CHALMERS

An investigation of the water vapour resistance

- the humidity detection sensor method in Versmaperm MkIV compared to the gravimetric method

Master's Thesis in Applied Physics

FRIDA BÖRJESSON

Department of Physics & Engineering Physics
Applied Physics
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

This project has been performed at SP, Technical Research Institute of Sweden, in Borås. SP is a research institute where they are not only involved in different research areas, they are also able to provide quality assurance and certifications. Different companies turn to SP for those services and it is therefore important that those tests are reliable but also time efficient. This project will focus on one quality that the subgroup Polymer Technologies provide; the measurement of the permeability on polymeric building materials.

Traditionally the permeability of polymeric building materials is measured by the well-established gravimetric method. This method tends to take a very long time, from weeks up to several months depending on the materials and in which humidities those are measured. It is therefore preferable to find alternative methods for those measurements. SP has recently invested in a new machine called *Versaperm MkIV WVTR Meter*, which measures the permeability using a RH-sensor based method, i.e. by measuring the relative humidity (RH) change. This RH-sensor based method is much faster than the gravimetric method. Those measurements can be done in some hours or in a couple of days, also depending on the sample and the RH. In the end one would like to find a correlation between those two methods.

This thesis will include an investigation of the machine itself and Versaperm MkIV WVTR Meter turned out to have some limitations of how permeable materials that can be tested. The range of a material's water vapour resistance needs to be between $\sim 2.5 \cdot 10^4 - 5.0 \cdot 10^6$ s/m to be able to give a result when measuring against a RH of 2% on the dry side. When measuring against a higher RH Versaperm will give a higher water vapour resistance than the gravimetric method which will give almost the same value in all conditions.

Keywords: Polymers, Permeance, Water vapour resistance, Gravimetric, Humidity detection sensor

Acknowledgements

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Introduction

T HIS IS A Master's Thesis for the degree of science in Applied Physics at Chalmers University of Technology. The project has been performed at SP, Technical Research Institute of Sweden, in Borås during summer and autumn of 2012. SP is a leading international research institute where the Swedish government's holding company RISE Holding AB is the sole shareholder. At SP several technical research areas are covered. SP does not only apply basic and applied research, they also provide quality assurance and certifications. This project was done at the section Polymer Technology which lies within the Department of Materials Science and Chemistry and provides researches and testing on polymers. A large part of the work in Polymer Technology lay the base for certification of products for use in many different areas. This project is focused on one quality of polymeric building materials, its permeance.

1.1   Background

The knowledge about a material's water vapour permeance is important in a row of applications. This can range from roofing materials and medical packaging, where it needs to be low, to wind-breaking films where one does not want moisture to build up, and the permeability must be high. Because of SP being capable of certification, many companies turn to SP to get their products approved. The time taken for a test can be critical, not only for SP but also for the customer who may need a quick answer.

   The way of measuring the permeance of polymeric building materials is traditionally done by gravimetric methods. This tends to take a very long time and it is therefore preferable to find other alternative methods that gives same results but in much shorter time.

1.1.1 Water vapour permeability

To begin with the water vapour permeability will be introduced to give an understanding in how this can be measured and presented. This to be able to present the aim of this thesis.

There is a slight difference between permeability and permeance. This report will talk much about the permeability, but in the end it is the permeance that is measured.
Permeance and permeability are connected to each other by the mass flux, j_x, of moisture through a material, [1]. The permeability, P, is defined in terms of a partial pressure gradient

$$j_x = -P\frac{\partial p}{\partial x}$$

and the permeance, W, is defined in terms of a vapour pressure difference

$$j_x = W\Delta p.$$

These indicate how much water vapour can diffuse through a material during a specific time, depending on the pressure and temperature. The gradient might be different within the material, depending on its complexity, which will affect the permeability. For the permeance only the difference in pressure around the sample is taken into account. The materials in this work are thin and a difference of the gradient within the sample is therefore being neglected. The measurements done in this study will also only measure the difference in pressure which will give the permeance and not the permeability. When expressing the ability to let through water one usually do that in the water vapour resistance in relation to vapour content, Z_v [s/m]. This quantity will therefore also be used in this work. How this quantity is developed will be shown in the theory.

Heat and moisture transport are coupled phenomena in most building construction, this means that it is difficult to only control one of them without affecting the other, [2]. When measuring the water vapour permeance it is therefore of great importance to keep the temperature at a constant value. The gravimetric method used in this project follows ISO 12572 that indicates that the water vapour permeance only can be determined under isothermal conditions, [3].
There are materials where the water vapour permeance is considered non-linear, meaning that it changes with the applied differential relative humidity in a non-linear way. For some materials it has been reported that the permeability increases exponentially with relative humidity [4]. However, if the material does not interact with the water vapour the permeance is expected to be a linear function of the differential relative humidity. Meaning that the flux through the material will increase linearly with the difference of the relative humidity (RH) on both sides of the sample. Making two tests with a different difference in RH for those samples will therefore be enough to tell about the flux for all RH differences.

By presenting the ability for water vapour to penetrate a sample in Z_v one takes the

different vapour pressures on both sides of the sample into account. For many materials it will therefore be a constant value of Z_v independent of in which RHs it is measured. There are however other ways of describing the water vapour permeability, for example by the water vapour transmission rate, WVTR [g/m^2·24h]. This is actually what is measured in the gravimetric method, how much vapour in weight that has penetrated through the sample over a specific time, here per day. It is this value that will increase linearly with the pressure difference if there is no interaction between the material and the vapour. Another way of measuring the permeability is by using a relative humidity (RH) detection sensor method which measures the relative humidity. The WVTR and Z_v can be calculated by measuring the change in RH on one side of the sample. This is what will be done in this project and how this is done will be described more in detail.

The WVTR can at first sight be the most intuitive way of expressing the permeability, but the WVTR does not take the pressure due to humidity into account. A highly permeable material can therefore have the same WVTR as a material with low permeance but in different testing conditions.

1.2 The aim of this thesis

Because of the importance of hastening the measurements of the permeability of polymeric building materials, SP has invested in a new machine called *Versaperm MkIV WVTR Meter* which is supposed to measure the permeability of those materials using RH-sensors. The aim of this thesis is therefore to investigate the reliability of this new machine and its RH-sensor based method to measure the permeability and how it compare with the gravimetric method.

The layout of this report will first include a theory part of the underlying physics of polymers and their gas transports. After that the theory behind the gravimetric method and the RH-sensor based method for determining the water vapour resistance will be described. The methods themselves will be described in more depth in chapter 3, where also the whole procedure of the investigation will be presented. Finally the results of both methods will be followed by an analysis and conclusion of the measurements and of the Versaperm MkIV WVTR Meter.

The methods used in this report is based on the international standard ISO 12572 for the gravimetric method and ISO 15106-1 for the RH-sensor based method. The conditions and environment of all the materials will be the same. This to be able to present not only the Z_v, but also the WVTR.

2

Theory

T O BE ABLE to understand how it is possible to measure the permeability of a polymer membrane one first needs to understand the underlying physics of the gas transport through the membrane. This theory part will first introduce the different types of polymers and which type of polymer the materials in this work belong to. The mechanism of gas transports relevant for those materials will be described. Finally the theory behind the different methods used in this project for estimating the permeability for the different polymers will be presented.

2.1 Different polymer types

The gas transport through a polymer depends on the morphology of the polymer. There are liquid crystalline, crystalline, semi-crystalline and amorphous polymers. The amorphous polymers can be divided further into rubbery and glassy polymers. The semi-crystalline polymers consists of two phases, the crystalline and the amorphous. Where the amorphous phase can be either rubbery or glassy.

The gas transport in liquid crystalline polymers is in general very low and the gas diffusion is not well defined, [7]. The gas transport in the amorphous polymers is different depending on if it is a rubbery polymer or a glassy polymer. A completely crystalline polymer lacks the ability of both sorption and diffusion. In semi-crystalline polymers the gas transport therefore almost only depends on its amorphous part.

Glassy vs. rubbery polymers

The mechanism behind the gas transport in the different amorphous polymers differ significantly. This is mainly because the glassy polymers are not in a true state of equilibrium as is the case for rubbery polymers, [8].

Diffusion in polymers is divided into two different kinds of diffusion, Fickian diffusion and non-Fickian diffusion. The Fickian diffusion was derived by Adolf Fick and explains

the diffusion in rubbery polymers. The diffusion in all rubbery polymers follow Fick's law of diffusion which describes this diffusion very well.

The gas transport models in glassy polymers are based upon statistical, mechanical-structure and thermodynamic considerations, [7]. The diffusion in this type of polymer belongs to the non-Fickian diffusion. The non-Fickian diffusion is a gathering of the different diffusion theories for the glassy polymers. Those are much more complicated and are basically derived from the free volume molecular theory. This theory states that the movement of gas molecules is dependent on the free volume in the polymer matrix and on the energy the gas molecules need to overcome the attractive forces between the chains in the polymer, [7].

The amorphous part of a polymer can be either glassy or rubbery depending on its glass transition temperature, T_g. This is the temperature where the glassy state in the polymer passes to the rubbery state, meaning that an amorphous polymer is rubbery above this temperature.

2.1.1 Polymers in this project

In this project nine different materials are laying the ground for the measurements in the different methods, the gravimetric method and the RH-sensor based method. Table 2.1 shows what types of polymer the different materials are made of.

Table 2.1: Different polymers in this project: polyethylene (PE), polypropylene (PP), polyether urethane (PU), polyethylene terephthalate (PET)

Polymer	Amount	Note
PE	3	
PP	2	one including an ether
PP-based	1	with a mesh fabric of a PE-copolymer
PP-based	1	with an outer layer of a PE-mesh
PU	1	
PET	1	

Polyethylene (PE) is a semi-crystalline thermoplastic with a $T_g \sim -120°C$, [9], meaning that its amorphous part is rubbery in room temperature. Polypropylene (PP) is also a semi-crystalline thermoplastic but with a $T_g \sim -10°C$, [9], this also means that the amorphous phase is rubbery. There is a wide range of polyether urethanes (PUs), therefore T_g can vary depending on its morphology. In this project the PU will be assumed rubbery. Polyethylene terephthalate (PET) which also is a semi-crystalline thermoplastic has got a $T_g \sim 70°C$, [9], which indicates that its amorphous part is in the glassy state in room temperature.

2.1.2 Properties affecting permeability

There are many general properties for all polymers and their permeability, some of them will be described here.

The polarity of a molecule affects the attraction between molecular chains and will therefore affect the structure of the polymer. This will in turn affect the solubility and therefore also the permeability, [5]. Generally polar polymers are more permeable to water than nonpolar polymers. Both PE and PET are nonpolar polymers meaning that they are hydrophobic and has therefore a low water sorption. There are however attractive forces between the polymer chains due to the Van der Waals forces, but thermal motion at room temperature can usually overcome or disrupt them, [5]. The water uptake in the polymer types in this project is very low. Within 24 hours the water uptake is $< 0.01\%$ for PE and 0.3% for PET, [9]. The water uptake in PP is $0.01 - 0.03\%$ and in thermoplastic PU it is $0.7 - 0.9\%$, [9]. The permeability can be presented as $P = HD$, where H is the sorption coefficient and D is the diffusion coefficient, [10]. A low water uptake in the materials gives a sorption coefficient that will lower the permeability.

Another property that can affect a polymer's permeability is the crystallinity. The degree of crystallinity does not only depend on the polymer but also on the processing technique. Polymers such as PE crystallize quickly and can reach high levels of crystallinity, [5]. Crystalline phases are generally inaccessible to most penetrants and a higher crystallinity will therefore usually lead to lower permeation rates, [6]. This will be described more ingoing in the next section.

2.1.3 Semi-crystalline polymers

All polymers in this work are semi-crystalline, it is therefore in place to describe this type of polymer more ingoing.

A semi-crystalline polymer, as mentioned before, consists of two phases; the impermeable crystalline phase and the permeable amorphous phase. The amorphous phase could be either rubbery or glassy depending on the glass transition temperature, T_g, for the material. This temperature can change within the same polymer type depending on the molecular weight, its thermal history and age, the measurement method and on the cooling or heating rate, [11]. It should also be mentioned that T_g refers to what happens to the amorphous part of the material, not the crystalline part.

Addition of plasticizers, low molecular weight compounds, can lower the value of T_g. This means that the amorphous phase of a polymer will be rubbery at a much lower temperature than normal, [11]. This is done to reduce the brittleness which occurs in glassy polymers, it is therefore not usual to add a plasticizer to a rubbery polymer.

Initial investigations of the solubility in a semi-crystalline polymer showed that the sorption was directly related to the crystallinity of the polymers [7]. The solubility, S, for the two phase model for a rubber amorphous phase was then represented as

$$S = S_a \cdot \Phi_a \tag{2.1}$$

where S_a is the solubility coefficient for pure amorphous polymer and Φ_a is the amorphous volume fraction. Negative deviations were shown from further investigations. This was explained by the presence of an unstable crystal structure which had higher density than the average density. The low density crystallites were assumed to cause this deviation because of the amorphous volume fraction which was based on average density measurements [7].

The diffusion in semi-crystalline polymers is related to its spatial distribution of the two phases. The polymer chains in the two phases are cross-linked by tie chains which reduces the mobility for the chains in the amorphous phase [7]. This cross-linking requires a higher activation energy for gas diffusion and the effects are accounted for in the diffusion coefficient, D, by introducing a factor β. The diffusion coefficient is then defined as

$$D = \frac{D_a}{\tau \cdot \beta} \qquad (2.2)$$

where D_a is the diffusivity of gas for a completely amorphous polymer and τ is the tortuosity factor accounting for the hindrance to the gas molecules due to the presence of the crystalline phase, [6]. This meaning that $\tau = l/L$ where l is the length of the penetrants path and L is the thickness of the membrane. The magnitude of β would increase if the size of the penetrant increase or if the crystallite size decrease. The penetrant's way through the material can be visualised as a sequence of diffusion steps, where it must pass over potential barriers separating one position from the next. This process requires energy available for the penetrant but also for the rearrangements of the polymer chain segments to create "holes" which then act as steps in the diffusion path, [6]. In polymers above its glass temperature those "holes" are constantly disappearing and reforming due to thermal fluctuations. One major factor that affect those segmental motions is the temperature. A higher temperature provides more energy which increases the motion. To hold the temperature constant during measurements of a material's permeability is therefore crucial.

To get a deeper understanding on how the permeability depends on the crystallinity the permeance of the three different polyethylenes (PE) in this work will be compared in respect to their crystallinity.

2.2 Fickian diffusion

This section will cover the Fickian diffusion theory, this because most of the materials used in this work are semi-crystalline with a rubbery amorphous phase where the gas diffusion belongs to the Fickian diffusion.

In polymer membranes it is appropriate to look at the equation for conservation of

species in one dimension given by

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x} j_x \tag{2.3}$$

where c is the concentration of the diffusing species, t is the time and j_x is the flux in the x direction, which is along the thickness of the membrane and the only direction in which the mass transfer is taking place. Here equation (2.3) assumes that there is no convection, which needs to be taken into account in the three-dimensional case, [10]. The dynamics gets one-dimensional if $A^{1/2} >> L$, where A is the area of the face of the membrane and L the membrane thickness. When working with membranes this is usually the case and will be the case for the samples in this project.

The diffusion in the polymer needs to be converted into a boundary value problem in the concentration, c, this is simplest done by employing Fick's law of diffusion

$$j_x = -D\frac{\partial c}{\partial x} \tag{2.4}$$

where D is the diffusivity, i.e. the diffusion coefficient which is the proportionality constant between the molar flux due to molecular diffusion and the driving force for diffusion (the gradient in the concentration of the species), [10].
Combining equation (2.3) and (2.4) one gets

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}(D\frac{\partial c}{\partial x}) \tag{2.5}$$

which is commonly referred to as Fick's second law of diffusion, [10].
   If the diffusivity, D, is constant equation (2.5), becomes

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{2.6}$$

Equation (2.6) is also referred to as Fick's second law of diffusion and is similar to the heat conduction problem, but with a concentration instead of a temperature and the diffusivity D instead of the thermal diffusivity, [10]. In the steady state condition, provided the diffusion coefficient is constant, equation (2.6) reduces to

$$\frac{d^2 c}{dx^2} = 0. \tag{2.7}$$

Integrating equation (2.7) twice with respect to x and introducing the boundary conditions, at $x = 0$ and L, one obtains

$$\frac{c - c_1}{c_2 - c_1} = \frac{x}{L} \tag{2.8}$$

where the concentration changes linearly from c_1 to c_2, [7]. The rate of transfer is the same across all sections in a membrane and therefore the flux, equation (2.4), is calculated by

$$j_x = -D\frac{dc}{dx} = \frac{D(c_1 - c_2)}{L}. \tag{2.9}$$

The diffusion coefficient can be extrapolated from the flow rate if the thickness and the concentrations are known. If D is a function of the concentration the solution gets more complicated, and equation (2.5) can be expressed as

$$\frac{\partial c}{\partial t} = \frac{\partial D}{\partial c}(\frac{\partial c}{\partial x})^2 + D\frac{\partial^2 c}{\partial x^2}. \tag{2.10}$$

Some simplifications can be made, for example the diffusivity which is an increasing function of concentration can be represented as

$$D = D_0 e^{\alpha c} \tag{2.11}$$

where D_0 and α are constants, [10].

