

Determination of the nitrogen gas transmission rate (N₂GTR) of ethylene vinyl alcohol copolymer, using a newly developed permeation measurement system

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ABSTRACT

The oxygen (O₂) barrier properties of ethylene vinyl alcohol copolymer (EVOH) have been widely investigated, but for other gases the available data are usually limited to dry conditions due to limitations in measurement equipment. Innovative permeation measurement systems with low detection limits are required to determine the gas transmission rate (GTR) of other gases, such as nitrogen (N₂) at varying temperature and relative humidity. This study presents the design and development of a versatile permeation measurement system consisting of two subsystems: a permeation system and a detection system using gas chromatography and a pulsed discharge helium ionization detector. The measured O₂GTR and N₂GTR of three different 20 µm-EVOH grades containing 32, 44 and 48 mol% ethylene are in good accordance to those obtained on validated MOCON OX-TRAN® modules and a GC-differential pressure method respectively, with differences within the analytical uncertainty of each method.

1. Introduction

Ethylene vinyl alcohol copolymer (EVOH) is one of the most commonly used plastic barrier materials against gases and other volatile organic compounds (VOC) in a wide range of applications, such as: food, clinical and pharmaceutical packaging to increase shelf life, as well as pipes for floor heating to prevent corrosion in the boiler, fuel tanks to prevent fuel emissions, and geomembrane films to reduce methane (CH₄) release in landfills, amongst others [1–5]. The barrier properties of EVOH are dependent on its resistance to sorption and diffusion of foreign molecules such as permanent gases, aromas, flavours and solvents. The three steps of a permeation process are shown in Fig. 1: (i) the adsorption of permeant molecules on the polymer surface on the high concentration side, (ii) the diffusion of the permeant through the film matrix and finally (iii) the desorption of the permeant from the polymer surface on the low concentration side [6–9].

This process is based on Fick's First Law of diffusion and Henry's Law of solubility. Fick's First Law describes the diffusion through a polymer

as (1).

$$J = -D \frac{dc}{dx} \quad (1)$$

where J is the diffusion flux in mol/(m²·s), D is the diffusion coefficient in m²/s, but can also be expressed by any other unit in area/time, c is the permeant concentration in mol/m³ and x is the distance in the flow direction in m.

The adsorption and desorption depend on the solution or sorption behaviour between the permeant and polymer. The ideal sorption isotherm is described in Henry's Law (2).

$$c_s = S \times p \quad (2)$$

in which c_s is the permeant concentration at the solid-phase film surface in mol/m³, S is the solubility coefficient in mol/(m³·atm) or in any other unit expressing amount/(volume x pressure) and p is the partial pressure of the permeant in atm. The product of S and D is the permeability

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coefficient (P) given in formula (3), which is the barrier characteristic of a polymer commonly referred to as permeability or permeation rate.

$$P = S \times D \quad (3)$$

The unit of P is thickness and pressure normalized (amount x film thickness)/(area x time x pressure) and expressed at a given temperature and relative humidity (RH). In this paper the unit is expressed in $\text{cm}^3 \cdot \mu\text{m}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$. The gas transmission rate (GTR), on the other hand, is the actual measured amount of gas permeating through the sample, regardless of its structure, which is detected in $\text{cm}^3/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at a given temperature and RH.

Maes et al. [10] recently summarized the gas permeability properties of EVOH. It is known that in addition to intrinsic factors (crystallinity, ethylene content, etc.), permeation is drastically influenced by extrinsic factors such as RH and temperature. A lot of data on the oxygen (O_2) gas transmission rate (O_2GTR) of EVOH in different conditions are available, however, relevant permeation data on other permanent gases such as nitrogen (N_2) and carbon dioxide (CO_2) are usually only measured in dry conditions with limited information on the applied test method. The lack of permeability data of other gases than O_2 in different environmental conditions can be explained by the limited (commercially) available equipment. Permeation measurements of other permanent gases require different methods and detectors than those used to measure the permeation of O_2 , for which a broad range of instruments with selective (e.g. coulometric) detectors is available on the market [10].

Most (inter)national standardized methods rely on 3 different permeation measurement principles, which make use of differential pressure (Fig. 2A), equal pressure (Fig. 2B) and static methods, respectively. However, when taking a closer look at these standards, many describe similar methods and most of them are specific for O_2 and water vapour permeation testing. In Tables 1–3 the international used standards of the International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM) are listed according to their respective measurement principle, with comparable standards next to each other.

1.1. Differential pressure methods to determine permeability

The first category contains the differential pressure methods (Table 1). Usually, a test specimen is mounted in a cell between two compartments, with one compartment being fed with a gas (mixture),

while the other compartment is evacuated, creating a vacuum with a lower pressure than the feeder side. These methods are based on the ideal gas law ($PV = nRT$) where the permeation is quantified by measuring the increase in pressure (manometric method, ISO 15105-1 Annex A [11], ISO 2556 [12], ASTM D1434 M method [13]) or the increase in volume (volumetric method, ASTM D1434 V method [13]) as is illustrated in Fig. 2A. This concept allows the permeation measurement of all kinds of different gases and mixtures. The GDP-C Gas Permeability Tester (Brügger Feinmechanik GmbH, München, Germany) can be used to measure all dry, non-corrosive and non-flammable gases and applies the manometric method [14]. The Deltaperm Permeation Tester (Technolox Ltd., Oxford, UK) also applies the manometric method, but uses higher pressures than atmospheric pressure to decrease the breakthrough time and accelerate the experiment [15]. The Deltaperm Permeation Tester can also be used to determine the water vapour transmission rate (WVTR) according to ISO 15106-5 [16]. Even though these methods can be used to measure permeation of nearly all gases and chemicals, it is limited to only one component at the time, for it can only measure the total permeation and not the individual fluxes of each component that might be present in a gas or chemical mixture. Another disadvantage is that the gas permeation can only be measured in dry conditions due to the possibility of co-permeation of water molecules. Moreover, there is a poor correlation with other methods, which might be material dependent or due to the stress which the test specimens experience from the difference in pressure in the two cell compartments [14,17].

In addition, Annex B of ISO 15105-1 [11] also describes a differential pressure method using gas chromatography (GC) analysis. The advantage of the GC methods is the higher sensitivity compared to other methods and the ability to measure different components simultaneously. The idea behind this method is to connect a permeation system to a GC to separate and analyse the components. Another major advantage is that this method is very versatile in its application as different types of sampling methods, GC columns and detectors can be used [17]. So far only GTR Tec (Kyoto, Japan) and Labthink Instruments Co. Ltd. (Jinan, China) have such commercially available measurement systems, but several research groups and institutes have built their own test systems based on the same principles as will be discussed below. GC-analysis can also be used to determine the WVTR, as described in the ISO 15106-4 [18].

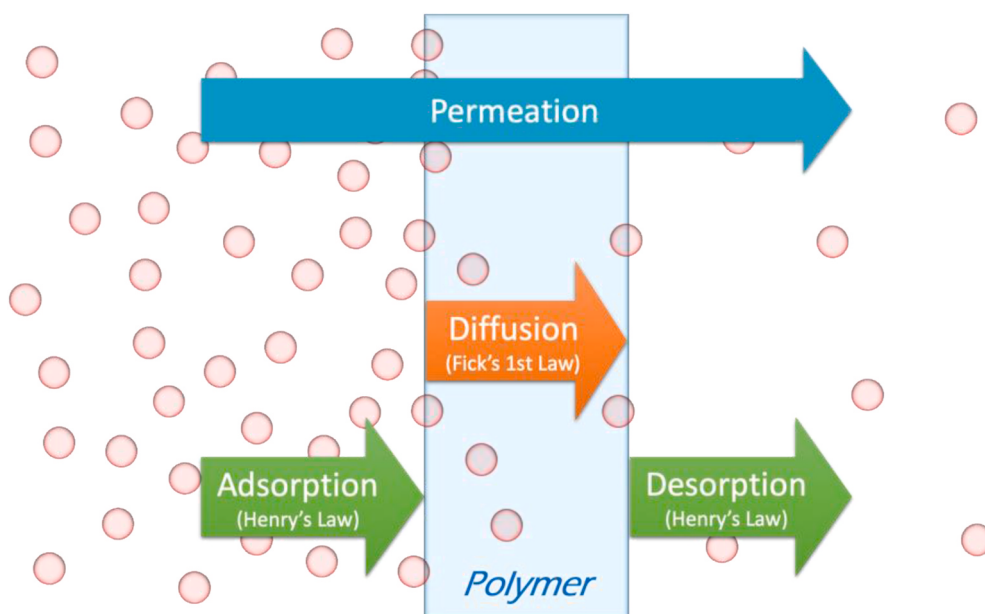


Fig. 1. Mechanism of permeation through a polymer.

