = pCO2out - (pCO2out - pCO2i0)*exp(k4*t);

PCO2_5 = Pco2_1* exp((Ep/(R*10^(-3)))*((1./T_0)-(1./T_5)));% permeability
constant CO2[m3m/m2dayPa]PA6
k5 = -((PCO2_5/Vn)*A*R*T_5)/(L*V); % [1/day]
pCO2i_5 = pCO2out - (pCO2out - pCO2i0)*exp(k5*t);

PCO2_6 = Pco2_1* exp((Ep/(R*10^(-3)))*((1./T_0)-(1./T_6)));% permeability
constant CO2[m3m/m2dayPa]PA6
k6 = -((PCO2_6/Vn)*A*R*T_6)/(L*V); % [1/day]
pCO2i_6 = pCO2out - (pCO2out - pCO2i0)*exp(k6*t);

plot(t,pCO2i_1,'r');
xlabel('Time [Days]')
ylabel('Pressure [Atm]')
hold on
plot(t,pCO2i_2,'g');
hold on
plot(t,pCO2i_3,'y');
hold on
plot(t,pCO2i_4,'b');
hold on
plot(t,pCO2i_5,'k');
hold on
plot(t,pCO2i_6,'c');
legend('pCO2i_1= 0C','pCO2i_2= 10C','pCO2i_3= 20C','pCO2i_4= 30C',…
'pCO2i_5= 40C','pCO2i_6= 50C')
```