Before the steady state condition is established the flux and concentration are varying with time. After the steady state condition is reached one can obtain the permeability. When working with materials that do not interact with the vapour the permeance is assumed to be a linear function. The diffusion coefficient for a material can therefore be assumed to be constant. If one assumes that the polymer membrane is initially free of diffusant and that the diffusant (gas or vapour) is introduced at one side of the membrane at a constant pressure, p_1, the other side will slowly rise its pressure, p_2, as the diffusant is being transferred to this side of the membrane, [10]. If the magnitude of the pressures are such that $p_1 >> p_2(t) \simeq 0$ the total amount of diffusant, Q_t, that has permeated through the membrane in time, t, is given by

$$\frac{Q_t}{Lc_1} = \frac{Dt}{L^2} - \frac{1}{6} - \frac{1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^2}{n^2}e^{-\frac{Dn^2\pi^2 t}{L^2}}. \tag{2.12}$$

c_1 is the concentration on the high-pressure side and $c_2 = 0$. Henry's law states that the solubility of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas, the pressure a gas would have if it alone occupied the volume, this at a constant temperature and in equilibrium with that liquid, [12]. When this law can be applicable on polymers, the diffusion coefficient is known to be concentration independent and holds that

$$c_1 = Hp_1 \tag{2.13}$$

where H is the Henry's law coefficient, the solubility, [10]. When t increases one approaches the steady state condition. The exponential term in equation (2.12) becomes negligibly small and by using equation (2.13), with some rewriting, one gets

$$\frac{LQ_t}{p_1} \simeq DH(t - \frac{L^2}{6D}). \tag{2.14}$$

Equation (2.14) can be derived to

$$\frac{L}{p_1}\frac{dQ_t}{dt} \simeq DH = P \tag{2.15}$$

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where P is the permeability, [10]. When plotting LQ_t/p_1 against time, equation (2.15) shows that the slope gives the permeability and equation (2.14) that an intercept on the t axis at $L^2/6D$ the diffusivity, see figure 2.1. This is one of many ways to find the diffusion coefficient, D, and the permeability, P. It is not necessarily that $p_1 >> p_2(t) \simeq 0$ is the case in the measurements taking place in this work. The pressure on each side of the membrane will not be measured, but the partial vapour pressure due to the temperature and the relative humidity on each side will be calculated.
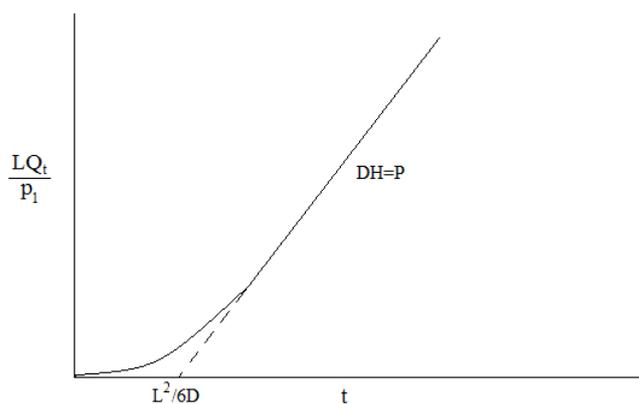
Figure 2.1: *Plotting equation* (2.14) *with respect to the time t shows that the slope at steady state gives the permeability and that the diffusivity can be calculated from the intercept on the t axis.*

2.3   Non-Fickian diffusion

The non-Fickian diffusion theories are widely diverse, i.e. there are different theories that suits different materials, even if all of them are derived from the free volume theory, [7]. There have been relatively few studies in the behaviour of hydrophobic glassy polymers, [14], the polymer type PET belongs to. There has however been an investigation for the sorption and diffusion of water in a PET-film where accurate sorption rate curves and the diffusion coefficient were obtained. In this investigation it turned out that the sorption in thin PET-films was done according to Fickian-type sorption and that the diffusion coefficient showed to be concentration-dependent, [14]. This will not be discussed further, instead an investigation due to the gravimetric and RH-sensor based method of this material will be done in the same way as the other materials. It can be good to have in mind that this might give a slightly different WVTR-rate on the material made of PET in this project, compared to the other materials, depending on the concentrations it is tested in as well as the concentration-difference.

2.4 Determining the water vapour resistance

There are different ways of expressing the ability to transfer water vapour through a material, one common way for building materials is by using the physical quantity water vapour resistance in relation to vapour content, Z_v [s/m]. This quantity takes the partial pressure into account and can therefore be compared to other materials without mentioning in which humidity it was tested. The methods used in this project will therefore be concentrated on how to determine this physical quantity. The environment for all materials being tested will however be the same and the water vapour transmission rate, WVTR [g/m^{2}24h], will also be presented.

As mentioned before there are different methods of measuring the water vapour resistance in materials. One common way to do this is by the gravimetric method, but there are other alternative methods to measure the resistance; like the relative humidity (RH) detection sensor method or by using an infrared sensor. This project will compare the established gravimetric method with the RH-sensor based method used in Versaperm MkIV WVTR Meter and the theory on how those different methods work will therefore be described.

2.4.1 The gravimetric method

The gravimetric method is a well-established method to calculate Z_v where you simply weigh the sample and measure the weight loss or gain. What you really measure is the WVTR, how much moist in gram that goes through a specific area of the polymer membrane per day. This way of presenting the permeability does not take the environmental conditions into account and can therefore be misleading, instead the WVTR is converted into Z_v. The gravimetric method used in this work follows the international standard ISO 12572 and is described in chapter 3.

In the gravimetric method the polymer sample is attached to a cup filled with either water, a salt solution or a desiccant. The cup is thereafter sealed and put in an environment with a constant RH and temperature. The cup is weighed in appropriate time intervals for the specific sample. The cup will either gain or lose weight depending on its content and the environment.

By weighing the sample in time intervals one gets a measure in kg/s, the weight of how much water vapour that has penetrated in a specific time. In steady state a regression line between mass and time can be calculated, the slope of this line is the water vapour flow rate through the specimen, G [kg/s]. The permeance, W, is then given by

$$W = \frac{G}{A \cdot \Delta p_v} \tag{2.16}$$

where A is the exposed area of the sample and Δp_v is the difference in the partial vapour pressure, p_{sat}, of each side of the sample, see equation (2.27).

The reciprocal of the water vapour permeance gives the vapour resistance in relation to vapour pressure, Z_p [Pa·m^2·s/kg]

$$Z_p = \frac{1}{W}.$$ (2.17)

The vapour resistance in relation to vapour content, Z_v [s/m], can in turn be calculated by

$$Z_v = \frac{Z_p}{R_v \cdot T}$$ (2.18)

where R_v is the gas constant for water vapour and T the absolute temperature. Again, this is the quantity that is used in this project.

There are other quantities that usually are presented when measuring and calculating the vapour resistance, one of them is the sample's equivalent air gap, s_d [m], at 1013.25 hPa. s_d is calculated by

$$s_d = \frac{\Delta p_v \cdot \delta_a}{g} - s_a$$ (2.19)

where g is the density of the water vapour flow rate, see equation (2.20), δ_a is the water vapour permeability of air with respect to the partial vapour pressure, see equation (2.21), s_a is the air gap between the content in the cup and the sample and Δp_v is as before the difference in p_{sat}. s_a may only be taken into account if highly permeable materials are investigated, when $s_d < 0.2$ m, otherwise it can be set to zero, [3].

g is given by

$$g = \frac{G}{A}$$ (2.20)

and δ_a is expressed as

$$\delta_a = \frac{D_v}{R_v \cdot T}$$ (2.21)

D_v is the vapour diffusion coefficient and can be based on, particularly, five different empirical functions formulated by Krischer, VDI Heat Atlas, De Vries, Vos and Schirmer, all shown further down, [13]. The following empirical function was applied by Krischer

$$D_v = 2.34 \cdot 10-5(\frac{T}{273.15})^{2.3}.$$ (2.22)

The VDI Heat atlas gives

$$D_v = \frac{2.252}{p_0}(\frac{T}{273.15})^{1.81}$$ (2.23)

where p_0 is the standard barometric pressure. De Vries approach gives

$$D_v = 2.17 \cdot 10^{-5}\frac{p}{p_0}(\frac{T}{273})^{1.81}$$ (2.24)

where p is the mean barometric pressure over the test. According to Vos one gets

$$D_v = (22.2 + 0.14 \cdot (T - 273.15)) \cdot 10^{-6}$$ (2.25)

and Schirmer gives

$$D_v = 2.31 \cdot 10^{-5} \frac{p_0}{p} (\frac{T}{273.15})^{1.81}. \tag{2.26}$$

The different vapour diffusion coefficients are plotted in figure 2.2 as a function of the temperature. The formula originally suggested by Schirmer deviates at temperatures above 50°C, this is not seen in the equation (2.26) but is illustrated in the figure. This should be considered when working at those temperatures.
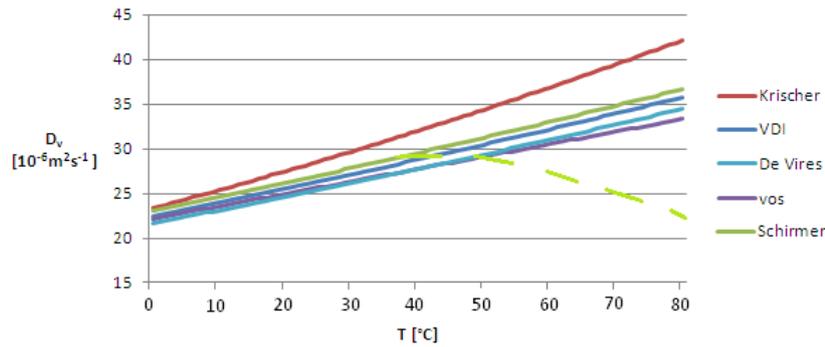
Figure 2.2: *A comparasion between the diffusion coefficients according to the different authors and where the dashed line illustrates how Schirmer originally suggested.*

The different coefficients do not vary significantly and may all be used. To be able to compare different materials with another there must however be a regulation. In Europe the empiric correlation according to the Schirmer formula is used, also seen in ISO 12572 and is therefore used in this work.

There are also different ways of expressing the partial vapour pressure, p_{sat}, used to determine Δp_v. The most common p_{sat} is coming from an equation called Magnus formula, in Sonntag et al. from 1982, which is also used in this work for the gravimetric method. The partial vapour pressure according to Magnus formula can be calculated in a temperature range from $0\,°C$ to $110\,°C$, [13], and depends on the absolute temperature T as

$$p_{sat} = \phi \cdot e^{(\frac{A}{T} + B - C \cdot T + D \cdot T^2 + E \cdot \ln(T))} \tag{2.27}$$

where ϕ is the relative humidity, see (2.29), and the constants $A = -6096.9385$, $B = 21.240964$, $C = 2.711193 \cdot 10^{-2}$, $D = 1.673952 \cdot 10^{-5}$ and $E = 2.433502$. Magnus formula for the partial vapour pressure is not presented in ISO 12572, instead the pressure is given as

$$p_{sat} = \phi \cdot 610.5 \cdot e^{\frac{17.269 \cdot \theta}{237.3 + \theta}} \tag{2.28}$$

where θ is the Celsius temperature. In this work equation (2.27) is used to calculate p_{sat} instead of equation (2.28), this according to BIPM, Bureau International des Poids et Mesures.

2.4.2 Measurements of the change in RH

The relative humidity (RH), ϕ, is defined by

$$\phi = \frac{p_w}{p_{ws}} \cdot 100\% \tag{2.29}$$

where p_w is the partial pressure of water vapour in the mixture and p_{ws} is the saturated vapour pressure.

The RH-sensor based method used in this work follows the standard ISO 15106-1 which will be described more in next chapter. The theory behind it will be presented below.

In Versaperm MkIV WVTR Meter the sample is attached between two chambers; one lower "wet" chamber where the RH is held constant and one upper "dry" chamber where the change in RH is measured. Those chambers are separated by the sample and it is the water vapour that diffuses through this sample that increases the RH in the dry chamber.

The time for the humidity to increase a given amount can be converted into a water vapour transmission rate, WVTR, [17]. This could be illustrated by

$$\text{WVTR} = \frac{\text{mass H}_2\text{O lost}}{\text{time} \times \text{area}} = \frac{\text{flux}}{\text{area}}. \tag{2.30}$$

Equation (2.30) can be expressed by the difference in the partial vapour content Δv_s like this

$$\text{WVTR} = \frac{\Delta v_s \cdot V}{t \cdot A} \cdot 3600 \cdot 24 \tag{2.31}$$

where V is the volume over the sample, A the area of the sample and t the time it takes for the RH to increase from a specified percent to another. Those RHs are also taken into account in v_s as

$$v_s = p_{sat} \cdot \frac{M}{R_v T} \tag{2.32}$$

where p_{sat} is the partial pressure as before, see equation (2.27) or (2.28), M is the molar weight for water, R_v is the general gas constant and T the absolute temperature.

According to the standard the WVTR is calculated by

$$\text{WVTR} = \frac{S \cdot T_R}{T_S} \cdot \frac{A_R}{A_S} \tag{2.33}$$

where S is the WVTR of a reference specimen connected to the machine, T_R and T_S is the time for the RH in the upper dry chamber to increase from its initial value to its final for the reference specimen and the test specimen respectively. A_R and A_S are the transmission areas of the reference specimen and test specimen. In this project no reference specimen will be used and equation (2.31) will be used to calculate the WVTR instead of equation (2.33).

The WVTR can in turn be converted into the water vapour resistance Z_v. This is first done by determining the water vapour resistance in relation to vapour pressure, Z_p, as

$$Z_p = \frac{3600 \cdot 24 \cdot \Delta p_v \cdot 10^3}{\text{WVTR}} \tag{2.34}$$

where Δp_v is as before the difference between the partial vapour pressure on both side of the sample, but in this method equation (2.28) is used for p_{sat}. The difference of the two partial vapour pressure, p_{sat}, is however very small where the biggest difference between them is $<1\,\%$.

Now Z_v can be calculated from Z_p as before by using equation (2.18).

3

Method

BECAUSE THE GRAVIMETRIC method for determining the permeability is well-established and reliable the results from those measurements will be seen as the true values of the samples. To be able to evaluate Versaperm MkIV WVTR Meter one needs to compare the results from this machine with the gravimetric results. The Z_v and WVTR of the materials being tested in this project is therefore first measured with the gravimetric method. After that the same materials are tested in the machine. Before this is done one first needs to know that the sensors in the machine work correctly. This is first done by calibrating the device. When the sensors in the different chambers shows the correct RH one must consider leakage in the chambers. The leakage where the upper and lower chamber connects may be prevented by a gasket and an investigation on the leakage of different gaskets needs to be done. After this the measurements can take place in the machine and the results can be compared with the gravimetric results.

There will also be a crystallinity test on three different materials, all made of polyethylene (PE), to see how this can contribute to the permeance. This to get a deeper knowledge about the polymers behaviour.

3.1   The different materials

In this work nine different polymeric materials were tested; four samples with a low permeability, with a $Z_v \sim 10^6$ s/m; two samples in the middle region, $Z_v \sim 10^5$ s/m, and three samples with a high permeability, $Z_v \sim 10^4$ s/m. The full name of the materials will not be mentioned but table 3.1 will give an insight in what kind of materials it concerns.

The type of polymer in each sample was tested using Fourier transform infrared spectroscopy, FTIR. The spectrum for each material is shown in Appendix A, here also

Table 3.1: The different materials being tested

Material	Type	Characteristic	Z_v
Material 1	PP	Windbreaking film	$\sim 0.5 \cdot 10^4$ s/m
Material 2	PU	Windbreaking film	$\sim 1.0 \cdot 10^4$ s/m
Material 3	PP with ether	Windbreaking film	$\sim 2.0 \cdot 10^4$ s/m
Material 4	PP-based	Air and vapour barrier	$\sim 1.5 \cdot 10^5$ s/m
Material 5	PET	Reference material	$\sim 6.5 \cdot 10^5$ s/m
Material 6	PP-based	Waterproofing foil	$\sim 2.5 \cdot 10^6$ s/m
Material 7	PE	Air and vapour barrier (0.11 mm)	$\sim 2.5 \cdot 10^6$ s/m
Material 8	PE	Air and vapour barrier (0.20 mm)	$\sim 4.5 \cdot 10^6$ s/m
Material 9	PE	Air and vapour barrier (0.20 mm)	$\sim 5.5 \cdot 10^6$ s/m

the spectrum for clean PE, PP, PU and PET are shown for comparison.

3.2 Gravimetric measurements

The gravimetric method used in this project was done according to the international standard ISO 12572.

To begin with the sample needs to be sealed to a cup, this is done using a wax. In this project only glass cups are used, but metallic cups can also be used. There is a need for at least two different cup tests for each material, a dry cup test and a wet cup test. This to see that the Z_v for the different cups are equal and the materials show a linear behaviour. The cup is in turn filled with either a saturated salt solution or a desiccant to obtain the desired humidity inside the cup. An illustration of those cups is shown in figure 3.1. The sample will lose weight if it is a wet cup test and gain weight if it is a dry cup test. For the wet cup test the cup is filled with distilled water to get a RH of 100 % under the specimen. For the dry cup test there will instead be a RH of 0 % by adding calcium chloride, CaCl, as a desiccant. The cups are placed in a chamber where the temperature is held constant at 23 °C and the RH is 75 %, this means that both types of cups will have this RH over the sample. Figure 3.2 shows the chamber where the cups are placed.

The air space between the water or desiccant and the sample shall be 15 ± 5 mm, this is of greater importance if the specimen has a high permeability.