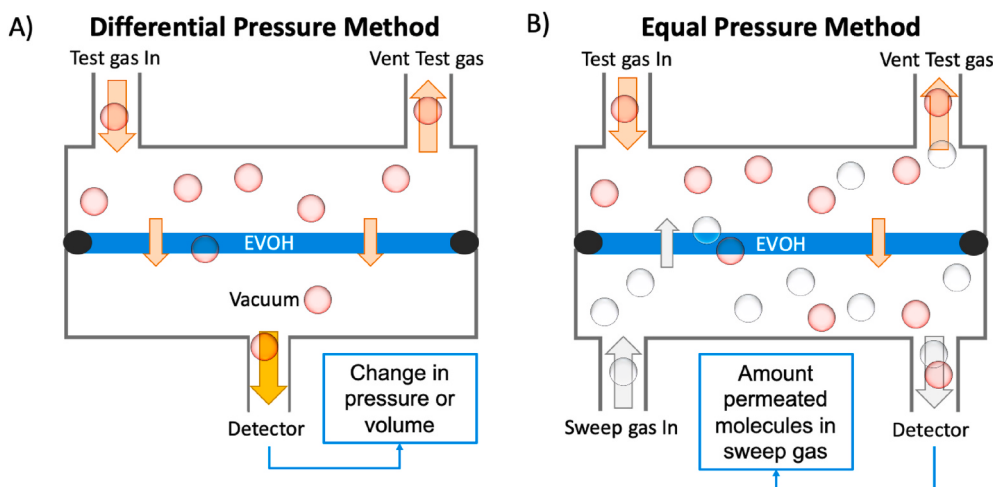


Fig. 2. Principle of the differential (A) and equal (B) pressure method.

Table 1

Overview of ISO and ASTM standards for permeation measurements using the principle of differential pressure.

Type	ISO and ASTM standards			Permeant
Differential pressure methods	ISO 15105-1 Plastics – Film and sheeting – Determination of gas-transmission rate – Part 1: Differential-pressure methods - <u>A</u> : Method <u>using a pressure sensor</u>	ISO 2556 Plastics – Determination of the gas transmission rate of films and thin sheets under atmospheric pressure – Manometric method	ASTM D1434 Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheet – <u>M method</u>	Gases
	ASTM D1434 Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheet – <u>V method</u>			
	ISO 15105-1 Plastics – Film and sheeting – Determination of gas-transmission rate – Part 1: Differential-pressure methods - <u>B</u> : Method <u>using a gas chromatograph</u>			
	ISO 15106-4 Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 4: Gas chromatographic detection sensor method			Water vapour
	ISO 15106-5 Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 5: Pressure sensor method			

1.2. Equal pressure methods to determine permeability

The second category contains the equal pressure methods which are summarized in Table 2. These methods are like the differential pressure methods, but instead of using a vacuum, a carrier or sweep gas flows through the other compartment. Permeation is triggered by the difference in partial pressure of the feeder gas (upstream flow) and the sweep gas (downstream flow). The sweep gas flushes the compartment and transfers the permeated molecules to a detector as shown in Fig. 2. Most of these methods describe the use of selective detectors like a coulometric detector for the determination of O₂ permeation (ISO 15105-2 Annex A [19], ASTM D3985 [20], ASTM F1307 [21], ASTM F1927 [22], ASTM F2622 [23]), which are used in the OX-TRAN® modules (AMETEK - MOCON Inc., Minneapolis, MN, USA), the C230 and OX2/231 (Labthink Instruments Inc.), the QT-OPT series (Qualitest International Inc., Richmond Hill, Canada), the Oxygen Permeation Analyzer series (Systech Illinois Ltd., Thame, UK) amongst others, whereas an infrared detector can be used to measure CO₂ permeation (ASTM F2476 [24]), i.e. in PERMATRAN-C® modules (AMETEK - MOCON Inc.) [25].

Similar to ISO 15105-1 [11], ISO 15105-2 [19] Annex B also describes the use of GC-technology for the detection of the permeants when applying the principle of equal pressure. The standard explicitly mentions that the use of various GC-columns and detectors can be considered depending on the gas of interest. GTR Tec is the only supplier who offers commercial equipment using either differential or equal pressure permeation systems connected to a GC. However, there are research groups and institutes who constructed systems based on these principles as will be explained below.

Several methods to determine the WVTR can be considered equal pressure methods as they use a constant flow on the downstream side to take the permeated water vapour molecules towards the detection system. There are several detectors, which can serve this purpose. However, similar as to the coulometric detector for O₂ permeation measurement, most of these detection methods are limited to the detection of water vapour. The PERMATRAN-W® Models 3/33, 3/34, 3/61 and 700 (AMETEK - MOCON Inc.), the W405 Water Vapour Permeability Analyzer (GBPI Guangzhou Biaoji Packaging Equipment Co., Ltd., Guangzhou, China), and the W3/230 and C390 M Water Vapour Transmission Rate Test Systems (Labthink Instruments Co., Ltd.) are examples of equal pressure methods using an infrared sensor (ISO 15106-2 [26] and ASTM F1249 [27]). Some instruments use an electrolytic sensor (ISO 15106-3 [28]) such as the AQUATRAN® modules (AMETEK - MOCON Inc.), the WDDG Water Vapour Permeability Tester (Brügger Feinmechanik GmbH), W202 and W203 Water Vapour Permeability Analyzer (GBPI Guangzhou Biaoji Packaging Equipment Co., Ltd.), and C330 Water Vapour Transmission Rate Test System and TSY-W3 Electrolytic Detection Method Water Vapour Permeability Tester (Labthink Instruments Co., Ltd.). The ISO 15106-6 [29] is a less commonly used standard, which describes the use of an atmospheric pressure ionization mass spectrometer (API-MS) detection. The last standard mentioned in Table 2 is the ASTM D6701 which uses the principles of equal pressure method with a humidified feeder gas on one side and a dry sweep gas on the other side, which takes the permeated water molecules towards an unspecified detector like in the PERMATRAN® 101K module (AMETEK - MOCON Inc.) [30].

Table 2

Overview of ISO and ASTM standards for permeation measurements using the principle of equal pressure.

Type	ISO and ASTM standards		Permeant
Equal pressure methods	<i>ISO 15,105-2</i> Plastics – Film and sheeting – Determination of gas-transmission rate – Part 2: Equal-pressure method - <i>A: Method for the determination of the oxygen-transmission rate using a coulometric sensor</i>	<i>ASTM D3985</i> Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheet Using a Coulometric Sensor <i>ASTM F1307</i> Standard Test Method for Oxygen Transmission Rate Through Dry Packages Using a Coulometric Sensor <i>ASTM F1927</i> Standard Test Method for Determination of Oxygen Gas Transmission Rate, Permeability and Permeance at Controlled Relative Humidity Through Barrier Materials Using a Coulometric Detector <i>ASTM F2622</i> Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheet Using Various Sensors	O ₂
	<i>ASTM F2476</i> Standard Test Method for the Determination of Carbon Dioxide Gas Transmission Rate (CO ₂ TR) Through Barrier Materials Using an Infrared Detector		CO ₂
	<i>ISO 15105-2</i> Plastics – Film and sheeting – Determination of gas-transmission rate – Part 2: Equal-pressure method - <i>B: Detection by gas chromatography</i>		Gases
	<i>ISO 15106-2</i> Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 2: Infrared detection sensor method	<i>ASTM F1249</i> Standard Test Method for Water Vapour Transmission Rate Through Plastic Film and Sheet Using a Modulated Infrared Sensor	Water vapour
	<i>ISO 15106-3</i> Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 3: Electrolytic detection sensor method		
	<i>ISO 15106-6</i> Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 6: Atmospheric pressure ionization mass spectrometer method		
	<i>ASTM D6701</i> Standard Test Method for Determining Water Vapour Transmission Rates Through Nonwoven and Plastic Barriers		

1.3. Static methods to determine permeability

Next to the differential and equal pressure methods, the third category represents the static methods (Table 3). These methods do not measure permeation in a continuous flow, but rather measure the dynamic accumulation or loss inside a cell or package. The gravimetric method according to the ISO 2528 [31] and ASTM E96 [32] standards, also known as the dish or cup test, is the most commonly used method to determine the WVTR. The test can be performed in two ways: either water is brought inside the test dish, then the test film is sealed on top and permeation is measured by weight loss over time, or an absorbent is placed inside the test dish before sealing the film on top, in this case the weight gain is measured. This method is relatively easy and can also be used for other substances. The substance is brought inside a test dish in liquid or solid phase and analysed for weight loss, similar to the static method ASTM D2684 [33], which describes a method to determine the loss of packaged reagents of proprietary products. These methods are simple but have a rather limited sensitivity due to the relatively small test area (in the cup test) combined with the limitations of the lab balances. Another disadvantage is that the measurements and calculations must be performed manually. Also, it takes a relatively long time to reach equilibrium and the results do not always show good reproducibility [17]. It is also possible to measure the WVTR by the use of a RH sensor (ISO 15106-1 [34] and ASTM E398 [35]), where the time needed to increase the RH with a certain amount is converted into a WVTR, i.e. in PERMATRAN-W® Models 1/50 and 398 (AMETEK - MOCON Inc.), the Lyssy L80-5000 module (Systech Illinois Ltd.) and W3/130 module (Labthink Instruments Co., Ltd.). A less common method to measure the WVTR is the calcium corrosion method (ISO 15106-7 [36]), by analysing the reaction rate of a calcium film deposited on top of the film sample through optical measurement (Annex A), electrical measurement (Annex B) or evaluation of the corrosion area (Annex C) the WVTR can be determined.