Ten different cups of each specimen is made, five for the wet cup test and five for the dry cup test, in accordance with the standard. An empty cup, with neither water or CaCl but with a small weight, is also made for each specimen. This to be able to make corrections for different atmospheric pressure different days. Figure 3.3 shows the
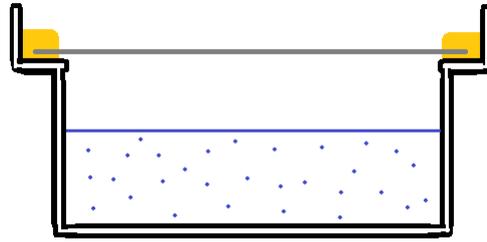
Figure 3.1: *An illustration of the cup test. The specimen is sealed with a wax on a glass cup filled with either water or a desiccant.*

Figure 3.2: *The chamber where the cups are placed. It is containing a saturated sodium chloride (NaCl) bath to keep the RH at a value of 75 %.*

cups for Material 1. The weighing in this project was done manually at time intervals selected according to the specimen. The balance for the measurements is connected to a computer that calculates the sample's equivalent air gap s_d and the resistances Z_p and Z_v. The weighing continues until five successive determination of change in mass per time for each specimen are within $\pm 5\,\%$ of the mean value for the specimen. For specimen with a low permeability this can take months, since weighing with high enough accuracy is difficult.

Due to values on the wet test in Versaperm MkIV Gradient WVTR Meter that did not seem to be correct according to the theory or to the gravimetric values, see chapter 4, a further investigation on the reference material, Material 5, was done. This because the values measured in Versaperm MkIV WVTR Meter on this material seemed to agree well with the gravimetric values for the dry test, see table 4.3. Four new gravimetric cup tests were done for this material. The first test had cups filled with the desiccant CaCl

Figure 3.3: *The cup tests for Material 1. The cups are filled with either water or CaCl, by a closer look one can see the pressure on the samples due to the different humidity inside and outside the cups.*

to give a RH of 0 % inside the cup. The second test had cups filled with the salt solution sodium chloride, NaCl, to give a RH of 75 %. The third test had cups filled with water for a RH of 100 %. Those three cup tests were put in a room with a RH of 50 %. The fourth test had cups also filled with water but were put in a desiccator filled with CaCl.

This test was done to see how the values in the machine vary with different partial pressures compared to the gravimetric values, but also if the RH in the dry upper chamber matters in the measurements.

Material 4 and 7 were also tested in Versaperm MkIV WVTR Meter with different RH in the dry chamber. This to see if those materials behaved in the same way as Material 5.

3.3 Measurements in Versaperm MkIV WVTR Meter

The RH-sensor based method used in this report is done according to the standard ISO 15106-1, but with some differences.

The machine is equipped with six different chambers where the specimens can be placed. A chamber is separated by the specimen that is tested. One side of the chamber, the lower part, will be supplied with water vapour and act as the wet chamber. The other side of the specimen, the upper part, will act as the dry chamber, whereto the specimen will transmit water vapour. A schematic over one chamber is shown in figure 3.4.

The temperature is held constant in the machine during the whole measurement at 23°C within ±0.3 °C. According to the standard only three specimens need to be tested but for some products testing more than three specimens can give a more reliable result.

The machine used in this work is however not capable of only using one chamber at a time, all chambers need to be used at the same time. The measurements will therefore always be on six samples and this for all specimen. The machine is shown in figure 3.5.
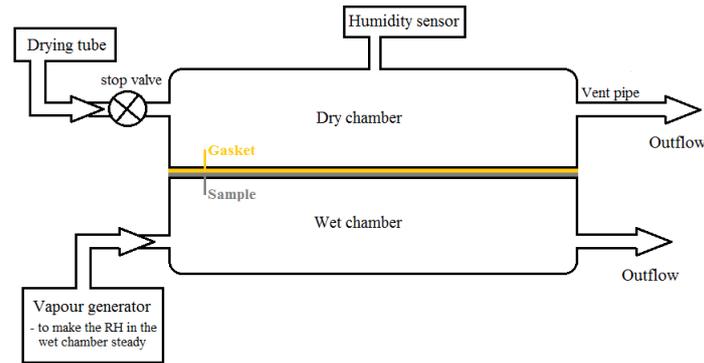
Figure 3.4: *A schematic over the whole chamber. The sample and gasket are placed between the dry and wet chamber before closing.*

In the wet chamber, the relative humidity is controlled by mixing two air flows, one with 100 % RH and one with 0 % to get the desired RH. This RH is being let in to the lower chamber and will be held constant during the complete measurement. The dry chamber will store the water vapour being transmitted until the RH reaches a specified value, then it is dried by a flow of compressed dry air. After the upper chambers are dried the process is repeated. The change in humidity is detected in the dry chamber by a RH-sensor.

The specimens in the different chambers should be of the same material and condition when making a measurement. The measurements in this work use the interval of 1 % lower than the specified RH to 1 % higher. In this project the RH for the "dry cup test" is selected to 2 %, meaning that the measurement starts at the RH 1 % and ends at 3 % and with the wet chamber put to 75 %. For the "wet cup test" the upper dry chamber is instead set to measure between the RH 74 % to 76 % and with the wet lower chamber set to 100 %. The tests made on Material 4, 5 and 7 with other RHs were done in the same way, always with the lower chamber as the wet chamber and the upper chamber as the dry chamber.

First the dry chamber needs to reach the lower RH, this done by the air flow. When the value is reached the air flow is turned off and the measurement of the time taken to reach the higher RH begins. When this value is reached the air flow is again drying the upper chamber and a second measurement can take place. This procedure shall continue until two consecutive times are recorded within ± 5 %, [17].

Versaperm MkIV WVTR Meter differs slightly from the standard. Here one needs

Figure 3.5: *All the six chambers are shown. Chamber 1, 2 and 3 shows when the chambers are closed. Chamber 4, 5 and 6 shows when the chambers are open, it is here the sample is placed before closing. The containers on the front, the bubblers, contains distilled water which will keep the RH steady on the wet side of the sample.*

to tell the device how many cycles the measurements shall continue in advance. The different chambers are also connected to each other and are not dried until all of them have reached the required value. The time is still taken at the time it should according to the standard and are not supposed to affect the result of the WVTR. In ISO 15106-1 a reference material is also mentioned, but is not used in this machine.

One difference to the gravimetric method that should be mentioned is that the driving force is decreasing with time, this when the dry side is getting a higher RH. In the gravimetric method the RH, and therefore the driving force, is constant.

The RH-sensors in the machine are capacitive hygrometric sensors. A capacitor is composed by two adjacent metal plates insulated from ecah other by a dielectric. Changes in the amount of water vapour in the air alter the capacitance in those capacitive hygrometric sensors. The change in capacitance is proportional to the change in relative humidity. The accuracy in the sensor in this machine is $\pm 2\,\%$ RH in the range of 5-95 % RH and at $25\,^{\circ}$C, but could be worse without calibration. This sensor is capable of detecting changes in humidity with a response of 10 seconds within the range of 5-95 % RH.

This means that a calibration needs to be done to get reliable results. An investigation of gaskets also needs to be done to be able to make adjustments for leakage.

3.3.1 Calibration of Versaperm MkIV WVTR Meter

The humidity sensors in each chamber in Versaperm MkIV WVTR Meter must work correctly and be valid. A calibration was done using a convenient method, by adding different saturated salt solutions. Different solutions gives different fixed RH values at a specific temperature. A salt is mixed with distilled water until it is saturated, some more salt is added to the solution so it will stay saturated even if there is moist in the chambers from the beginning. After the solution is placed in the different chambers the calibration can begin.

Two different solution was used, pure distilled water and sodium chloride (NaCl). When the air in the chambers was saturated, with the solution placed in the chamber, the sensors were calibrated. The RH on the sensors was put to 100 when calibrating with pure distilled water and 75.4 when calibrating with NaCl, which is the RH for those specific solutions. A scale parameter on each sensor in the machine was defined and the sensors shall now work properly.

3.3.2 Test of gaskets

The chambers in Versaperm MkIV WVTR Meter, where the test specimens are placed, are closed by a pneumatic piston. Between the chamber halves the test specimen is clamped by the pressure and a leakage due to unevenness in the surfaces may occur. To prevent this a gasket can be helpful. Different kinds of gaskets were investigated using a test specimen made of aluminium foil.

Aluminium is impermeable. It will therefore not be any gas transmission through the specimen whether from the wet lower chamber or the dry upper chamber. All changes in RH will be regarded as some kind of leakage. This test was done for both a dry and a wet test. In the dry test one investigates how long time it will take for the upper chamber to increase its RH from 1 to 3 %. This will in turn be converted into a WVTR and Z_v assuming that the water actually came through the sample and not the gasket. This value was used to make corrections for the WVTR or Z_v directly for the test specimen. The same calculations will be done for the wet test, but here one investigate the leakage out of the upper chamber. This is done by placing a distilled water drop on the surface of the aluminium sample and run a normal test cycle. The RH will increase to a specified value and then be dried by the air flow into the chamber. If the chamber is not fully dried after this the RH will rise again and if it does not reach the limit for drying the water will slowly transfer through the gasket, now one can measure the time it takes for the RH to decrease 2 %, for example 76 to 74 % which can be appropriate to chose when the wet samples are tested at a RH of 75 %. Some chambers did not reach this high RH after being dried and could not be a part of the measurement.

When a gasket is in a range for what could be accepted in leakage, depending on the material being tested, the measurements on the materials in Versaperm MkIV WVTR Meter can be started. Now the WVTR and Z_v for the gasket can be taken into account when taking measurements on the test specimens. What should be kept in mind is

that the difference in RH is between the dry chamber and the environment outside the chamber. It usually varies between 10-50 % depending on the season. When taking the leakage into account the WVTR was used and converted to a Z_v depending on the RHs of the measurements. The WVTR would of course also change with season but was not taken into account in this work. When presenting the Z_v for the gasket the outer RH was set to be 50 %, which is a bit high.

The first gasket that was tested was a PU foam which had a very high leakage, to get rid of the air passages the material was greased with a desiccator grease which gave a lower permeability and therefore a better gasket. A PE foam with almost the same qualities was also greased and tested.

To grease a gasket is not preferable when it tends to take time. The grease itself could also be pressed out from the gasket on to the sample being tested, this might affect the water vapour transmission significantly. A search for a new gasket ended up in testing a material made of ethylene propylene diene monomer (epdm), which turned out to be the best so far. There was however a problem with materials with a rough surface. A gasket that could seal these samples needed to be found. An adhesive material of butyl seemed to be able to do this. There was however no time to investigate this butyl gasket further

3.4   Crystallinity

To get a deeper knowledge in how different materials made of the same type of polymer can differ in permeability a crystallinity test was done for the three different polyethylenes, Material 7, 8 and 9. As mentioned before different crystallinity can give different diffusion coefficients.

The method used to determine the crystallinity followed the international standard ISO 11357-3 using a differential scanning calorimetry (DSC). To determine the crystallinity one first holds the sample at a constant temperature of 25°C for five minutes to make it stabilize, after that the sample is heated in steps of 10 °C every minute until it reaches 180 °C where it is again held constant for five minutes. This procedure is called the first heating and will erase the history of the polymer, which otherwise can give a misleading result in the crystallinity and melting point. The sample will then decrease in temperature until it reaches 0 °C, also made in steps of 10 °C every minute. After being cooled the temperature is again held constant for five minutes before it is heated in the second heating which is done in the same way as the first heating. This is where the crystallinity and melting points can be calculated. The heating and cooling of the sample is done with nitrogen. No oxygen is present to prevent oxidation. The diagram of how the enthalpy changes for the material when making this change in temperature is shown in figure 3.6.
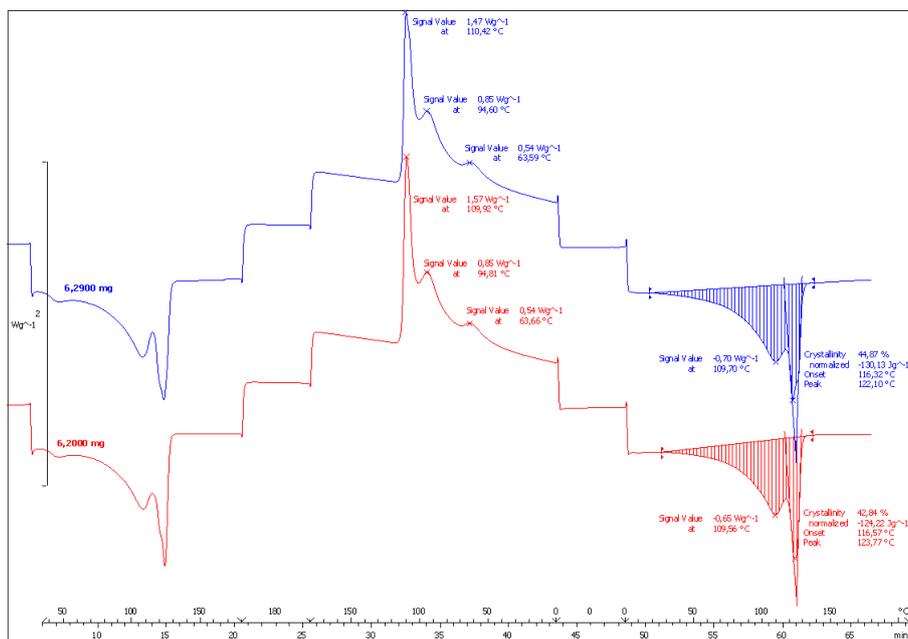
Figure 3.6: *The procedure in the DSC method. The change in enthalpy is shown over time and temperature changing, an increase meaning a loss of enthalpy in the material. The dashed area is where the crystallinity is measured. The plot shows the change for Material 7.*

To be able to calculate the crystallinity percentage called % crystallinity, one needs to know the enthalpy of melting for 100 % crystalline material, ΔH_{100}. For polyethylene $\Delta H_{100} = 290 \, \text{J/g}$. The % crystallinity is then calculated from

$$\% \, \text{crystallinity} = \frac{\Delta H_m}{\Delta H_{100}} \cdot 100 \tag{3.1}$$

where ΔH_m is the enthalpy of melting for the PE sample, [15]. The enthalpy of melting is calculated by integrating the area of the DSC peak on a time basis. The PE melts over a narrow temperature range where the peak is situated at the melting point, T_m, which varies with % crystallinity. A lower crystallinity gives a lower T_m. If the polymer is completely amorphous there is no T_m, the melting is instead done continuously. Also, variations in chain lengths produce lamellae of varying thickness which in turn gives different T_m, [16].

Three different PE samples were tested using this method; Material 7, 8 and 9. There is a specific size of the sample that needs to be cut out and put into a small aluminium container. The weight of this sample must be more than 5 mg and in all three cases more than one piece of this specific size needed to be put in the container. This shall not play a part in the measurements because the sample is melted into a unit. Two tests of each specimen were done.

To be able to compare the % crystallinity of the different materials with its permeability the thickness of each material needs to be taken into account. According to equation (2.15) the permeability changes linearly with the samples thickness. This can also be seen in equation (2.9) where the flux changes inverse to the thickness of the sample. The WVTR is calculated from flux/area. The area of the samples are the same, so by multiplying the result from the WVTR for each material with its thickness one will get a new WVTR where the thickness of the material is taken into account. Now the WVTR of the different materials can be compared with each other due to its % crystallinity, i.e. same % crystallinity will give the same value of this new WVTR.

4

Results

F IRST THE RESULTS from the gaskets will be presented to give a feeling of how much those affect the results on the different materials. The result in how the measurements made in Versaperm MkIV WVTR Meter using a RH-sensor based method compare to the gravimetric measurements will be presented for each material separately. In the dry cup test all the materials were compared, here a correlation graph will be shown. After that the results from the wet cup test and the further tests for Material 4, 5 and 7 will be featured. Here three different graphs will be shown, one for each material.

The result from the crystallinity test will be presented separately.

4.1   The gasket

Three different gaskets were fully investigated; the greased PU, the greased PE and the epdm. Those were tested in both a dry test and a wet, i.e. how much vapour that would transfer into the chamber when measuring against a RH of 2 % and how much vapour that would transfer out from the chamber when measuring against a RH of 75 %. The results are shown in table 4.1 for the dry test and in table 4.2 for the wet test. Both the Z_v and the WVTR with its standard deviation σ will be presented for each gasket. A minimum of four chambers were chosen to overcome the RH of 76 % in the wet test, this to give a reliable result.

For the calculation of Z_v the other side was assumed to have a RH of 50 %, this RH is depending on the season or the environment of the room where Versaperm is placed. This should be held in mind when studying the results of the gaskets.

Table 4.1: The results of the contribution to the Z_v and WVTR from the gaskets in the dry test in Versaperm.

Gasket	Z_v [s/m]	σ	WVTR [g/m^{2}24h]	σ
PU greased	$1.85 \cdot 10^7$	$0.29 \cdot 10^7$	0.047	0.0069
PE greased	$1.02 \cdot 10^7$	$0.15 \cdot 10^7$	0.085	0.012
epdm	$5.14 \cdot 10^7$	$1.22 \cdot 10^7$	0.017	0.0040

Table 4.2: The results of the contribution to the Z_v and WVTR from the gaskets in the wet test in Versaperm.

Gasket	Z_v [s/m]	σ	WVTR [g/m^{2}24h]	σ
PU greased	$-1.77 \cdot 10^7$	$0.36 \cdot 10^7$	-0.026	0.006
PE greased	$-6.45 \cdot 10^6$	$1.18 \cdot 10^6$	-0.069	0.012
epdm	$-1.49 \cdot 10^7$	$2.86 \cdot 10^6$	-0.030	0.006

4.2 Correlation between the two methods

Because the gravimetric method is a well-established method, the results of the Z_v and WVTR from those measurements are seen as more reliable. The results will therefore be presented in values of the results from the Versaperm MkIV WVTR Meter divided by the results from the gravimetric measurements to see how those differ. This meaning that a value closer to 1 shows a better agreement between the two different measurements. All individual results for the Z_v and WVTR from the dry and wet test will be shown in Appendix B.1 and B.2. The values from the further measurements on Material 4 and 5 will be presented in Appendix B.3.