The amount of O₂ can be measured using the principle of fluorescence decay. Here, a chemically coated dot is embedded into a test cell (ASTM F3136 [37]) or into the headspace of a (flushed) package (ASTM F2714 [38]). The O₂ molecules present inside the package or cell

interact with the chemical coating of the dot and affect its fluorescent response, which is monitored using a light emitting device directed at the dot. By comparing the measured decay with those of known concentrations of O₂, the concentration can be determined. However, this method is only possible for transparent or translucent packaging materials or packaging containing a transparent window. The Oxygen Analyzer 5250i and 325i (Oxysense Inc., New Castle, DE, USA) and the OpTech®O₂ Model P (AMETEK - MOCON Inc.) are examples of instruments which apply this principle.

Finally, ASTM F1115 [39] focusses on the loss of CO₂ in beverage containers, which can be measured either by the use of sensitive pressure and temperature monitoring or by measuring the carbonation level inside the package through a CO₂ analyzer.

1.4. Permeation measurement systems coupled to GC-analysis

The use of gas chromatography as detection system in a permeation measurement method shows the most potential for the (simultaneous) determination of permeation of various molecules. The GC can be equipped with a wide range of GC-columns and different types of detectors, which allow the detection of a broad selection of permeants. In addition, the permeation system can be adapted to accommodate the test conditions and set-up to the needs of the application in which the permeants are used. Table 4 summarizes permeation and detections systems for selected permeants and their respective limitations as described in the literature. These studies clearly indicate the versatility of the application of GC technology in permeation measurement systems. However, to our current knowledge, none of these systems focus on the permeation of other gasses than O₂ and CO₂, and most systems are unable to measure permeation in varying RH settings. Several systems even require manual manipulations during the sampling as well, making them time-consuming.

1.5. Design and development of the PEBaMeT module

As the conventional methods to measure permeation of molecules through film materials and associated equipment are not all useful for

Table 3

Overview of ISO and ASTM standards for static permeation measurements methods based on dynamic accumulation or loss.

Type	ISO and ASTM standards		Permeant
Static methods	ASTM F3136 Standard Test Method for Oxygen Gas Transmission Rate through Plastic Film and Sheet using a Dynamic Accumulation Method	ASTM F2714 Standard Test Method for Oxygen Headspace Analysis of Packages Using Fluorescent Decay	O ₂
	ASTM F1115 Standard Test Method for Determining the Carbon Dioxide Loss of Beverage Containers		CO ₂
	ASTM D2684 Standard Test Method for Permeability of Thermoplastic Containers to Packaged Reagents or Proprietary Products		Packaged Reagents
	ISO 2528 Sheet materials – Determination of water vapour transmission rate (WVTR) – Gravimetric (dish) method	ASTM E96 Standard Test Methods for Water Vapour Transmission of Materials	Water vapour
	ISO 15106-1 Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 1: Humidity detection sensor method	ASTM E398 Standard Test Method for Water Vapour Transmission Rate of Sheet Materials Using Dynamic Relative Humidity Measurement	
	ISO 15106-7 Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 7: Calcium corrosion method		

testing a variety of new molecules in different conditions of temperature and RH, the development of new innovative test equipment is required. The objective of this study is to develop an automated permeation measurement system coupled to a GC separation and detection method to measure the GTR of EVOH in different environmental conditions for permanent gases (such as O₂, N₂ and CO₂ amongst others). The up- and downstream humidity control should be separated in order to simulate different conditions on either side, i.e. for packaging concepts for dry products in a humid environment and vice versa. Additionally, the simultaneous measurement of different film samples should be possible. The detection limit in the low ppb region (<50 ppb) for permanent gases is especially challenging due to the known low gas permeation rates of O₂ through thin EVOH layers and N₂ is even known to have lower permeation rates than O₂. Finally, it would be an asset if the detection system is able to detect all gases simultaneously, allowing the system to study co-permeation effects.

The equipment is developed by combining different techniques and advanced optimization of the permeation and detection systems. The resulting permeation measurement equipment to measure barrier properties of EVOH films under various climatic conditions is referred to as the PEBaMeT module. In which PEBaMeT is an acronym for **P**ermeability **E**VOH **B**arrier **M**easurement **T**ool.

The permeation measurement of N₂ was chosen to validate the PEBaMeT for two reasons: 1) N₂ is known to show permeation values lower than those of O₂, making it an ideal component to test the detection limits of the system, and 2) because air mainly consists of N₂ (79%), the leakage or infusion of this gas into the system is the most significant. In order to determine the low N₂GTR, the leakage must be suppressed to the minimum.

2. Materials and methods

2.1. Gases

The following gases (with respective purity) were used: CO₂ (4.5), high-purity N₂ (6.0), O₂ (4.5), high-purity He (6.0),¹ forming gas H₅ (95% N₂ and 5% H₂) and a calibration gas, which according to the supplier's certificate consisted of 9.35 ppm H₂, 10.8 ppm O₂, 15.5 ppm N₂, 9.75 ppm CO₂ and 9.32 ppm carbon monoxide (CO) in He. All gases were obtained from a local gas supplier (Messer Belgium NV, Zwijndrecht).

¹ 6.0 is an industrial grade with a purity of 99.9999%. If the industrial grade is for instance 4.5 this means 99.995%.

2.2. EVAL™ EVOH test samples

Three different EVAL™ EVOH grades were used for the experiments: EVAL™ F171B film, EVAL™ E105B film and EVAL™ G156B film containing respectively 32 mol% ethylene (EVOH32), 44 mol% ethylene (EVOH44) and 48 mol% ethylene (EVOH48). These samples were either used as monolayer structures of 20 µm or laminated (//) on a single 50 µm polypropylene layer, resulting in EVOH//PP (20//50 µm) structures. Because the processing drastically impacts crystallinity and hence the barrier properties, all film samples received a pre-heat treatment according to ISO 14663-2 norm of 10 min at 20 °C below the melting point (*T_m*) of the EVOH grade, in order to erase the thermal history of the processing, prior to experimentation [40]. For the permeation measurement, the samples were preconditioned at the desired RH in desiccators containing salt solutions or a moisture adsorbent for approximately a week. The used test surface was 50 cm².

2.3. Permeation measurement system: PEBaMeT

The PEBaMeT, developed in cooperation with Interscience bv (Breda, The Netherlands), is based on the principles of a permeation system combined with a separation system (GC) and a pulsed discharge helium ionization detector (PDHID) for the detection of different permeants according to the equal pressure method described in ISO 15105-2 Annex B. Fig. 3 shows a schematic representation of the PEBaMeT in which the subsystems, the permeation system and the detection system, are clearly visible. Inline calibration is possible by connecting a calibration gas to the Dilution Unit.

2.3.1. PEBaMeT: permeation system

A detailed representation of the permeation system is given in Fig. 4. A customized EasyCal Unit (Umwelttechnik MCZ GmbH, Bad Nauheim, Germany) functions as a mass flow controller (MFC) and humidifier for both the upstream (test gas) and downstream (sweep gas) flows of the cells. At the input side of the test gas to the EasyCal Unit, a 2-way switching valve (AFP, Analytical Flow Products) is connected, which makes it possible to switch the gas supply of the upstream flow automatically between sweep gas for individual zero measurements and test gas for the permeation measurements. The flow for the test and the sweep gas is regulated separately by two EL-FLOW® gas MFC (Bronkhorst High-Tech B.V., Ruurlo, The Netherlands) and two µ-FLOW® liquid MFC control the absolute amount of water coming from a reservoir at the back of the EasyCal Unit. The resulting gas and liquid flows are combined in a mixing and evaporator chamber where the water is vaporized into the gas flow, allowing humidification of approximately 0%–100% RH depending on the temperature and demanded flow.

A custom-built convection oven functions as a permeation box (Global Analyzer Solutions – Interscience bv branding) with a maximum

Table 4

Summary of permeation studies using GC-analysis for permeant detection.