4.2.1 The dry cup test

All nine materials were tested in the dry cup measurements with the epdm gasket. The results from Versaperm MkIV WVTR Meter is divided by the gravimetric results to compare how much they differ, both for the Z_v and the WVTR. Table 4.3 shows the results from the dry tests.

The results shown in table 4.3 are illustrated in figure 4.1. Here the quotient $\frac{\text{Versaperm}}{\text{gravimetric}}$ is shown as a function of the increasing gravimetric Z_v.

A log-log plot of the real Z_v from both methods is shown in figure 4.2. Also a log-log plot of Z_v from both methods for the materials lying in the middle and low permeability region, Material 4, 5, 7, 8 and 9, is shown in figure 4.3. Material 6 is excluded when it is a more complex material showing values from Versaperm way off the gravimetric values.

Table 4.3: The results from the measurements done in Versaperm divided by the results from the gravimetric method, this for the dry test. A complete matching would give the value 1.00 for both Z_v and WVTR.

Versaperm/gravimetric	Z_v	WVTR
Material 1	4.28	0.25
Material 2	2.87	0.36
Material 3	1.23	0.80
Material 4	0.85	1.15
Material 5	0.96	1.03
Material 6	0.17	5.74
Material 7	0.79	1.23
Material 8	0.86	1.13
Material 9	0.908	1.074
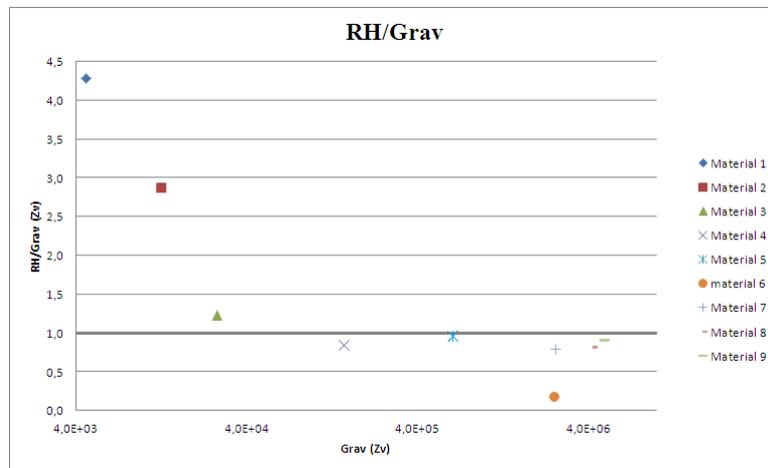
Figure 4.1: *The result from the divided Z_v shown in table 4.3 against the gravimetric Z_v. Material 4, 5, 7, 8 and 9 lies within a small different range from each other and the gravimetric value. The closer to the thick line at 1.0 the dot is situated, the closer the result from the measurements done in Versaperm is to the gravimetric.*

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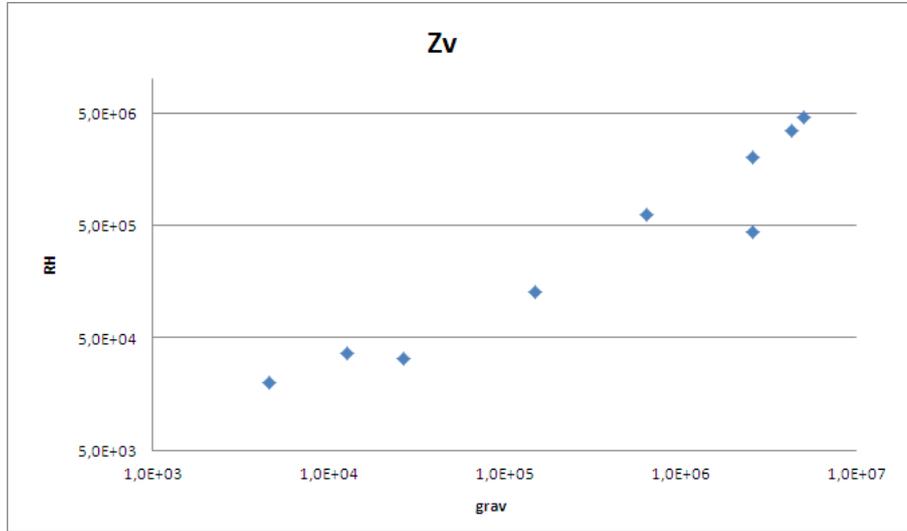
Figure 4.2: *A log-log plot of Z_v on the dry test. The gravimetric values on the x-axis and the values from Versaperm on the y-axis.*
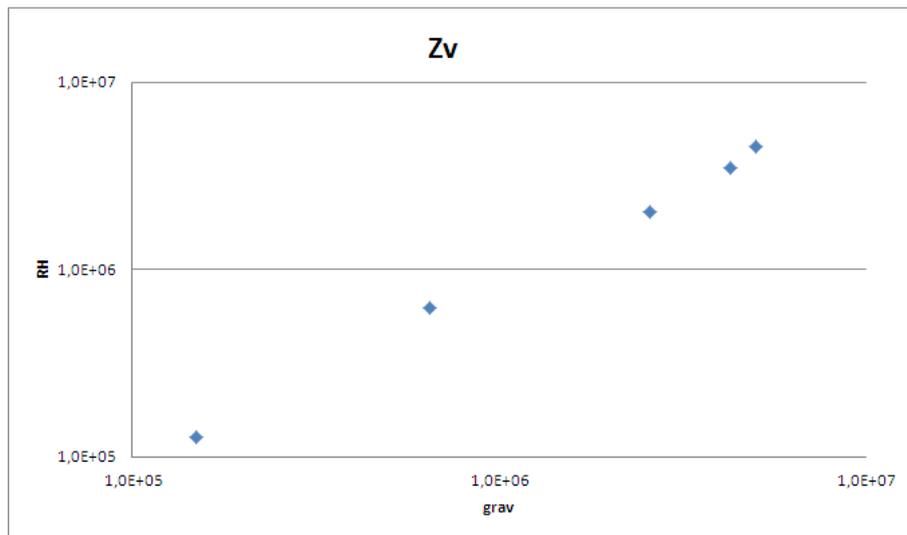
Figure 4.3: *A log-log plot of Z_v on the dry test for Material 4, 5, 7, 8 and 9. It shows an almost straight line which would have been preferable for all materials being tested.*

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4.2.2 The wet cup test

Only Material 4, 5 and 7 were tested in the wet test, this because of bad compliance between the results from the two methods. The results from Versaperm is again divided with the gravimetric results and are shown in table 4.4.

Here one chamber often seemed to be out of range compared to the rest of the chambers, sometimes another chamber were way off the rest of the chambers. If any chamber showed a result that was more than two standard deviations away from the mean value of the rest of the chambers it was not taken into account. One chamber had values that were almost always beyond this restriction.

Table 4.4: The result from Versaperm divided by the gravimetric result, this for the wet test. A complete matching would give the value of 1.00.

Versaperm/gravimetric	Z_v	WVTR
Material 4	2.37	0.40
Material 5	3.36	0.31
Material 7	2.68	0.38

4.2.3 Results from Material 4, 5 and 7

The PET-film, Material 5, had the best agreement between the two methods in the dry test and were therefore further investigated. The results from Versaperm MkIV WVTR Meter seemed to follow a pattern and by presenting this in a different way this was made very visible. By dividing the WVTR with the difference in RH on both sides of the sample the theory for Fickian diffusion predict that this will give the same value for all measurements, this is the same theory that give us the same Z_v in different RHs. This value will be plotted against the difference in RH, see figure 4.4.
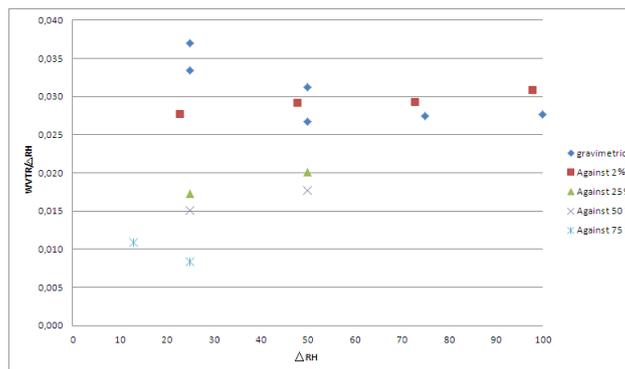
Figure 4.4: *The results for Material 5 when measuring against different RHs on the dry side. The results from the gravimetric values are also shown. What can be seen in this plot is a decrease of WVTR when increasing the RH on the dry side in Versaperm.*

When measuring against a RH of 2 % the result lies within the range for the gravimetric values, despite different RHs on the wet side of the sample. When measuring against a RH of 25 % the WVTR decreases. It decreases more when measuring against a RH of 50 % and even more when measuring against 75 %. The measurements in Versaperm MkIV WVTR Meter also show the most horizontal lines within those different RH, this in agreement with the theory.

To see if this pattern followed other materials the results from Material 4 and 7 will be presented in the same way as the result from Material 5, see figure 4.5 and 4.6.
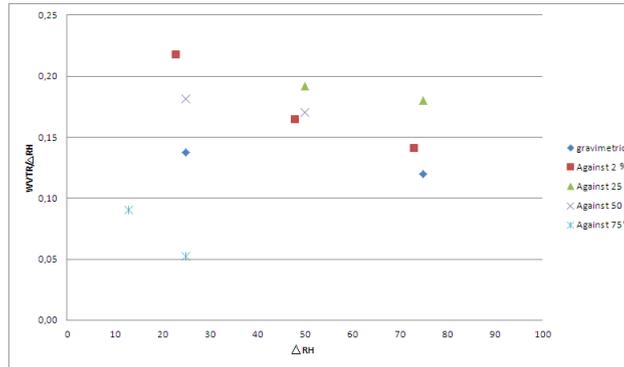
Figure 4.5: *The results for Material 4 when measuring against different RHs on the dry side. The results from the gravimetric wet and dry cup tests are also shown. In this plot no clear connection to the different RHs are shown.*
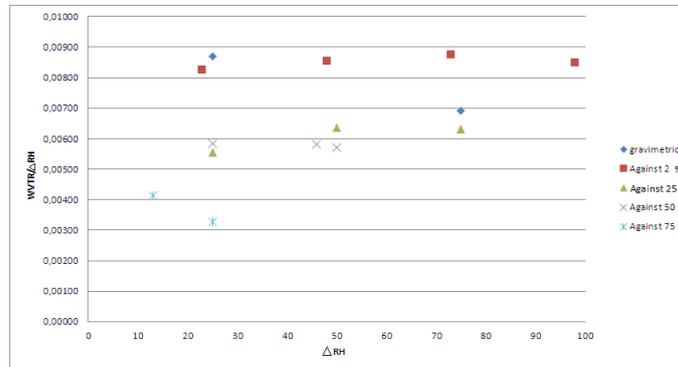
Figure 4.6: *The results for Material 7 when measuring against different RHs on the dry side. The results from the gravimetric wet and dry cup tests are also shown. Here the decrease in WVTR is connected to the increase of RH of the dry side in Versaperm.*

4.3 Crystallinity

The crystallinity test was done for Material 7, 8 and 9. The results of the % crystallinity are compiled in table 4.5. The crystallinity is compared to the WVTR multiplied with the thickness, L, of the sample to see if it agrees with the theory.

The figures over the DSC peak for each material at where the enthalpy of melting, ΔH_m, is calculated which in turn gives the % crystallinity is presented in Appendix C. The melting point, T_m, can also be seen in those figures.

Table 4.5: The % crystallinity for the three PE materials and its WVTR, [g/m²·24h], multiplied with the thickness L, [mm], of the sample. WVTR$_d$ stands for the dry test and WVTR$_w$ stands for the wet test.

Material	% crystallinity	WVTR$_d$ · L	WVTR$_w$ · L
Material 7	43.86 %	0.060	0.025
Material 8	45.44%	0.062	0.023
Material 9	45.06%	0.054	0.024

5

Analysis

T HE RESULTS FROM the measurements done in the Versaperm MkVI Gradient WVTR Meter using the RH-sensor based method will in this chapter be analysed and compared to the gravimetric method and results. The % crystallinity of the three different polyethylenes will also be analysed.

5.1 Preferable gaskets

The gasket used in all measurement, both in the dry and the wet test, was the epdm. In the dry test the epdm showed the best result, the leakage into the chamber was only $0.017\,\mathrm{g/m^2 24h}$. As mentioned in Methods the leakage is seen as if it is through the material being tested, this to be able to make adjustment for the leakage. This leakage was taken into account for all measurements but could have been neglected when the material had a high permeability. For the materials with a lower permeability this leakage will have a greater impact. The corresponding resistance, Z_v, for the epdm-gasket was $5.14 \cdot 10^7\,\mathrm{s/m}$. This lies in a higher range than all materials being tested, which can be seen as a requirement for the gasket. The greased gaskets were also in this range for the dry test, but not as high as the epdm.

In the wet test the leakage out of the chamber was greater than the leakage into the camber for the dry test. Here the best result was from the greased PU with $0.026\,\mathrm{g/m^2 24h}$, also seen if it was through the material and not the gasket itself. Even if this PU gasket gave the best result the epdm gasket was used with a leakage of $0.030\,\mathrm{g/m^2 24h}$. This is not far away from the PU gasket and it was used because it was more convenient. Another reason is because of the grease in the PU that could be squeezed out of the gasket on to the material and act as a non-permeable layer. To work with greased gaskets is therefore not preferable. It is also time consuming to grease a gasket and it can be hard to tell when it is time to grease it again because of grease getting stuck on the sample tested. The shape of those greased gaskets changed during

use and could be hard to fit in the machine. The corresponding resistance, Z_v, for the epdm in the wet test was $1.49 \cdot 10^7$ s/m which is higher than all materials that were tested.

The first measurements on the epdm gaskets gave worse results then later measurements, this is because this material needs to be conditioned. The material itself can loose moist but sorption could also occur. Therefore different gaskets of this material were made depending on if it was for the dry or the wet test. The gaskets made for the dry test were put in a desiccator dried with the desiccant CaCl to prevent the epdm to take up any moist when not in use. The epdm gaskets made for the wet test were instead placed in a chamber with a 75 % RH made by a bath of saturated NaCl.

5.2   How the methods compare

The results from Versaperm MkIV Gradient WVTR Meter compared to the gravimetric results differed depending on if it was a dry or a wet test. This section will therefore be divided into three subsections, the first analysing the dry test, the second the wet test and the third analysing the PET material, Material 5, in different RHs and the result from the measurements on Material 4 and 7 made in Versaperm MkIV WVTR Meter.

5.2.1   The dry cup test

In the dry test the methods were comparable. This test was done at least two times for each material.

For the reference material, Material 5, which is a PET there were almost no difference between the results in the two methods. For the four air and vapour barriers, Material 4, 7, 8 and 9, the resistance Z_v was around 10-20 % lower than in the gravimetric dry cup test. Material 7, 8 and 9 are all PE films and it is not strange that those materials act the same way.

For the two materials with a high permeability, Material 1 and 2, the resistance Z_v seemed to be 3-4 times higher than the gravimetric values. For Material 3 the Z_v also seemed higher, but only around 20 %. To be able to measure those materials the air flow into the upper chamber needed to be much higher than for the other materials. This to be able to lower the RH in the dry chamber faster than the moist transferred through the membrane. This flow needed to be higher for Material 1 and 2 than for Material 3. This flow could have been the reason for the high values on the Z_v. This high air flow could have dried the wet lower chamber through the sample to a much lower RH than it was supposed to have. In one chamber this flow also seemed to dry the tubes where the moist from the bubblers enter. This means that there will be a delay in the resistance due to an air layer. Or this air could have caused a condensation drop in the tube which also would have affect the measured resistance for the sample. In one of those tests, with Material 2, one of the six chambers was measured without a sample, this chamber gave almost the same resistance as the other five which proves the theory of the tubes getting dried as well. Another thing that can increase the measured resistance is the

RH-sensors not being able to measure as fast as they need to for this increase in RH. 10 seconds might not be accurate enough for those samples.

Material 6, which lies in the lower permeability range, gave a totally different result than the other materials. This material is a PP, but with an outer layer of diffusible PE-mesh. This layer is diffusible because of its structure with many air passages. This layer could transfer moist out or into the chambers. The gasket, epdm, that was used in all measurements was not preferable for this kind of material. Instead an investigation with another gasket made of butyl was started. This butyl is self-adhesive and by attaching the sample between two layers of this material it might prevent moist from transferring out or into the chamber. The sample is not covering the whole gasket and the edges of the butyl are sealed because of this adhesive surface. This investigation was not complete and any conclusion from this can not be presented, but it gave an indication of a result closer to the real values for this material. A further investigation of this gasket and types of materials can be seen as a next step in this dry cup test. What can be said about the butyl gasket is that it also needs to be conditioned like the epdm gasket and it can only be used once.