Permeation system and detection system summary	Permeant	Limitations	Ref
Permeation: Permeation cell made of consumable glass bottle, film mounted on the neck of the bottle; toluene/methanol in cell and downstream side continuously flushed Detection: Cryogenic cold trap connected to a GC with a Flame Ionization Detector (GC-FID)	toluene/methanol mixtures	No RH control; supercritical cooled N ₂ needed	[52]
Permeation: Pervaporation cell with two compartments; model fuel mixture circulated from stainless steel reservoir to upstream side and vacuum on downstream side Detection: Cryogenic cold trap connected to a GC-FID	fuel containing alcohols	No RH control; supercritical cooled N ₂ needed	[53]
Permeation: Permeation cup with open top inside Dynamic Vapour System (DVS); aromas inside cell and vacuum on downstream side Detection: Purge-and-trap fast GC with FID (P&T f-GC-FID)	limonene and ethyl butyrate (aromas)	Only RH control on downstream; one sample at a time	[54]
Permeation: None: Sorption and diffusion experiments Detection: GC-FID (sorption) and Fourier transform infrared spectroscopy (FTIR, diffusion)	α -pinene and ethyl butyrate (aromas)	Manual/time-consuming sampling; permeation not measured	[2]
Permeation: None: Sorption and diffusion experiments Detection: P&T GC-MS	BTEX	Manual/time-consuming sampling; permeation not measured	[55, 56]
Permeation: Permeation cell with two compartments; gas/vapour feed to upstream side and vacuum on downstream side Detection: GC (pressure)	gas/vapour mixture: O ₂ , CO ₂ and methanol	No RH control; one sample at a time	[57]
Permeation: Permeation cell with two compartments; spiked paperboard in cell and downstream side continuously flushed Detection: Electrically cooled trap connected to GC-FID	mineral oil hydrocarbons	No RH control	[58]
Permeation: Permeation cell with two compartments; spiked gas flow injected in upstream compartment by syringe and downstream continuously flushed Detection: Electrically cooled trap connected to GC-FID	mineral oil hydrocarbons	No RH control	[59, 60]
Permeation: Packaging inside glass container with solid-phase micro-extraction (SPME) Detection: GC-FID	aroma compounds of wine	SPME fibres manually put on GC; careful calibration needed	[61]
Permeation: Permeation cell with two compartments; vapour injected in one side and both sides sampled with airtight syringe at regular intervals Detection: GC-MS	dimethyl disulphide (fumigant)	Sampling manual and time-consuming	[62]

temperature of about 120 °C. The permeation box can also be cooled to about 10 °C by a cooling circuit in the bottom of the box, which is connected to a Microcool MC250 unit (Lauda Dr. R. Wobser GmbH & Co. KG, Lauda-Königshofen, Germany).

Four remote test cells with a test surface of 50 cm² (AMETEK - MOCON Inc.) are built into the permeation box. The transfer lines for both the test and sweep gas coming from the MFC and Humidifier enter the permeation box and are both divided across four flow paths, which results into a flow of approximately 10 mL/min per cell. In case of the upstream side, the test gas fills the bottom compartment of each cell with test gas which is subsequently individually vented to the outside of the permeation box. On the downstream side, the four cells are constantly flushed with a He flow, which is led to the detection system in sequence by switching a rotating 6-port-multi-position valve (Vici AG International, Schenkon, Switzerland). Ports 1 to 4 of this valve are connected with the downstream flow coming from the four cells; one cell at the time is selected for analysis on the detection system. The two additional ports are used for a reference measurement and calibration gas measurements. The reference measurement is used to evaluate the changes in impurities in the sweep gas, which might influence the outcome of the permeation measurement. For the calibration measurements a μ EasyCal (Umwelttechnik MCZ GmbH) is used as a Dilution Unit to make standards with different concentrations, by blending the calibration gas with high-purity He (6.0).

2.3.2. PEBaMeT: detection system

The detection system (Fig. 5) is composed of a TRACE 1300 GC High Purity Analyzer (HPA) (Thermo Fisher Scientific Inc.), which is expanded with a heated valve box combined with a PDHID detector. The TRACE 1300 is equipped with two channels each with a sample loop of 350 μ L for injection, a pre-column to backflush components that are damaging to the main analytical column.

The main column of channel one is a Rt-Msieve 5 A fused silica PLOT (30 m $\times$ 0.53 mm i.d., 50 μ m film thickness; Restek). The backflush column is a CP-Silica PLOT (15 m $\times$ 0.53 mm i.d., 6 μ m film thickness; Agilent). This channel is used for the separation of H₂, O₂, N₂, and CO. In addition, this channel is able to separate light hydrocarbons up to C₃ (e.g. CH₄) and all other noble gases such as argon (Ar), krypton (Kr), xenon

(Xe) etc. All heavy and polar gases (e.g. water vapour, CO₂) are back-flushed to vent on this channel.

The second channel can separate CH₄ and other light hydrocarbons up to C₅, CO₂, sulphur and nitrous gases, e.g. nitrous oxide or laughing gas (N₂O). The molecules (H₂, O₂, Ar, N₂ and CO) separated by the first channel co-elute as one peak on this channel. A Rt-U-BOND PLOT (15 m $\times$ 0.53 mm i.d., 20 μ m film thickness; Restek) is used as a pre-column to backflush H₂O and a Rt-Q-BOND PLOT (30 m $\times$ 0.53 mm i.d., 20 μ m film thickness; Restek) functions as the main column for channel two.

The GC-oven operates in an isothermal mode of 35 °C throughout the entire analysis and the combination of the two channels leads to a complete separation of all components mentioned. The heated valve box contains three switching valves (AFP). Two 10-port gas sampling switching valves are used to switch either channel between injection and backflush mode and one 6-port gas sampling switching valve is used to select which of the two channels is connected to the PDHID. The data analysis is performed by the Chromeleon 7 software (Thermo Fisher Scientific Inc.), which also controls the valves in the equipment.

Because the detection of the permanent gases at low ppb levels is required, the used helium (6.0) gas is additionally purified by two Helium Purifiers (Vici Valco Instruments Co. Inc.) to a purity of about 7.0.

2.4. Permeation measurements

2.4.1. Permeation measurements using the PEBaMeT

The O₂GTR validation experiments were measured on the laminated structures with EVOH32 and EVOH48 at 20 °C and 0% RH and on monolayer EVOH44 at 30 °C and 65% RH.

The N₂GTR measurements were performed on both monolayer and laminated structures. The experiments on the EVOH32 samples were performed in quadruple and those on the EVOH44 and EVOH48 were performed in duplicate. The laminated structures were only used for measurements in dry conditions, and similar as with the measurements on the PERMATRAN-C® 4/41, the samples were mounted with the EVOH side of the sample facing to the downstream side. Dry N₂GTR measurements were conducted on EVOH32 at 20, 30, 35, 40, 45 and 55 °C, and measurements at varying RH were executed at 35 °C at approximately 15, 25, 35, 50 and 65% RH. The N₂GTR of EVOH44 and

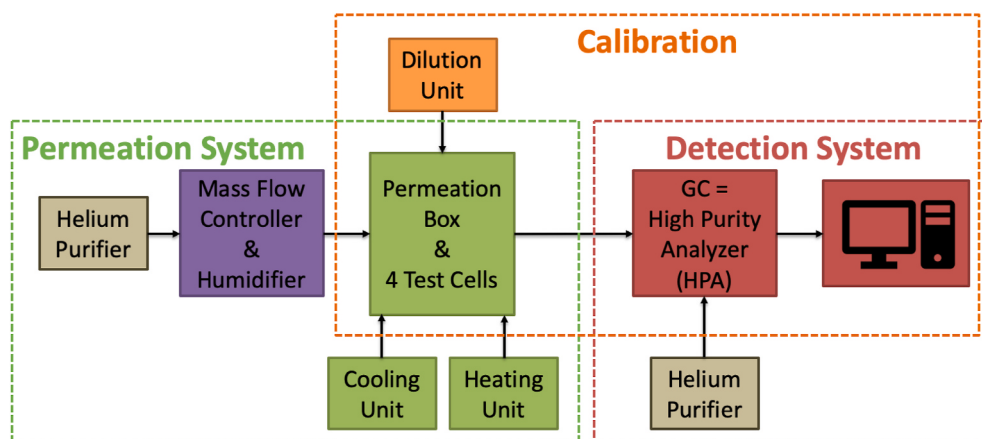


Fig. 3. Schematic overview of PEBaMeT.