5.2.2 The wet cup test

Not all the materials were tested in the wet cup test, because of a big difference to the gravimetric result. First the reference material, Material 5, was tested with more than three times higher resistance than in the gravimetric measurements. Material 4 and 7 were also tested to see if they behaved in the same way, which they did. A three times higher Z_v cannot give any trustworthy result. There are a few things that can give those high resistances. One of them can be because of the high RH of 100 % which might provide condensation in the tubes from the bubblers which in turn will hinder the moist from reaching the lower chamber. The working range for the sensors is as mentioned before 5-95 % which can cause some trouble. The condensation will give a smaller gradient between the lower and upper chamber which will show as a higher resistance. By measuring the RH of the air flow out of the lower chambers one could get a hint of the real RH inside the chamber. The temperature outside the machine is lower than inside, namely 20 °C, this gives a higher RH for the same amount of water vapour. With a RH of 100 % inside the wet chamber condensation showed in the pipes outside the machine as expected. When measuring with a RH of 75 % in the wet chamber a RH of ~89 % was measured outside the machine, also as expected. This gave an indication that the bubblers were able provide the correct RH inside the wet chambers. Therefore there might not be any condensation in the tubes into the chambers and this scenario might not be the case for the higher Z_v.

By looking into the theory the high resistance may be that the measurements are taking place when the material is not in steady state. By studying figure 2.1 it might be that the measurement is taking place before the linear region, this will show as a higher resistance. This is illustrated in figure 5.1. Because of the sample always being dried there can occur fluctuations within the material which will prevent a steady state.

The sample might get a lower concentration of water molecules when dried which needs to increase before steady state occurs, lowering the concentration within the material gives an increase of the Z_v. There will also be an energy barrier for the water vapour to overcome when entering and leaving the material, especially for hydrophobic materials like the ones in this work. In steady state this barrier is already crossed and shows a steady flow through the membrane. If the material is being dried between every cycle the water vapour needs to overcome this barrier in every measurement which will also increase the Z_v. The question is why this does not occur in the dry cup tests. The difference of the RH in the air flow and the dry chamber is however not as high in the dry test as in the wet test. If it is this energy barrier that is the problem and that the sample is getting dry when flushing with dry air a solution might be to flush with air with a RH closer to the RH of the measurement.
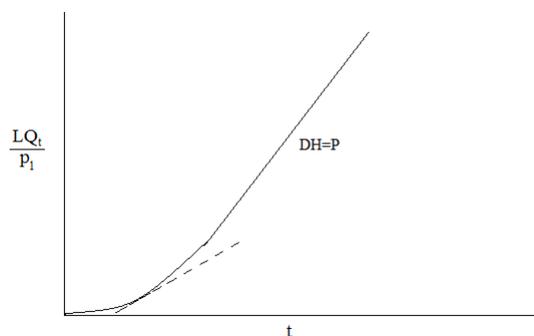
Figure 5.1: *Instead of measuring in steady state where the slope of the curve shows the real permeability a fictive permeability of the sample is measured. The dashed line shows this fictive slope for the permeability. In this case the measured resistance is higher than the real one.*

Plots over the weight of water that penetrates the samples over time is done for the gravimetric measurements for the wet cup test on Material 4, 5 and 7, see Appendix D. The curve for each material shows a linear increase which indicates that the measurements are taken when the sample has reached its steady state condition. The intercept is almost at $t = 0$ for Material 4 and 5, meaning that neither of the samples need a long time to reach steady state. For Material 7 the intercept occurs after some hours. The similar behaviour of the three materials, despite different intercepts, shows that it is not likely that the measurements are taking place before steady state.

Something else must lay the ground for this non expected behaviour. The measurements on Material 4, 5 and 7 were done for further investigation on this behaviour.

5.2.3 The further investigation on Material 4, 5 and 7

The results from the investigation of Material 5 did seem to follow a specific behaviour. The WVTR decreases when increasing the RH of the dry side of the sample. It could

almost be predicted where a new measurement would land in the plot in figure 4.4. The change does not follow a complete straight pattern. Again a plot of the amount of water vapour that has penetrated the sample at steady state is done for all different RH-differences of Material 5 by using the gravimetric measurements, see Appendix D. The different slopes of those curves seem to follow the theory and the intercept is again close to $t = 0$. Why this change in WVTR and therefore also Z_v occurs in the machine when changing the RH of the dry side cannot be explained by the theory. But if the air flow is flushing straight on the sample there still might be an energy barrier that needs to be overcome. Again; the intercept on the Q_t-plot is close to $t = 0$. Something else than the material itself must lay the ground for this behaviour.

By consulting with the constructor of the machine and how it is built a new theory of why this occur is discussed. The upper chambers are, as mentioned in chapter 3, dried when all of them have reached the higher RH in the measurement. This dry air is coming through a pipe which is divided into six small pipes leading into one chamber each. These small pipes represent a small volume that is connected to each chamber. This small volume will have a RH of $\sim 0\,\%$. Even if this volume is small it will appear bigger when measuring at a higher RH on the dry side. Because the RH in the volume will increase from zero to a much higher RH. When measuring against a RH of $2\,\%$ this small volume will not "steal" as much water vapour as when measuring against a RH of $25\,\%$. Even more water vapour will make its way to this small volume when measuring at a RH of $50\,\%$ and $75\,\%$. By calculating how much water vapour is needed to be absorbed to give the high resistance, shown in figure 4.4, one can calculate how big the volume needs to be for each chamber. By doing this calculation a volume of $\sim 3 - 5\,\mathrm{ml}$ was found and was depending on the RH in the dry chamber. According to the constructor the volume should however be much smaller than this and the pipe cannot alone give this rise in resistance.

What is satisfying by this theory of the dry extra volume is that it explains why this increase of Z_v is happening and it can also predict how much the WVTR and the Z_v will differ from the gravimetric value. However, if the volume alone would be the reason for the increase of Z_v for Material 5 the volume seems to change in size depending on the RH in the dry chamber, i.e. it is not possible to predict the difference.

To see if the same behaviour occurred when measuring on another material the same test was done on Material 4. Those measurements gave a complete different result than expected. This can however be because of the complexity of Material 4 which has an uneven surface covered with a mesh fabric. The material itself gave very different Z_v because of its construction.

It was preferable to do this test on another material, like Material 7. A further investigation on this behaviour was therefore done. The increase in resistance did seem to follow the same behaviour as for Material 5, but not with the same magnitude. So even if there is an expected behaviour one cannot predict what the result in a measurement will be for other materials or even on the same material when changing the RH on the

dry side. One should also have in mind that the leakage in the chamber for Material 7, when measuring with a small driving force, can be more than the measured resistance. This is not optimal and can also play a part in this behaviour.

5.3   Versaperm MkIV Gradient WVTR Meter

The Versaperm MkIV Gradient WVTR Meter gives different accuracy depending on the material that is being tested. If the permeability is high it is hard to dry the upper chamber to a low RH. The flow can be turned up but at some point the pressure will damage the sample. Even if it manages to lower the RH to a set value the sensors are not fast enough to measure with a high accuracy on those materials. A limit in how high permeance that can be measured may need to be set. The dry test for Material 3 did not differ much from the gravimetric value but did need a very high flow on the dry air to reach the low RH. Material 3 showed a higher Z_v in the machine compared to the gravimetric value while the other materials with a lower permeability showed a lower Z_v than in the gravimetric measurements. The higher Z_v for Material 3 can be due to the high air flow. The wet air on the other side may also dry if this air penetrate through the sample, this gives a lower driving force which will show as a higher resistance for those sample lying in this region. The lack of materials with a resistance between Material 3 and 4 makes is hard to say where exactly this limit should be, but should be somewhere between $2.5 \cdot 10^4$ and $1.5 \cdot 10^5$ s/m when measuring against a RH of 2%. When measuring on materials with a resistance lower than $1.5 \cdot 10^5$ m/s this phenomena must be considered.

To give an indication of how high resistance of a material the Versaperm MkIV WVTR Meter can measure the leakage can be seen as a limit. If the corresponding resistance of the leakage is lower than 10% of the measured resistance of the material one should consider if there is a good agreement with the real resistance of the material. The epdm gaskets showed a resistance of $5.14 \cdot 10^7$ s/m for the dry test, this gives a the higher limit of the resistance for material being tested as $5.14 \cdot 10^6$ s/m. In the wet test this higher limit will instead be $1.49 \cdot 10^6$ s/m.

The limits for the Z_v that can be measured in the machine are shown in table 5.1.

Table 5.1: The limitations for the Z_v that can be measured in Versaperm MkIV WVTR Meter.

	Low limit [s/m]	High limit [s/m]
Dry test	$2.5 \cdot 10^4 - 1.5 \cdot 10^5$	$\sim 5.1 \cdot 10^6$
Wet test	-	$\sim 1.5 \cdot 10^6$

When measuring on Material 5 with a higher RH on the dry side than 2% the Z_v in one chamber, and sometimes two, seemed far off from the others. A theory that the mean value of the RH in this dry chamber was higher than required came up. This could occur

if there is a lack of turbulence in the chamber that does not mix the air completely. This can make the sensor measure a RH that is lower than the average. When studying the log-files for the measurements an exponential increase of the RH in those chambers was found. In the other chambers a linear increase of water vapour in the dry chamber was found. This indicated that this theory was true, that the dry air flow in those chambers did not mix the air enough and therefore the RH-sensors showed a lower RH than the average. This problem might be fixed by making the air flow more turbulent. One way of doing this is by an increase of the flow. This might give the same problem that happened for Material 3, that the air in the wet chamber also dries. This is not likely for the least permeable materials, instead the dry air in some of the chambers will dry far more than they have to. This will increase the time of the measurement, especially when the driving force in those wet tests are not that high and the permeance in the materials low. A balance of the increase in time to the more stable measurement for all chambers must be found. To flush with air with a RH closer to the RH of the measurement might solve this problem too.

There is also this increase in Z_v of Material 5 when increasing the RH on the dry side of the sample which needs to be investigated further. The same increase happen for both Material 4 and 7 when measuring against 75 %, but the further investigation on Material 4 did not follow the same behaviour as Material 5.

For the moment there is no reference material connected to this machine, as mentioned in the standard ISO 15106-1. If a reference material is used it might compensate for some of the disagreements in the measurements. Earlier, Material 5 has been decided to be the reference material and it is therefore also appropriate to investigate this material further.

If some of the water vapour actually disappear into the small extra volume there can be some improvements. This by installing a simple valve that let dry air out of the pipe by the air pressure made by the air flow. When the air flow is turned off the valve would also hinder the moist to go into the small volume because of the difference in the water vapour pressures between the chamber and the small volume. This construction can be made by a plug in a cone shaped pipe, it opens when the pressure is in one direction and closes in the other direction.

In constellations for nozzles, where compressed dry air is coming through, sometimes contains a desiccant that could absorb some of the moist. An investigation of the nozzle into the chambers in the machine was done. This by first flushing with the dry air for some minutes with the chambers open and then close the chambers simultaneously as the air flow was stopped. If there would have been a desiccant in the nozzles into the chambers the RH in the chamber might have decreased after closing, this did not occur and there is probably no desiccant present.

5.4 The effect of crystallinity

The three different PEs were shown to have almost the same % crystallinity. According to the theory this indicated that those should have similar WVTR after compensating for the thickness of the sample. This is also what the result shows, see table 4.5. It is therefore hard to analyse how the % crystallinity affect the permeance by just analysing this result.

The magnitude of the melting points, T_m, differ between the different materials, see figures C.1, C.2 and C.3. Even if Material 7, 8 and 9 are all made of polyethylene (PE) the melting points can differ because of different size of the crystals within each material. As mentioned in the theory different thickness of the lamellae due to different chain length of the polymer chains can affect the melting point. The concentration of thicker lamellae might therefore be higher in Material 7 than in Material 8 and 9. This does not affect the % crystallinity and therefore not the permeance.

6

Conclusion

One question still remains about the Versaperm MkIV WVTR Meter, why the Z_v increases when measuring against a higher RH for Material 4, 5 and 7. If the results with different "dry sides" are separated it seems like the resistances lie in a narrow range. And when measuring against two the results seem to be even more accurate than the results from the gravimetric method. The measurements against a higher RH seem to follow a pattern for Material 5, but the increase in resistance does not seem to increase with the RH in a predictable way. Measurements of more values on the RH in the dry chamber might give an exact correlation between the two methods for this material. Now one can only see an indication in what the result in the Versaperm MkIV WVTR Meter will be.

The increase in Z_v could however be the reason why a reference specimen is mentioned in the standard and it is convenient to believe that this can "fix" the problem with the high RH on the dry side. The change in the results on Material 5 in the machine is not consistent with the change in the results on Material 4, this can be because of the complexity of Material 4. The further investigation on Material 7 showed a similar behaviour as Material 5, but was still not consistent. Even for the other materials, when measuring against a RH of 2 %, the result for Material 5 does not match. Material 4, 7, 8 and 9 differ 10-20 % from the gravimetric value and Material 5 only some few percent. It can therefore be appropriate to consider if Material 5 is good as a reference material. This material does also differ from the others in type of polymer. All of them are semi-crystalline but Material 5 with a glassy amorphous part and the others with a rubbery amorphous part.

The air the chamber is being flushed with can be another reason to this increase in Z_v. If this air instead got a RH that is a little bit lower than the RH that the sample is being measured against it might improve the measurements. This requires a change in the construction and a new investigation. The time it takes for the chamber to be dried

to its lower RH takes only a couple of minutes and the increase in RH of the "dry air" would not affect the total time of the measurement significantly.

As Versaperm MkIV WVTR Meter is constructed today there are however a low and a high limit in the resistance that can be measured. The lower limit is somewhere between $2.5 \cdot 10^4$ and $1.5 \cdot 10^5$ s/m when measuring against a RH of 2 %. The leakage into or out from the chambers sets the upper limit of the Z_v that can be measured. If the highest leakage is not more than 10 % the results from the epdm gaskets gives a higher limit of $\sim 1.5 \cdot 10^6$ s/m for measurements made against 75 % and $\sim 5.0 \cdot 10^6$ s/m for measurements made against 2 %. Those limits are quite low and a further investigation on the gasket would be preferable. A change in the pressure force connecting the chambers could also prevent the leakage. The leakage may also vary with the RH outside the machine. This variation would be fixed easy by placing the Versaperm in a room with constant RH and temperature. One could also measure the RH outside the machine all the time, but the driving force and therefore leakage would vary as well as the resistance depending on the RH.

If the Versaperm MkIV WVTR Meter would be able to measure more accurate the time it takes for materials in the range of $\sim 10^6$ s/m when measuring against 75 % takes some days or even a week to measure. This still lies in a much smaller time scale than the gravimetric measurements, where it would take at least six to seven weeks.

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A

Materials

To see what kind of polymers the materials in this project are made of a FTIR test was done on each of the nine different materials. The spectrum of each material is shown in next section, for comparison the spectrum for PP, PU, PE and PET are shown afterwards.