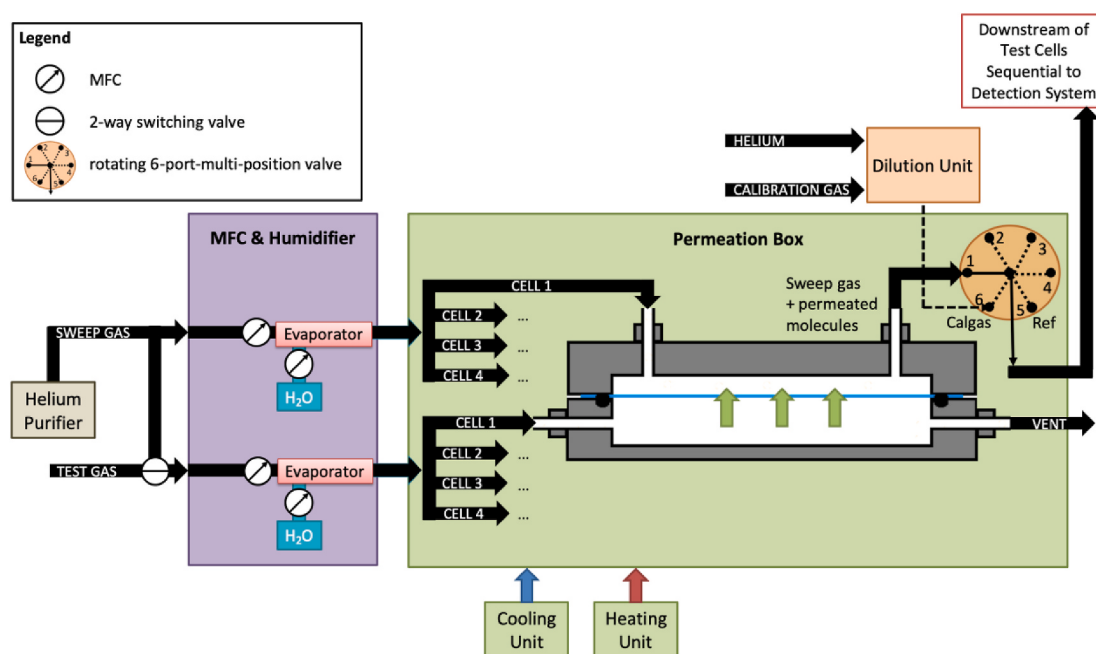


Fig. 4. Schematic of permeation system of PEBaMeT.

EVOH48 were measured in dry conditions at 20, 25, 30 and 35 °C, the experiments in varying RH were carried out at 35 °C at approximately 25, 35, 65% RH.

The permeation was measured on a sample surface of 50 cm² and expressed in cm³/(m²·day·atm).

2.4.2. Oxygen permeation measurements using commercial equipment

The O₂GTR is measured according to ASTM D3985 using an OX-TRAN® 2/22 model 10X and 2/21 ML (AMETEK – MOCON Inc.) at 20 °C and 0% RH and using an OX-TRAN® 2/22 model H at 30 °C and 65% RH. The film samples are mounted into the test cell, which is then purged with an oxygen-free carrier gas, in this case forming gas H₅. O₂ is introduced to the upstream side, while the downstream side, which is analysed by a coulometric detector on the presence of oxygen, is swept with the forming gas (Fig. 2B).

Additionally, O₂ permeation experiments were also performed on different OX-TRAN® modules by EVAL R&D – Kuraray Co. Ltd. (Kura-shiki, Japan) in varying conditions.

2.4.3. Nitrogen permeation measurements performed at GTR Tec

The N₂GTR of EVOH32 and EVOH44 was measured at GTR Tec (Kyoto, Japan) on a permeation system applying the differential pressure method (Fig. 2 A) combined with a GC, similar as to the equipment described by Uenishi et al. [41] The EVOH32 was tested at 20, 30 and 40 °C and the EVOH44 and EVOH48 were measured at only 20 °C. All measurements were carried out in dry conditions.

3. Results and discussion

3.1. Set-up and optimization of the PEBaMeT method

The starting point for the development of the PEBaMeT method was the combination of a permeation system using the equal pressure method and a GC-based detection system. The equal pressure method was chosen over the differential pressure method to avoid the sample from being exposed to mechanical stress that might be caused by the difference in pressure on both sides. The PEBaMeT is especially designed for the continuous measurement of the permeation of permanent gases, therefore its detection system is constructed to analyse low values of

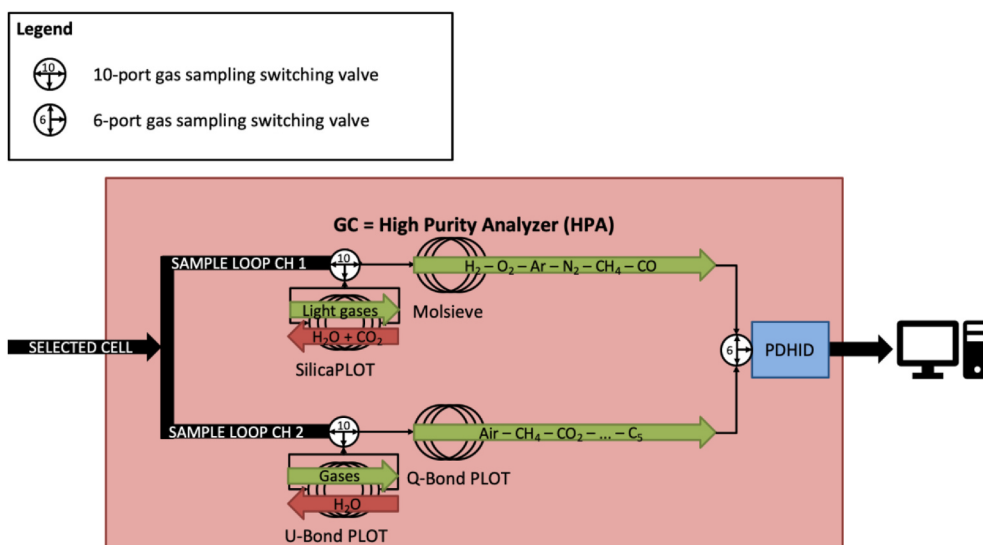


Fig. 5. Schematic of detection system (HPA) of PEBAmeT.

different permanent gases, such as O_2 , N_2 , CO_2 , CO , hydrogen (H_2), and noble gases amongst others, within a carrier gas (e.g. He). Additionally, the detection system is able to detect all gases simultaneously (allowing to study co-permeation). The next paragraphs describe i) the selection of GC columns, ii) the detector and its calibration and iii) the conversion of the detector output to a GTR value. During the method development the PEBAmeT has been optimized with a state-of-the-art approach in order to resolve reoccurring issues as well as preventing some known problems and shortcomings from previously established methods.

3.1.1. Selection of GC columns

GC-column separation is dependent on the mobile phase (carrier that flows through the column) and the stationary phase (column film or packing). According to the used stationary phases gas-solid chromatography (GSC), in which a solid adsorbent solid or porous layer is used and gas-liquid chromatography (GLC), in which a liquid film is used are defined. GLC is widely used in different applications opposed to GSC. However, GSC is well established for very specific applications, such as the separation of permanent gases and light hydrocarbons (HCs). Packed columns have been used in both GSC and GLC, but due to low resolution and long analysis time, they have mainly been replaced by capillary columns, which have enabled fast high-resolution GC analysis [42,43]. Capillary columns using a GLC stationary phase are called wall-coated open-tubular (WCOT) columns and those with a GSC stationary phase are called porous-layer open-tubular (PLOT) columns as shown in Fig. 6. In addition, there are also the support-coated open-tubular (SCOT) columns, which use a porous layer that is wetted with a liquid stationary phase [44].

For the separation of permanent gases, PLOT columns are the most suitable. Unfortunately, there is not a single type of PLOT column, which is able to separate all gases present in air completely in high resolution. Usually two or more columns are required to accomplish full separation [42,44,45]. Different types of PLOT columns and their performances are listed in Table 5. Because high resolution separation of O_2 and N_2 is required the molecular sieve 5 A is included in the PEBAmeT system. Due to its sensitivity to H_2O and CO_2 amongst others, pre-separation is applied to avoid these components from being adsorbed onto the column, by using a silica PLOT pre-column for back-flushing. This is important because the sample flows in the permeation system can be humidified. A second column that can separate CO_2 and other heavier components such as nitrous gases is selected to detect a broad range of different permanent gases simultaneously.

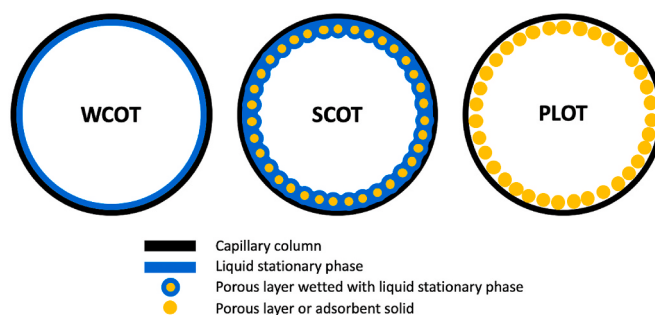


Fig. 6. Different types of capillary columns. Modified from De Lloyd [51].

3.1.2. Selection and calibration of the detector

The detection of permanent gases and light HCs requires a universal detector. A flame ionization detector (FID), which is most commonly used for efficiently detection of carbon containing compounds at low detection limits and large dynamic linear range, is not suitable for the detection of inorganic compounds (such as N_2 , O_2 , He, H_2S , H_2O and NO_2) with the exception of CO and CO_2 which can be detected by using a methanizer. A thermal conductivity detector (TCD) measures the difference in heat loss of a filament when the pure reference gas flow versus carrier gas containing the analytes flows over it, can detect all permanent gases depending on the choice of the carrier gas, as long as there is a significant difference in thermal conductivity. However, the major limitation is its detection limit of about 1–10 ppm for the gases of interest, whereas the permeation of EVOH in a flow of 10 mL/min for a test surface of 50 cm² requires a detection limit in the low ppb region [43]. The most interesting detector for this application is the PDHID. This universal detector generates a pulsed discharge in high-purity (≥ 6.0) He that leads to the emission of photons with an energy range of 13.5–17.7 eV. A small fraction of the analytes present in the carrier gas are ionized by these photons. The resulting free electrons are focussed onto a collector electrode and influence its standing current, this change is recorded as a change in signal in the chromatogram. With the exception of neon (Ne) and He itself all molecules can be ionized and therefore detected. The PDHID also has a detection limit that is three orders of magnitude more sensitive than the TCD in the detection of permanent gases [43,46,47].

The PDHID is a concentration sensitive detector, which measures an electric signal. This signal is plotted as a function of time providing

Table 5

Summary of different PLOT columns used for permanent gas separation [42–45, 63].

PLOT column	Advantages	Disadvantages
Molecular sieve: Natural or artificially prepared zeolites (aluminosilicates of sodium, potassium or calcium). – 5A: Calcium aluminosilicate with pore diameter of 5 Å can separate HCs up to C ₃ – 13X: Sodium aluminosilicate with pore diameter of 10 Å, lower resolution for O ₂ and N ₂ than 5 Å, but can separate HCs up to C ₁₂	Columns with highest resolution for N ₂ and O ₂ . Unique ability to separate other noble gases such as He, Ne, Ar, Kr, Xe above ambient temperature as well as H ₂ , CO and light HCs such as CH ₄	Absorbs CO ₂ , chlorine, sulphur and nitrous gases (not irreversibly), and water.
Carbon sieve: Carbonaceous particles obtained from pyrolysis of poly (vinylidene chloride) (PVDC) or other products, resulting in a very apolar, inert, high surface area column.	Used for separation of permanent gases such as H ₂ , O ₂ + N ₂ , CO, CO ₂ , water vapour, CH ₄ and other light HCs. Can separate CO and CO ₂ from air.	Limited resolution for O ₂ , N ₂ and CO.
Silica based: Silica gel and porous silica in a variety of surface areas and pore diameters.	Can separate H ₂ , air, CO, CO ₂ and light HCs. Analysis of moisture containing samples is possible. Inert to and can separate sulphur, nitrous and chlorine gases from air	Cannot separate O ₂ and N ₂ above ambient temperatures.
Porous polymer: Different types made of divinylbenzene (DVB) based copolymers, varying in polarity and selectivity. – Q-Bond: Conventional type using DVB homopolymer – U-Bond: DVB and ethylene glycol dimethacrylate, higher polarity than the Q-Bond	Can separate heavier permanent gases from air such as CO ₂ and water vapour and light hydrocarbons. Can be used for moisture containing samples.	O ₂ and N ₂ separation only possible at sub-ambient temperatures.

peaks in a chromatogram. The surface of these peaks are integrated generating area counts (time-normalized in pA·min), which correlate to a certain concentration of analyte. A careful calibration in the lower ppb region is necessary for more accurate measurements of films with lower GTR. This led to the implementation of the Dilution Unit to calibrate at different levels. By using the Dilution Unit, the calibration gas, containing approximately 10 ppm of each gas, can be mixed with pure He, which allows calibration in the low and medium ppb range.

The detector is calibrated with different standards ranging from low ppb up to low ppm levels, using the Dilution Unit. The standards are automatically injected on the HPA unit through the sample loop via port 6 of the rotating 6-port-multi-position valve inside the permeation box. The calibration curves (Fig. 7) for this experiment were based on 5 different standards. Each standard was injected 5 times on both GC channels. H₂, O₂, N₂ and CO were calibrated via channel 1 and CO₂ via channel 2. This resulted in linear correlations for all 5 components.

3.1.3. Conversion to GTR values

The calibration curves are used to calculate the amount of permeated gas in ppb levels, which are automatically converted by the Chromeleon software to GTR values in cm³/(m²·day·atm) using formula (4).

$$GTR = \frac{q_{GTR} \times 10^{-9} \frac{\text{cm}^3}{\text{mL}} \times \varphi_{\text{sweep}} \frac{\text{mL}}{\text{gas min}} \times 1440 \frac{\text{min}}{\text{day}}}{A_{\text{cell}} \times 10^{-4} \text{ m}^2 \times P_{\text{gas}} \text{ atm}} \quad (4)$$

In which q_{GTR} is the amount of permeated gas in ppb, A_{cell} is the surface area of the film inside the cell expressed in cm², $\varphi_{\text{sweep gas}}$ is the flow of the sweep gas on the downstream side of the cells in mL/min and P_{gas} is the partial pressure of the test gas in atm.

The PDHID and formula (4) can be used to determine the GTR of any other permanent gas, except for He and Ne, which cannot be detected.

3.2. O₂GTR validation experiments

To validate the PEBaMeT measurements in different conditions of RH and temperature, several O₂GTR permeation measurements were performed on different EVOH grades using both PEBaMeT and OX-TRAN® modules. Experiments were performed on EVOH32 and EVOH48 at 20 °C in dry conditions and an additional experiment was performed on EVOH44 at a higher temperature and higher RH, i.e. 30 °C and 65% RH. The results on the EVOH44 and EVOH48 are in good accordance with results obtained by the OX-TRAN® modules (Table 6). There was little discrepancy between the different modules for the EVOH32, which might be due to variation amongst samples, the modules sensitivity and the operator. Overall it can be stated that the results obtained using the PEBaMeT are in line with those of the OX-TRAN® modules (Table 6).

3.3. N₂GTR measurements

3.3.1. N₂GTR validation experiments

The N₂GTR of the 20 µm-EVOH32 was determined at 20, 30 and 40 °C in dry conditions on the PEBaMeT and compared with the results of a similar grade measured on a validated permeation measurement system using the GC-differential pressure method according to ISO 15105-1 Annex B at GTR Tec (Kyoto, Japan), similar as to the system described by Uenishi et al. [41]. The same was done for EVOH44 and EVOH48 at 20 °C and 0% RH. Results are shown in Table 7.

Overall, the results measured by the PEBaMeT are in accordance with the measured values on the GC-differential pressure method. However, there is some discrepancy between certain results, but it should be noted that there is no information available on the error of the GC-differential pressure method and the differences between the results of these two methods are comparable with the differences between the results of the different OX-TRAN® modules as was shown in Table 6. These deviations might also be explained by the difference in the test method, since the GTR uses a differential pressure method, whereas the PEBaMeT is based on the equal pressure method.

3.3.2. N₂GTR at varying temperature

Using the aforementioned method and formulas the N₂GTR of 20 µm-EVOH32 film was determined at 20, 30, 35, 40, 45 and 55 °C in dry conditions in order to plot an Arrhenius curve as shown in Fig. 8. Measurements were both performed on monolayer film samples as well as laminated structures. Initial measurements on EVOH32 films were performed solely on monolayer films, but in dry conditions the monolayer film samples became brittle and occasionally ruptured due to stress at higher temperature causing the experiment to fail. This issue could be resolved by using the laminated PP layer of 50 µm. The PP layer gives the sample additional mechanical strength and prevents the film from rupturing in dry conditions. Because the barrier properties of PP against N₂ (and other gases) are negligible, the N₂GTR of both the EVOH monolayer and EVOH//PP laminated structures can be considered the same. Even though the outcome was the same, it was found that laminated structures took a longer time to reach steady-state permeation when the RH conditions were changed, because PP is a good water barrier and it takes longer before the RH in the EVOH layer is at equilibrium. Monolayers showed steady-state permeation after a few hours,