A.1 Materials in this project
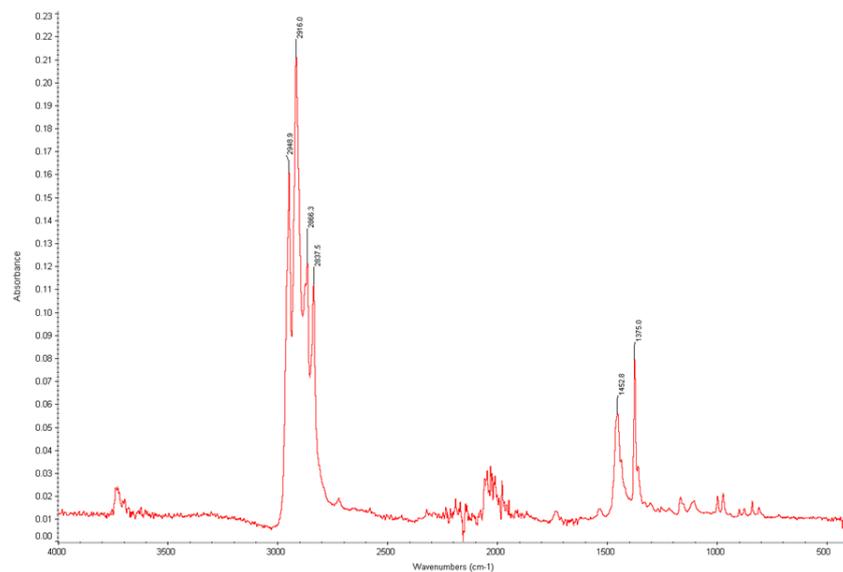
Figure A.1: *Material 1 shows a PP-spectrum*
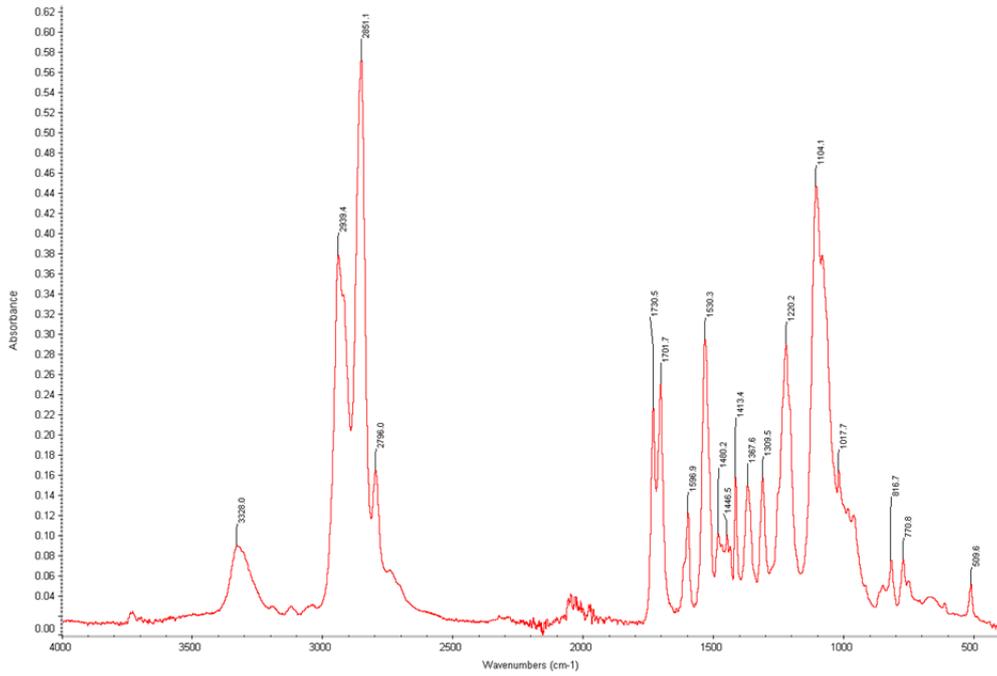
Figure A.2: *Material 2 shows a PU-spectrum*
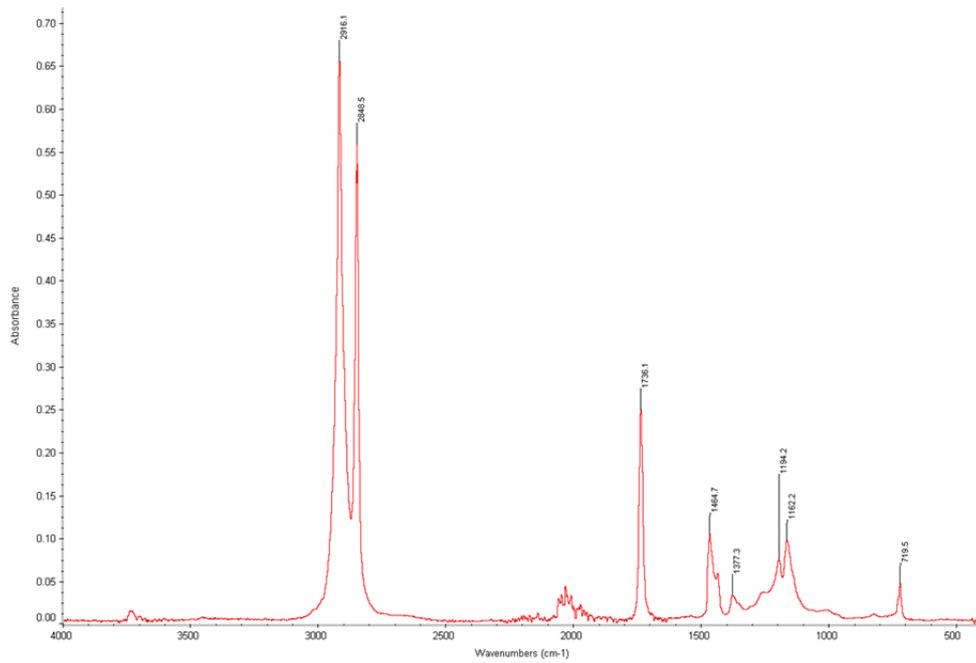
Figure A.3: *The film of Material 3 shows a peak at the wave number $1736cm^{-1}$, this indicates that there is an ether in the material.*
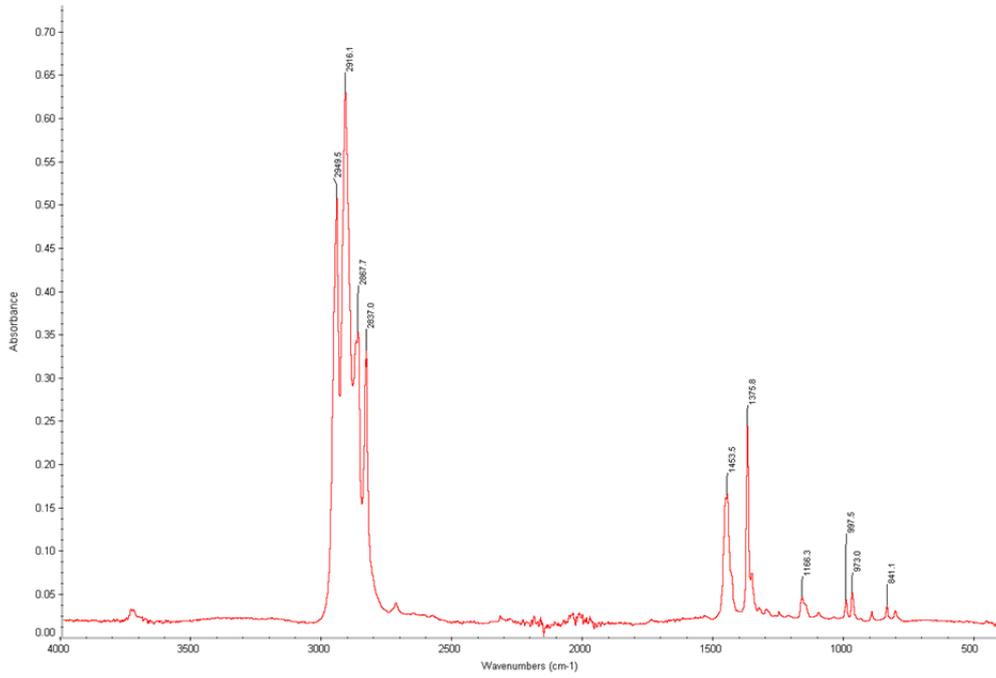
Figure A.4: *The coating on Material 3 shows a PP-spectrum*
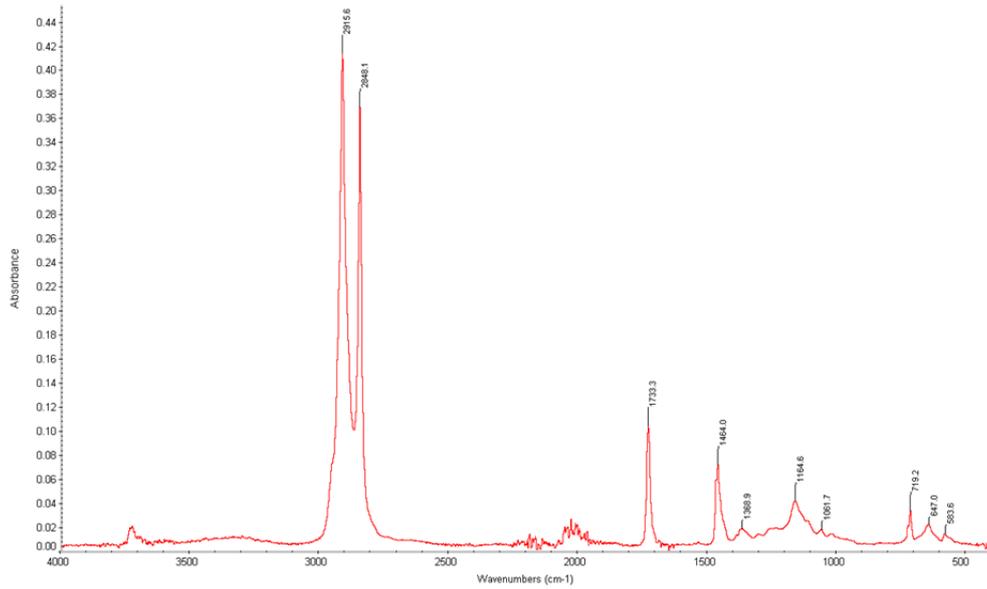
Figure A.5: *Material 4 shows a PP-spectrum, also with an ether. It also includes a PE-copolymer as a coating mesh.*
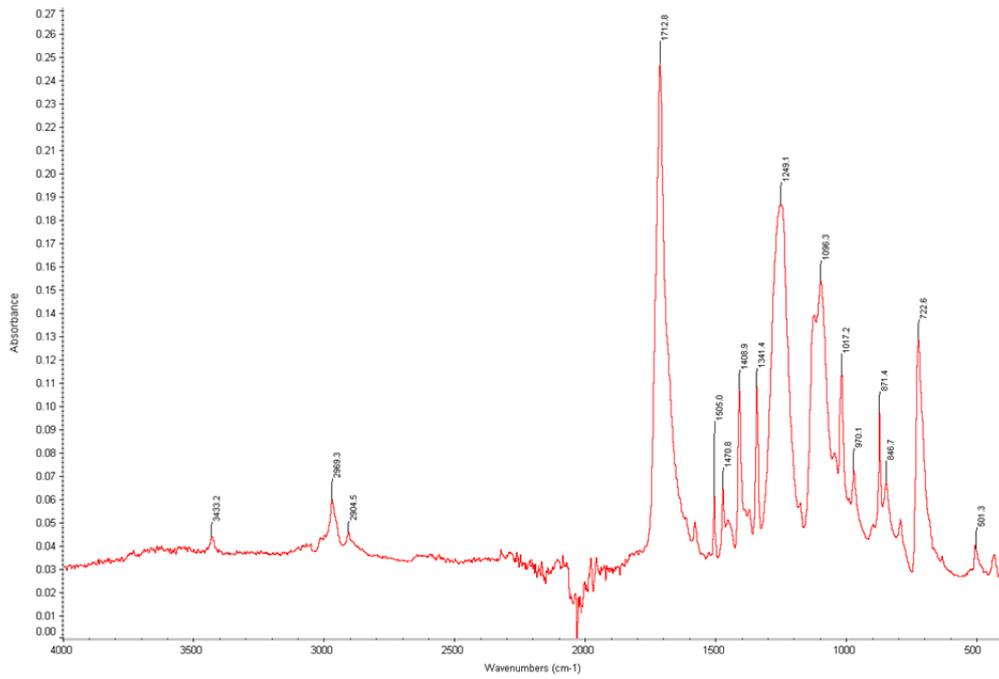
Figure A.6: *Material 5 shows a PET-spectrum*
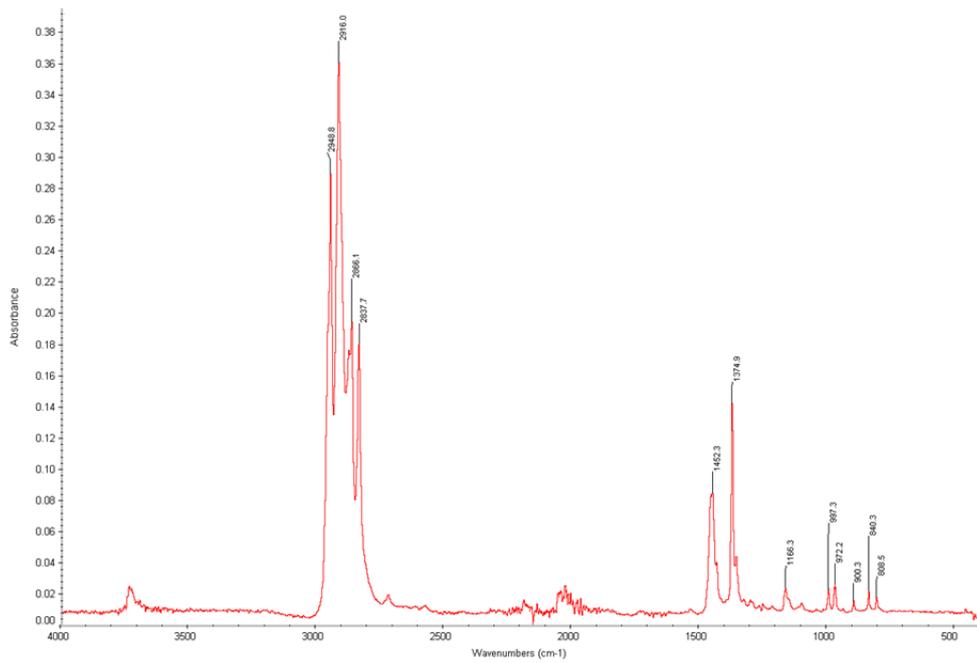
Figure A.7: *Material 6 shows a PP-spectrum.*
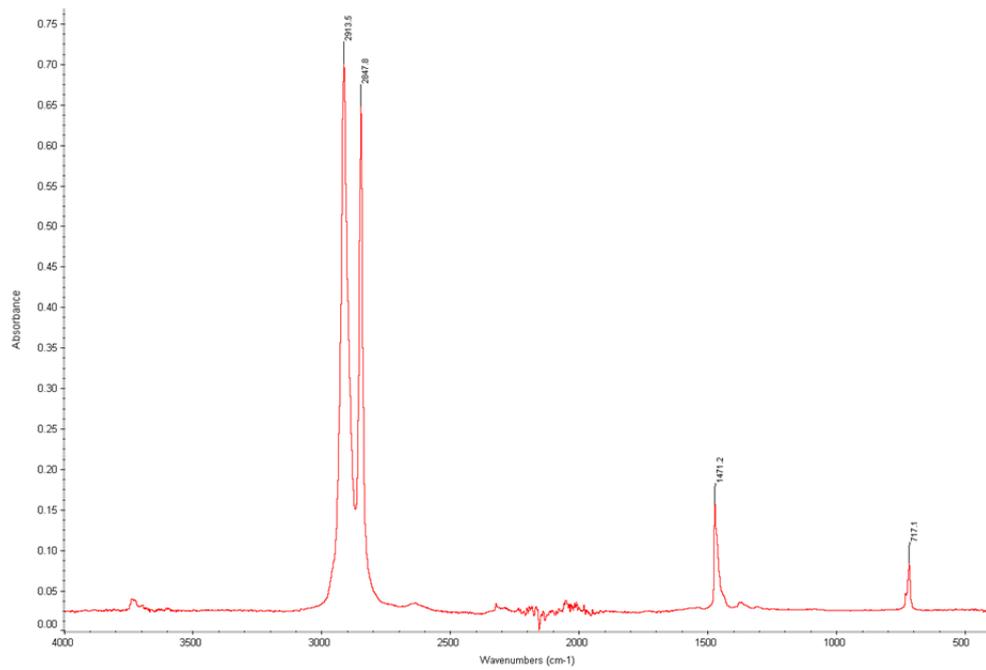
Figure A.8: *Material 7 shows a PE-spectrum.*
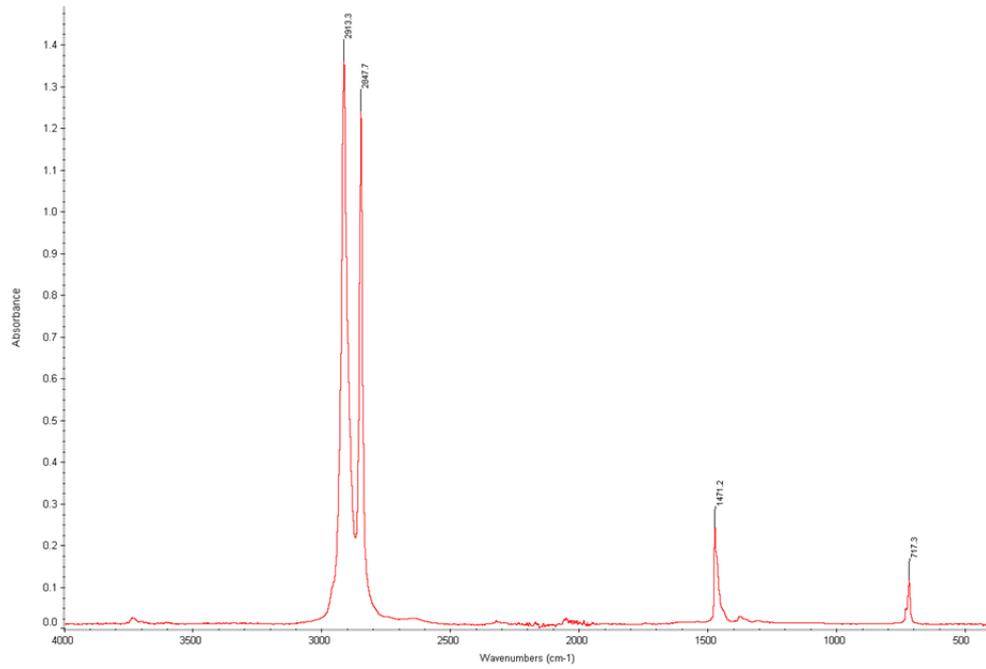
Figure A.9: *Material 8 shows a PE-spectrum.*
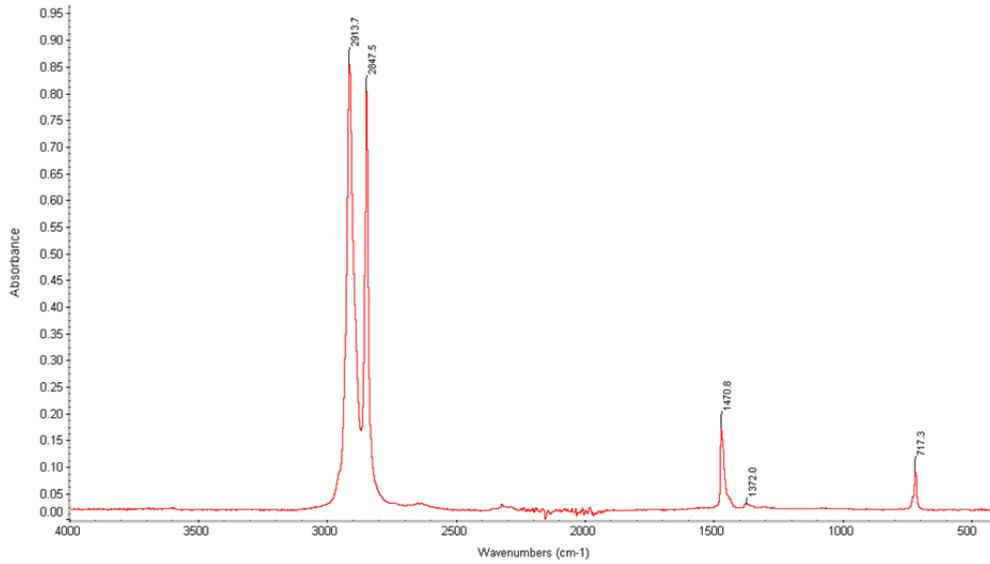
Figure A.10: *Material 9 shows a PE-spectrum.*

A.2   PP, PU, PE and PET
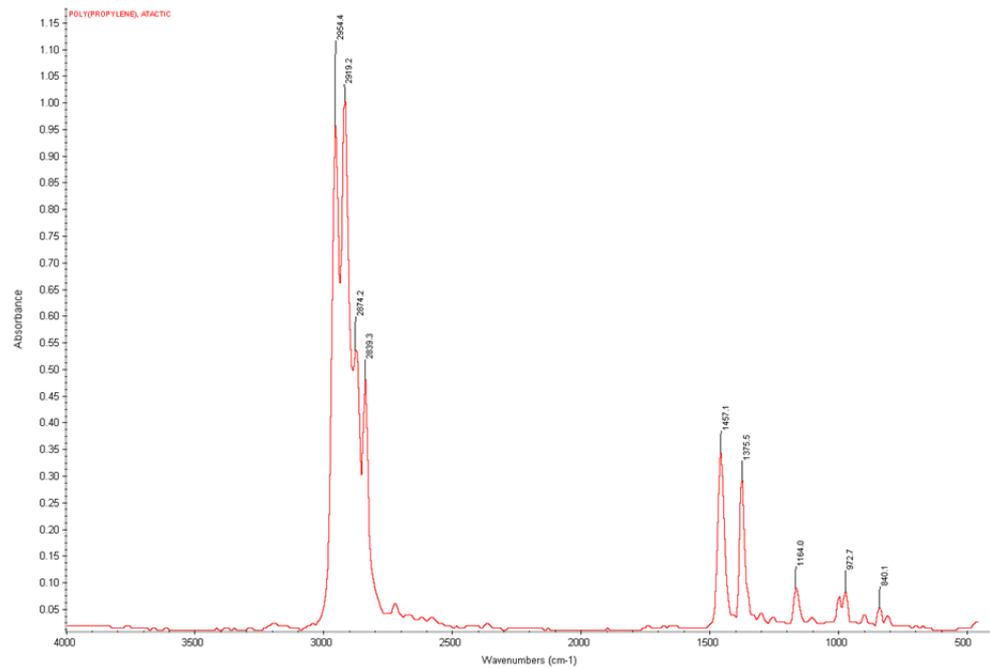
Figure A.11: *The spectrum of PP.*
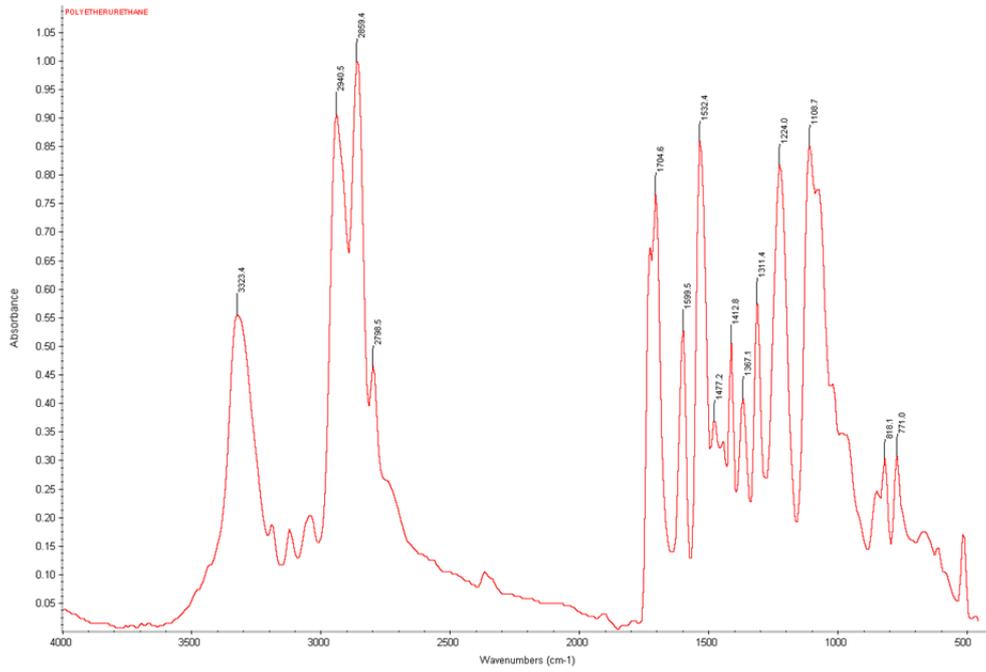
Figure A.12: *The spectrum of PU.*
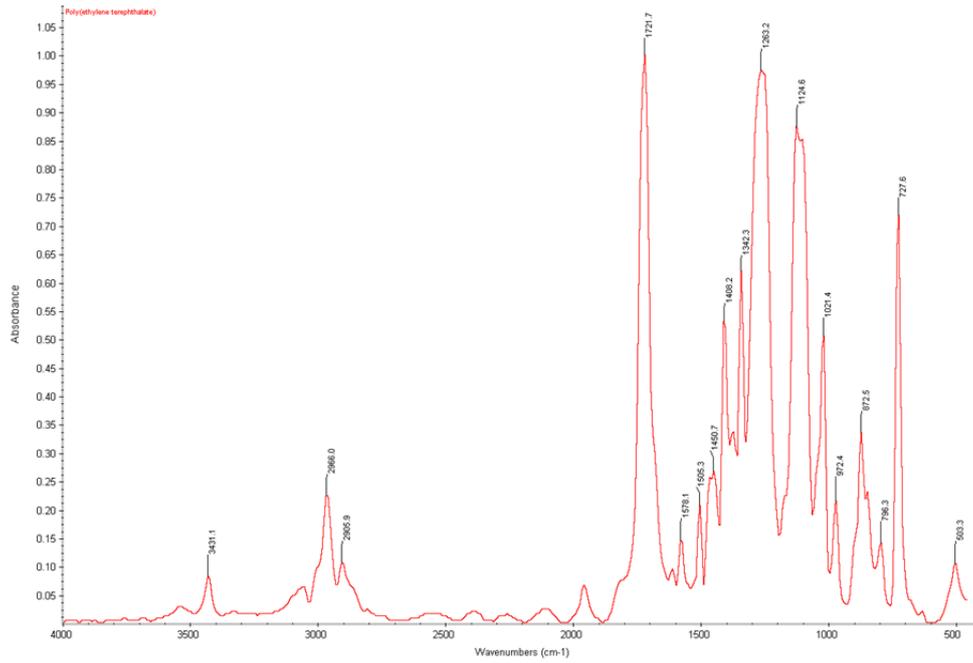
Figure A.13: *The spectrum of PET.*
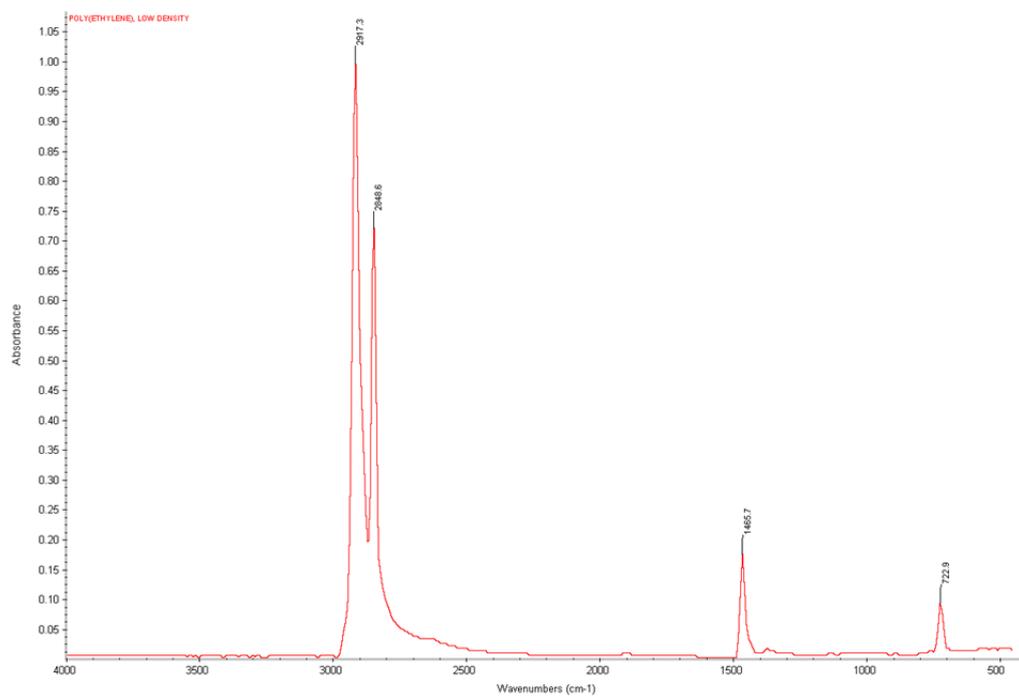
Figure A.14: *The spectrum of PE.*

B

Data

All gravimetric measurements were performed in a temperature of $\sim 23\,^\circ$C and in boxes with a RH of 75 % over the sample. The wet cups were filled with distilled water to get a RH of $\sim$100 % under the sample and the dry cups were filled with calcium chloride (CaCl) to get a RH of $\sim$0 % under the sample. An empty cup was measured every time to compensate for the day to day pressure difference. The measurements in Versaperm MkIV WVTR Meter were also performed in a temperature of $\sim 23\,^\circ$C. The RH on the wet side was $\sim$100 % and the RH on the dry side was measured around 75 %, this in the wet test. For the dry test the wet side had a RH of 75 % and the dry side a RH was measured around 2 %.

The results are being presented in Z_v [s/m] which takes the driving force in account. For a more visualizing picture the WVTR [g/m^{2}24h] will also be presented. Here one needs to be aware that the WVTR doesn't say anything about the testing conditions and can therefore be misleading. Materials with different permeability can have the same WVTR in different conditions. In this work the surrounding conditions have been the same for all measurements and the WVTR is therefore representative. The standard deviation, σ, is also presented.

B.1 The dry test

Table B.1: Results from the dry test for Material 1.

Material 1	Gravimetric	Versaperm
Z_v [s/m]	$4.62 \cdot 10^3$	$1.98 \cdot 10^4$
σ	$9.49 \cdot 10^2$	$2.69 \cdot 10^3$
WVTR [g/m^{2}24h]	265.05	66.66
σ	48.70	8.46

Table B.2: Results from the dry test for Material 2.

Material 2	Gravimetric	Versaperm
Z_v [s/m]	$1.279 \cdot 10^4$	$3.668 \cdot 10^4$
σ	$1.179 \cdot 10^3$	$7.073 \cdot 10^3$
WVTR [g/m^{2}24h]	100.561	36.681
σ	8.609	7.208

Table B.3: Results from the dry test for Material 3.

Material 3	Gravimetric	Versaperm
Z_v [s/m]	$2.681 \cdot 10^4$	$3.294 \cdot 10^4$
σ	$3.428 \cdot 10^3$	$2.311 \cdot 10^3$
WVTR [g/m^{2}24h]	49.436	39.516
σ	7.158	2.632

Table B.4: Results from the dry test for Material 4.

Material 4	Gravimetric	Versaperm
Z_v [s/m]	$1.497 \cdot 10^5$	$1.265 \cdot 10^5$
σ	$1.703 \cdot 10^4$	$7.789 \cdot 10^3$
WVTR [g/m^{2}24h]	8.967	10.281
σ	1.087	0.605

Table B.5: Results from the dry test for Material 5.

Material 5	Gravimetric	Versaperm
Z_v [s/m]	$6.468 \cdot 10^5$	$6.206 \cdot 10^5$
σ	$1.190 \cdot 10^4$	$4.106 \cdot 10^4$
WVTR [g/m^{2}24h]	2.059	2.126
σ	0.038	0.143

Table B.6: Results from the dry test for Material 6.

Material 6	Gravimetric	Versaperm
Z_v [s/m]	$2.562 \cdot 10^6$	$4.064 \cdot 10^6$
σ	$3.033 \cdot 10^5$	$8.011 \cdot 10^5$
WVTR [g/m^{2}24h]	0.520	3.356
σ	0.006	0.875

Table B.7: Results from the dry test for Material 7.

Material 7	Gravimetric	Versaperm
Z_v [s/m]	$2.574 \cdot 10^6$	$2.036 \cdot 10^6$
σ	$1.129 \cdot 10^5$	$1.059 \cdot 10^5$
WVTR [g/m^{2}24h]	0.519	0.638
σ	0.022	0.032

Table B.8: Results from the dry test for Material 8.

Material 8	Gravimetric	Versaperm
Z_v [s/m]	$4.062 \cdot 10^6$	$3.501 \cdot 10^6$
σ	$2.212 \cdot 10^5$	$2.490 \cdot 10^5$
WVTR [g/m^{2}24h]	0.329	0.372
σ	0.019	0.026

Table B.9: Results from the dry test for Material 9.

Material 9	Gravimetric	Versaperm
Z_v [s/m]	$5.01 \cdot 10^6$	$4.546 \cdot 10^6$
σ	$7.57 \cdot 10^4$	$2.398 \cdot 10^5$
WVTR [g/m^{2}24h]	0.266	0.286
σ	0.0040	0.015

B.2 The wet test

Table B.10: Results from the wet test for Material 4.

Material 4	Gravimetric	Versaperm
Z_v [s/m]	$1.299 \cdot 10^5$	$3.374 \cdot 10^5$
σ	$1.355 \cdot 10^4$	$6.572 \cdot 10^4$
WVTR [g/m^{2}24h]	3.433	1.362
σ	0.350	0.245

Table B.11: Results from the wet test for Material 5.

Material 5	Gravimetric	Versaperm
Z_v [s/m]	$5.320 \cdot 10^5$	$1.787 \cdot 10^6$
σ	$7.812 \cdot 10^3$	$3.840 \cdot 10^5$
WVTR [g/m^{2}24h]	0.825	0.259
σ	0.012	0.052

Table B.12: Results from the wet test for Material 7.

Material 7	Gravimetric	Versaperm
Z_v [s/m]	$2.11 \cdot 10^6$	$5.653 \cdot 10^6$
σ	$3.65 \cdot 10^5$	$1.22 \cdot 10^6$
WVTR [g/m^{2}24h]	0.217	0.082
σ	0.048	0.017

B.3 Test on Material 4 and 5

The tests on Material 5 were also done in the temperature range of 23±0.3°C. But instead of being put in the chamber with a RH of 75% the cups were put in a room with a RH of 50%, this RH may fluctuate due to people entering the room etc. One cup test is measured with a RH of 100% against zero, those cups are put in a desiccator filled with CaCl.

Some of the tests on Material 5 were only done in Versaperm MkIV WVTR Meter, those are presented further down. None of the tests made on Material 4 were done gravimetric.

Material 5 both gravimetric and in Versaperm

Table B.13: Results for material 5 with a RH of 50 against 0.

50 to 0	Gravimetric	Versaperm
Z_v [s/m]	$6.42 \cdot 10^5$	$6.03 \cdot 10^5$
σ	$8.25 \cdot 10^3$	$6.52 \cdot 10^4$
WVTR [g/m^{2}24h]	1.384	1.428
σ	0.018	0.153

Table B.14: Results for material 5 with a RH of 75 against 50.

75 to 50	Gravimetric	Versaperm
Z_v [s/m]	$5.36 \cdot 10^5$	$1.10 \cdot 10^6$
σ	$1.36 \cdot 10^4$	$4.22 \cdot 10^4$
WVTR [g/m^{2}24h]	0.841	0.405
σ	0.021	0.015

Table B.15: Results for material 5 with a RH of 100 against 50.

100 to 50	Gravimetric	Versaperm
Z_v [s/m]	$5.69 \cdot 10^5$	$9.85 \cdot 10^5$
σ	$1.10 \cdot 10^4$	$4.49 \cdot 10^4$
WVTR [g/m^{2}24h]	1.561	0.902
σ	0.031	0.042

Table B.16: Results for material 5 with a RH of 100 against 0.

100 to 0	Gravimetric	Versaperm
Z_v [s/m]	$6.37 \cdot 10^5$	$5.87 \cdot 10^5$
σ	$5.27 \cdot 10^3$	$4.77 \cdot 10^4$
WVTR [g/m^{2}24h]	2.786	2.98
σ	0.023	0.254

Material 5 only tested by Versaperm MkIV WVTR Meter

Those measurements were only done in Versaperm MkIV WVTR Meter.

Table B.17: Results for material 5 with a RH of 88 against 75.

88 to 75	Versaperm
Z_v [s/m]	$1.82 \cdot 10^6$
σ	$2.41 \cdot 10^3$
WVTR [g/m^{2}24h]	0.129
σ	0.017

Table B.18: Results for material 5 with a RH of 50 against 25.

50 to 25	Versaperm
Z_v [s/m]	$9.93 \cdot 10^5$
σ	$1.06 \cdot 10^5$
WVTR [g/m^{2}24h]	0.454
σ	0.071

Table B.19: Results for material 5 with a RH of 75 against 25.

75 to 25	Versaperm
Z_v [s/m]	$9.10 \cdot 10^5$
σ	$6.93 \cdot 10^4$
WVTR [g/m^{2}24h]	0.981
σ	0.068

Table B.20: Results for material 5 with a RH of 25 against 2

25 to 2	Versaperm
Z_v [s/m]	$6.80 \cdot 10^6$
σ	$9.05 \cdot 10^4$
WVTR [g/m^{2}24h]	0.612
σ	0.090

Material 4 only tested by Versaperm MkIV WVTR Meter

Those measurements were only done in Versaperm MkIV WVTR Meter.