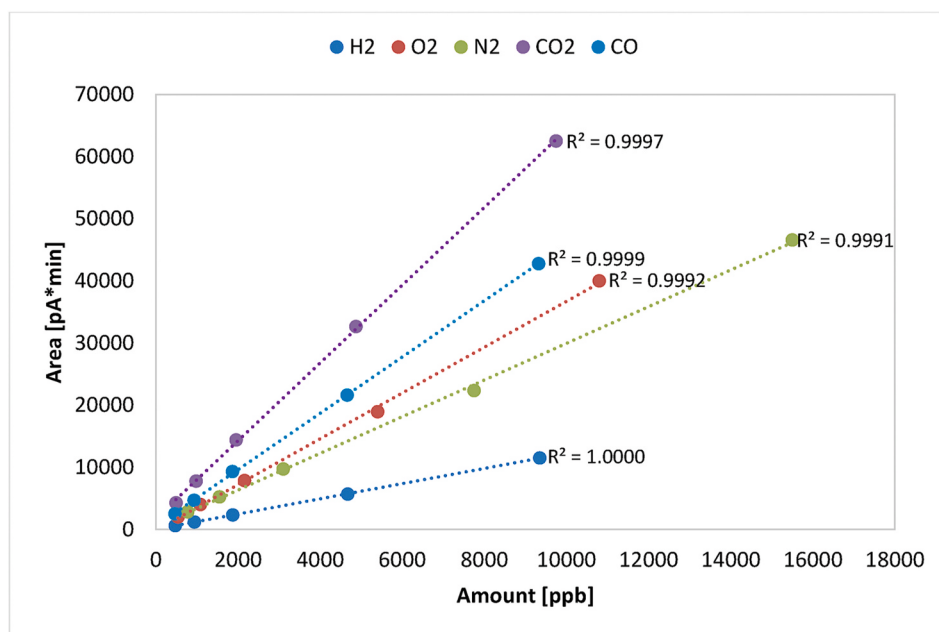


Fig. 7. PDHID calibration curves for H₂, O₂, N₂, CO₂ and CO.

Table 6

O₂GTR measured on different OX-TRAN® modules and the PEBaMeT module.

Sample	Test conditions	PEBaMeT	OX-TRAN® 2/22 10X	OX-TRAN® 2/21 ML	OX-TRAN® 2/22 H
			O ₂ GTR [cm ³ /(m ² ·day·atm)]		
EVOH32	20 °C, 0% RH	0.525 ± 0.006	0.349 ± 0.004	0.807 ± 0.009	
EVOH48	20 °C, 0% RH	8.39 ± 0.08	8.33 ± 0.03	8.81 ± 0.09	
EVOH44	30 °C, 65% RH	7.04 ± 0.05			7.10 ± 0.08

Table 7

Comparison of N₂GTR results of different EVOH film samples of 20 µm measured by PEBaMeT and GTR at different temperatures.

Sample	Conditions	PEBaMeT	GTR: GC-Differential pressure method
		N ₂ GTR [cm ³ /(m ² ·day·atm)]	
EVOH32	20 °C, 0% RH	0.06 ± 0.03	0.04
	30 °C, 0% RH	0.14 ± 0.01	0.14
	40 °C, 0% RH	0.35 ± 0.01	0.49
EVOH44	20 °C, 0% RH	0.55 ± 0.03	0.62
EVOH48	20 °C, 0% RH	1.13 ± 0.05	1.52

whereas laminated structures reached equilibrium after a day or two depending on pre-conditioning.

The Arrhenius curve of the N₂GTR of 20 µm EVOH32 in dry conditions (Fig. 8) shows a good correlation and has an R² of 0.9967, which indicates the system's integrity. The N₂GTR increases from about 0.06 ± 0.03 cm³/(m²·day·atm) at 20 °C to 1.00 ± 0.01 cm³/(m²·day·atm) at 55 °C. By using the Arrhenius equation, which can be obtained from the graph, the N₂GTR can be extrapolated to other temperatures. However, as can be seen in the graph, the error of the value measured at 20 °C, becomes substantial opposed to the other temperatures where the error is no longer graphically visible (n = 4). And this value might arguably be at the instrument detection limit (IDL) as the standard deviation of the leak into the system was 0.03 cm³/(m²·day·atm). The IDL is 3 standard deviations higher than the leak which results in a detection limit of nearly 0.1 cm³/(m²·day·atm).

In paragraph 3.3.1 it was already discussed how the N₂GTR of the

EVOH32 measured on the PEBaMeT differed from the measurements performed at GTR Tec (Kyoto, Japan). These results are represented in Fig. 9, where they are compared with the O₂GTR measured on the same samples. Opposed to the O₂GTR, the N₂GTR measurements performed by GTR Tec using the GC-based differential pressure method are much steeper. The N₂GTR measurements performed on the PEBaMeT, on the other hand, show a nearly parallel correlation with the O₂GTR. A possible explanation for this phenomenon lies within the difference in the total pressure which could cause plasticization and swelling effects [7,48]. Due to the higher pressure on one side in combination with a high temperature, which leads to an increase of kinetic energy, the gas molecules might be able to permeate faster than with the equal pressure method in the same conditions. Additionally, in the equal pressure method there are two gases involved, a test gas and a sweep gas, in which case permeation in two directions could cause competition [49].

3.3.3. N₂GTR at varying relative humidity

The PEBaMeT system was also used to measure the N₂GTR of the three different grades at one temperature and varying humidity, to define the RH dependence. The N₂GTR curve is plotted at 35 °C, with the RH ranging from dry conditions to approximately 65% as shown in Fig. 10. This temperature was chosen because the values at lower temperature were too close to or below the detection limit of 0.1 cm³/(m²·day·atm). The higher temperature also limits the RH to about 65% due to the maximum amount of water which can be vaporized into the gas flows.

As expected, the N₂GTR curves as a function of RH, show a quite similar trend to the O₂GTR curves as a function of the RH [1,10]. In case

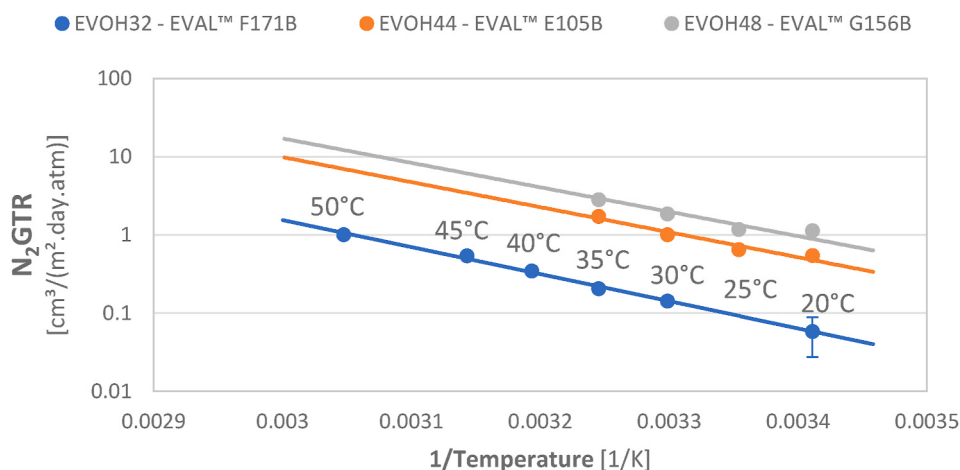


Fig. 8. Arrhenius curve of the N₂GTR of EVOH32, EVOH44 and EVOH48 measured on film samples of 20 μm at 0% RH.

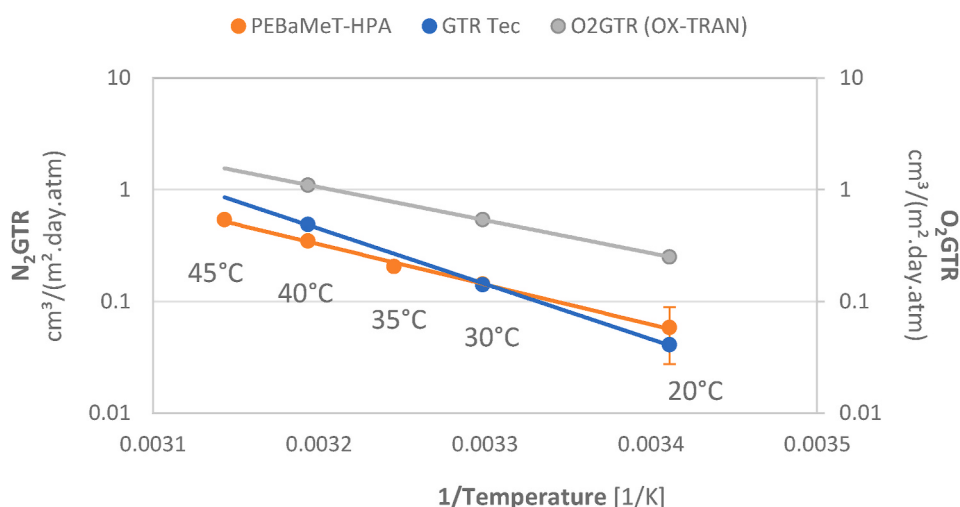


Fig. 9. The N₂GTR of EVOH32 (20 μm) at 0% RH determined on the PEBAmeT system using an equal pressure permeation system versus the measurements performed at GTR Tec (Kyoto, Japan) on a differential pressure permeation system. Comparison with O₂GTR on the same grade measured on OX-TRAN® modules at EVAL R&D (Kurashiki, Japan).