Table B.21: Results for material 4 with a RH of 25 against 2.

25 to 2	Versaperm
Z_v [s/m]	$8.39 \cdot 10^4$
σ	$1.32 \cdot 10^4$
WVTR [g/m^{2}24h]	4.998
σ	0.863

Table B.22: Results for material 4 with a RH of 50 against 2.

50 to 2	Versaperm
Z_v [s/m]	$1.09 \cdot 10^5$
σ	$1.21 \cdot 10^4$
WVTR [g/m^{2}24h]	7.88
σ	0.826

Table B.23: Results for material 4 with a RH of 75 against 25.

75 to 25	Versaperm
Z_v [s/m]	$9.48 \cdot 10^4$
σ	$1.57 \cdot 10^4$
WVTR [g/m^{2}24h]	9.65
σ	1.79

Table B.24: Results for material 4 with a RH of 100 against 25.

100 to 25	Versaperm
Z_v [s/m]	$1.02 \cdot 10^5$
σ	$1.98 \cdot 10^4$
WVTR [g/m^{2}24h]	13.52
σ	2.76

Table B.25: Results for material 4 with a RH of 75 against 50.

75 to 50	Versaperm
Z_v [s/m]	$1.02 \cdot 10^5$
σ	$1.86 \cdot 10^4$
WVTR [g/m^{2}24h]	4.52
σ	0.92

Table B.26: Results for material 4 with a RH of 100 against 50.

100 to 50	Versaperm
Z_v [s/m]	$1.07 \cdot 10^5$
σ	$1.94 \cdot 10^4$
WVTR [g/m^{2}24h]	8.61
σ	1.73

Table B.27: Results for material 4 with a RH of 88 against 75.

88 to 75	Versaperm
Z_v [s/m]	$2.11 \cdot 10^5$
σ	$6.14 \cdot 10^4$
WVTR [g/m^{2}24h]	1.17
σ	0.29

Material 7 only tested by Versaperm MkIV WVTR Meter

Those measurements were only done in Versaperm MkIV WVTR Meter.

Table B.28: Results for material 7 with a RH of 25 against 2.

25 to 2	Versaperm
Z_v [s/m]	$2.08 \cdot 10^6$
σ	$2.84 \cdot 10^5$
WVTR [g/m^{2}24h]	0.200
σ	0.0238

Table B.29: Results for material 7 with a RH of 50 against 2.

50 to 2	Versaperm
Z_v [s/m]	$2.09 \cdot 10^6$
σ	$1.88 \cdot 10^5$
WVTR [g/m^{2}24h]	0.412
σ	0.0343

Table B.30: Results for material 7 with a RH of 100 against 2.

100 to 2	Versaperm
Z_v [s/m]	$2.12 \cdot 10^6$
σ	$1.69 \cdot 10^5$
WVTR [g/m^{2}24h]	0.824
σ	0.0598

Table B.31: Results for material 7 with a RH of 50 against 25.

50 to 25	Versaperm
Z_v [s/m]	$3.45 \cdot 10^6$
σ	$5.57 \cdot 10^5$
WVTR [g/m^{2}24h]	0.131
σ	0.0179

Table B.32: Results for material 7 with a RH of 75 against 25.

75 to 25	Versaperm
Z_v [s/m]	$2.87 \cdot 10^6$
σ	$1.69 \cdot 10^5$
WVTR [g/m^{2}24h]	0.310
σ	0.0177

Table B.33: Results for material 7 with a RH of 100 against 25.

100 to 25	Versaperm
Z_v [s/m]	$2.85 \cdot 10^6$
σ	$1.35 \cdot 10^5$
WVTR [g/m^{2}24h]	0.467
σ	0.0215

Table B.34: Results for material 7 with a RH of 75 against 50.

75 to 50	Versaperm
Z_v [s/m]	$3.06 \cdot 10^6$
σ	$3.29 \cdot 10^5$
WVTR [g/m^{2}24h]	0.146
σ	0.0146

Table B.35: Results for material 7 with a RH of 94 against 50.

94 to 50	Versaperm
Z_v [s/m]	$2.95 \cdot 10^6$
σ	$2.44 \cdot 10^5$
WVTR [g/m^{2}24h]	0.266
σ	0.0219

Table B.36: Results for material 7 with a RH of 100 against 50.

100 to 50	Versaperm
Z_v [s/m]	$3.24 \cdot 10^6$
σ	$3.33 \cdot 10^5$
WVTR [g/m^{2}24h]	0.276
σ	0.0268

Table B.37: Results for material 4 with a RH of 88 against 75.

88 to 75	Versaperm
Z_v [s/m]	$4.33 \cdot 10^6$
σ	$3.92 \cdot 10^5$
WVTR [g/m^{2}24h]	0.0537
σ	0.00516

C

Crystallinity

The method used to determine the crystallinity followed the international standard ISO 11357-3 using a differential scanning calorimetry (DSC), this method is described in chapter 3. Method.
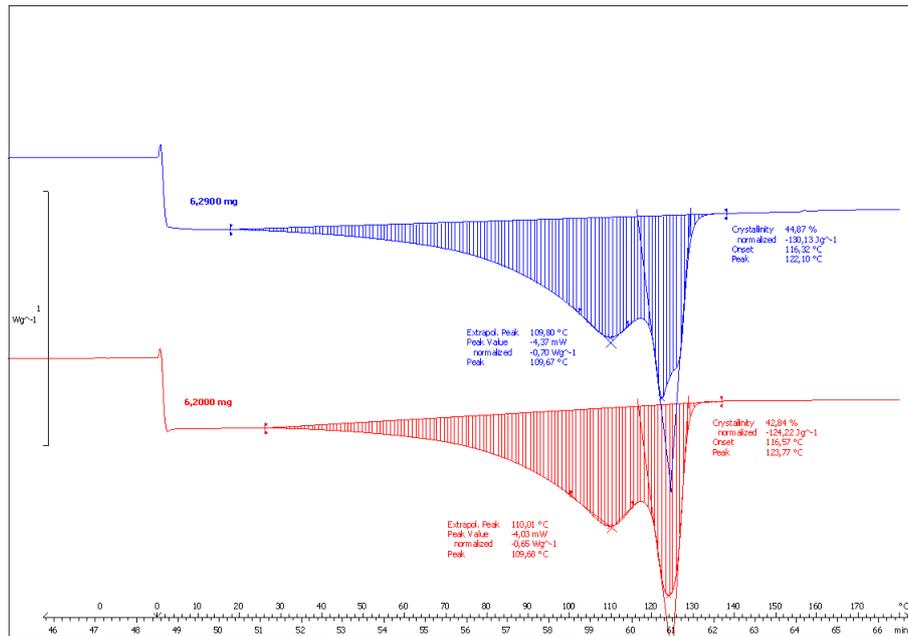
Figure C.1: *The enthalpy change in where the crystallinity is calculated for Material 7.*
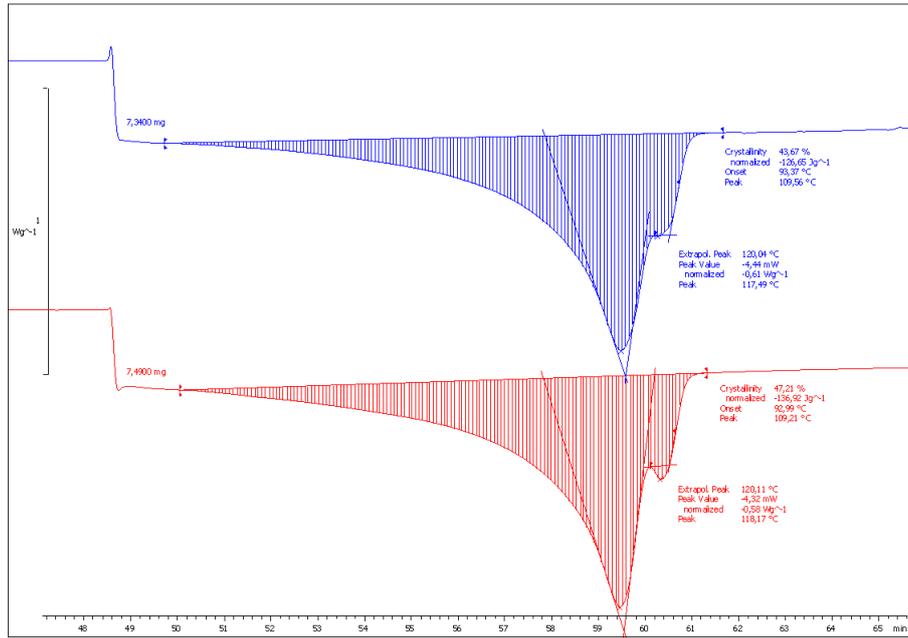
Figure C.2: *The enthalpy change in where the crystallinity is calculated for Material 8.*
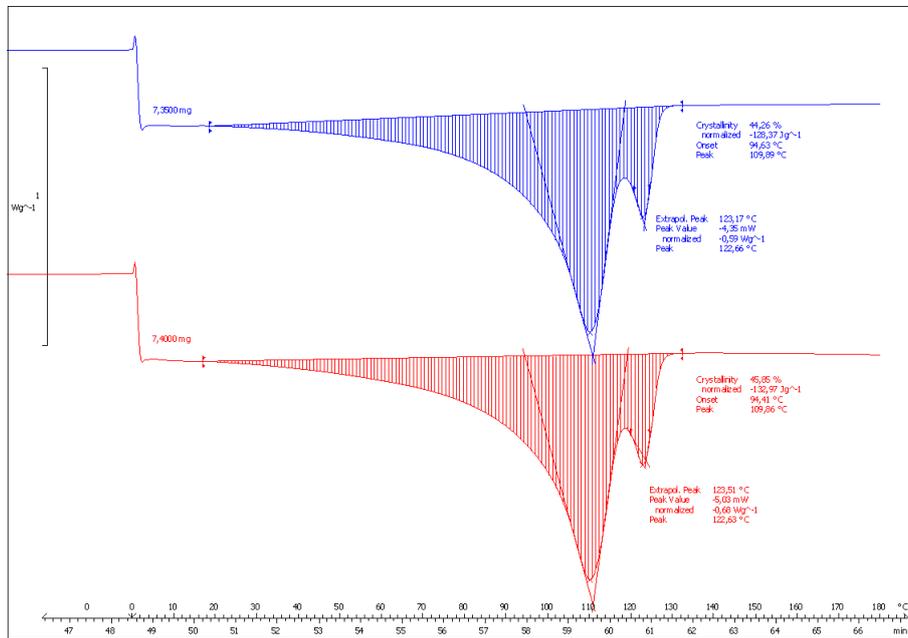
Figure C.3: *The enthalpy change in where the crystallinity is calculated for Material 9.*

D

Amount of penetrant in time

The amount of penetrant, Q_t, that has diffused through the material plotted against time to see if the interception of the curve lies close to $t = 0$. Is the interception on the x-axis far away from zero it takes time for the material to reach steady-state. This test was done on Material 4, 5 and 7 for the wet cup test. It was also done on Material 5 for all gravimetric measurements made on this material.
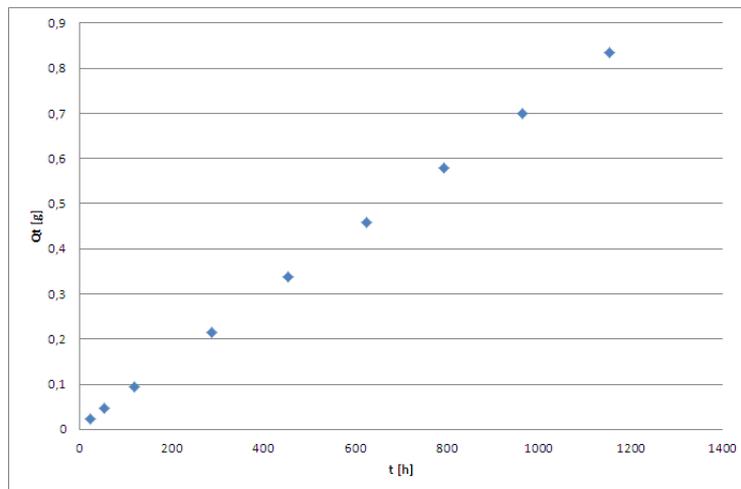
Figure D.1: *The amount of penetrant in gram that has diffused through Material 4 plotted against the time. This for the wet cup test.*
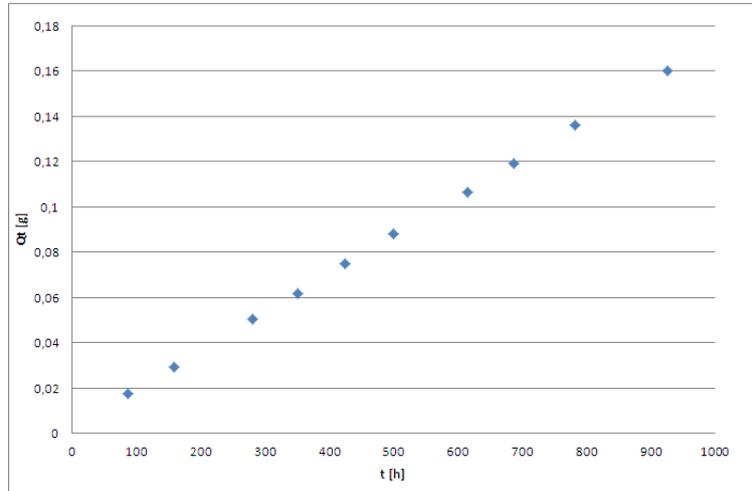
Figure D.2: *The amount of penetrant in gram that has diffused through Material 5 plotted against the time. This for the wet cup test.*
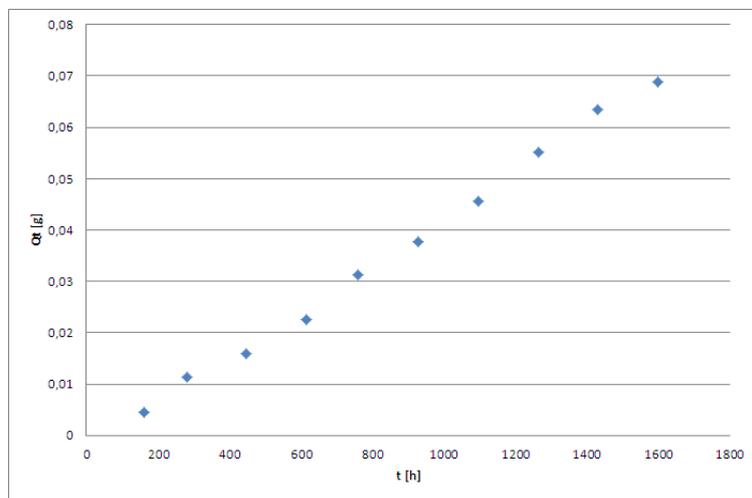
Figure D.3: *The amount of penetrant in gram that has diffused through Material 7 plotted against the time. This for the wet cup test.*

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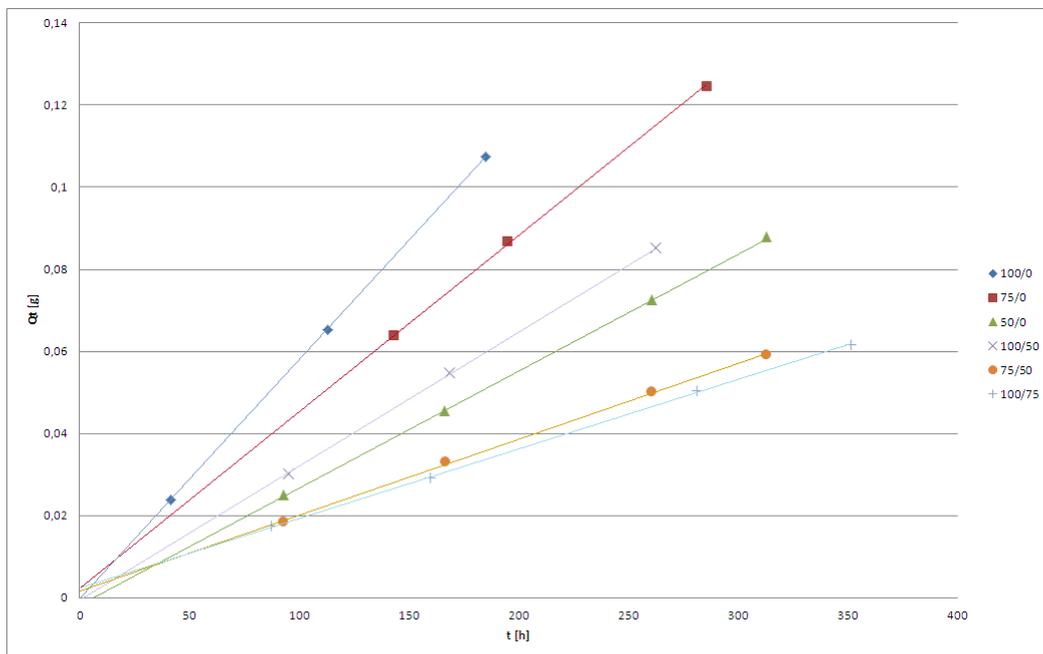
Figure D.4: *The amount of penetrant in gram that has diffused through Material 5 plotted against the time. This for all cup tests made on this material. The lines are made to make it easier to follow a sample.*