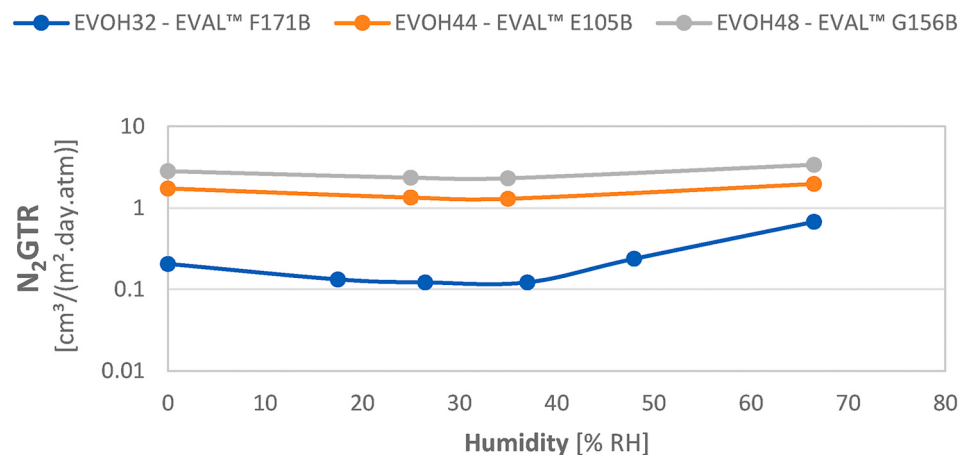


Fig. 10. N₂GTR of EVOH32, EVOH44 and EVOH48 film samples of 20 μm at 35 $^{\circ}\text{C}$ as a function of the RH.

of the EVOH32, the N₂GTR first slightly decreases from $0.21 \pm 0.01 \text{ cm}^3/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at approximately 0% RH before it reaches a minimum at around 30–35% RH of $0.12 \pm 0.01 \text{ cm}^3/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ and then

rapidly increases as the RH increases, i.e. $0.68 \pm 0.01 \text{ cm}^3/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at approximately 65% RH. Both the EVOH44 and EVOH48 are less affected by the change in RH between 0% and 65% due to their higher

ethylene content, the minimum value here is 1.30 ± 0.15 and 2.31 ± 0.22 $\text{cm}^3/(\text{m}^2\cdot\text{day}\cdot\text{atm})$ respectively at approximately 30% RH [10]. This decrease is due to the reduced chain mobility caused by strong interactions between water molecules and the polymer matrix at low RH as the water molecules effectively fill up the free volume between the polymer chains. When the RH is further increased the water molecules will act as a plasticizer and weaken the strong inter- and intramolecular hydrogen bonds which in turn will lead to an increase in the chain mobility, making it easier for the other gas molecules to permeate [10, 50].

3.4. Comparison of the GTR of EVOH with common polymers

The results obtained using the PEBaMeT confirm that EVOH has very good N_2 barrier properties. To compare them with the barrier of other polymers from literature, the GTR can be converted to a thickness normalized permeability coefficient expressed in $\text{cm}^3\cdot\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{atm})$. The O_2 permeability coefficient (P_{O_2}) and the N_2 permeability coefficient (P_{N_2}) of high-density polyethylene (HDPE), polypropylene (PP) and polyamide 6 (PA 6) is given in Table 8. EVOH32, EVOH44 and EVOH48 easily outperform polyolefins such as PP and HDPE as N_2 barrier, even when the EVOH grades were measured at higher temperature and in higher RH. Even PA 6 and PET are outperformed [7]. This is similar to the P_{O_2} of EVOH which is considered the lowest amongst polymers. PA 6 and PET have a P_{O_2} which is 1-3 orders of magnitude higher than EVOH and for PP and HDPE the P_{O_2} is over 3 orders of magnitude higher [10].

4. Conclusion

In this study a new permeation measurement system dubbed the PEBaMeT was successfully developed. The PEBaMeT consists of a permeation system equipped with four permeation test cells with an up- and downstream flow, which can be regulated and humidified separately, combined with a detection system (HPA), which measures the permeation of the four cells in sequential order through a rotating 6-port-multi-position valve. The combination of two analytical GC channels, each with a pre- and main column in the HPA leads to the full separation of all permanent gases. The components are detected and quantified by a PDHID, which requires a careful calibration from low ppb to low ppm levels by using the Dilution Unit in order to provide more reliable results across the required range. The detected amounts in ppb are automatically converted to GTR values by the Chromeleon software using formula (4).

It was also demonstrated that the PEBaMeT can be used to measure the permeation of O_2 and N_2 through high-barrier EVOH films at varying temperature and RH. The O_2 GTR measurements on the PEBaMeT were similar to those obtained on validated OX-TRAN® modules. The measured N_2 GTR values on the PEBaMeT through EVOH32, EVOH44 and EVOH48 films of 20 μm , where in good accordance with the values measured by a GC-differential pressure method and the differences were within the analytical uncertainty of each method.

The Arrhenius curve at 0% RH demonstrates good correlation and can be used to extrapolate the N_2 GTR at other temperatures. At 35 °C 20 μm of EVOH32, EVOH44 and EVOH48 illustrates optimal barrier properties against N_2 around 30% RH, where the N_2 GTR reaches a minimum of approximately 0.12, 1.3 and 2.3 $\text{cm}^3/(\text{m}^2\cdot\text{day}\cdot\text{atm})$ respectively. However, for the PEBaMeT system, temperature is a limiting factor in relation to the amount of water that can be vaporized in the gas flows, thus limiting the maximum RH (e.g. at 35 °C the maximum RH was approximately 65%).

The results clearly prove that EVOH has good N_2 barrier properties, as all three EVOH grades outperform HDPE, PP and PA 6 by several

Table 8

Comparison of the O_2 permeability coefficient (P_{O_2}) and the N_2 permeability coefficient (P_{N_2}) of EVOH with common polymers at varying conditions.

Polymer	P_{O_2} [$\text{cm}^3\cdot\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{atm})$]	P_{N_2} [$\text{cm}^3\cdot\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{atm})$]
EVOH32	7.0 (20 °C, 0% RH)	1.2 (20 °C, 0% RH)
		4.1 (35 °C, 0% RH)
		14 (35 °C, 65% RH)
EVOH44	64 (20 °C, 0% RH)	11 (20 °C, 0% RH)
		35 (35 °C, 0% RH)
		39 (35 °C, 65% RH)
EVOH48	170 (20 °C, 0% RH)	23 (20 °C, 0% RH)
		56 (35 °C, 0% RH)
		68 (35 °C, 65% RH)
HDPE	40,000–91,000 (23 °C, 50% RH) [7]	21,000 (unknown) [7]
PP	50,000–100,000 (23 °C, 50% RH) [7, 64]	18,000 (30 °C, unknown RH) [7]
PA 6	400–2000 (23 °C, 0% RH) [7]	350 (23 °C, 0% RH) [7]
PET	1000–5000 (23 °C, 50% RH) [7,64]	300 (23 °C, 75% RH) [7]

orders of magnitude, even at more stringent conditions of temperature and RH. The P_{N_2} at 35 °C and 65% RH is 14, 39 and 68 $\text{cm}^3\cdot\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{atm})$ for EVOH32, EVOH44 and EVOH48 respectively, opposed to 300 $\text{cm}^3\cdot\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{atm})$ for PET at 23 °C and 75% RH and 350 $\text{cm}^3\cdot\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{atm})$ for PA 6 at 23 °C and 0% RH.

Moreover, the principle of incorporating GC technology in permeation measurement systems could also be used to measure permeation of other substances such as aromas and chemicals. For this, different types of GC-columns would be required.

CRedit authorship contribution statement

Caroline Maes: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Validation, Writing - original draft, Writing - review & editing. **Maarten te Molder:** Methodology, Validation, Writing - review & editing. **Wout Luyten:** Conceptualization, Funding acquisition, Resources, Supervision, Writing - review & editing. **Geert Herremans:** Conceptualization, Funding acquisition, Resources, Supervision, Writing - review & editing. **Naomi Winckelmans:** Investigation, Methodology, Validation, Writing - review & editing. **Roos Peeters:** Supervision, Writing - review & editing. **Robert Carleer:** Conceptualization, Supervision, Writing - review & editing. **Mieke Buntinx:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2020.106979>.

Data availability

The data required to reproduce these findings are already presented in this paper.

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