Comparison of water vapour transmission rates of monolayer films determined by water vapour sorption and permeation experiments

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ABSTRACT

The water vapour transmission rate (WVTR) of packaging materials and edible coatings is one of their critical parameters for the shelf life of many food products. The water vapour transmission rates of flat bodies such as films are determined by permeation measurements which are a steady-state method. Another method is based on water vapour sorption measurements which is a non-steady-state method. It can be used only for mono-material flat bodies. It allows using smaller sample areas compared to permeation measurements. However, not much is known about how well both methods correlate with each other. Therefore, the aim of this study was to compare the WVTR results of different materials determined by both methods. The results of both methods differed by up to factor of three, measured at identical samples. In a few cases the difference was up to factor five. The exact reasons for these differences are unknown. Nonetheless, the water vapour sorption method is a suitable method to determine the magnitue of order of the water vapour transmission rate but not its exact value.

1. Introduction

The water vapour transmission rate (WVTR) of polymer films is one of their most important properties and it is often measured in quality control and to identify their suitability for use as packaging materials (Bleisch et al., 2014; Langowski, 2008).

The aim of this study has been to compare WVTR values determined by permeation experiments (steady-state) and sorption experiments (non-steady-state).

The WVTR is normally measured in steady-state by using the electrolytic detection sensor method (carrier gas method) or by using the gravimetric method referred as steady-state measurement (e.g. according to DIN 53122-1). For both methods the relative humidity (RH) gradient between both sides of flat samples is constant. The WVTR is the mass of water (m) that permeates in steady-state through a film with the thickness (l) and an area (A) per time (t) at a given temperature (T) and RH gradient (Eq. (1)). In applied science these values are often normalised to a film thickness of 100 μm (Bleisch et al., 2014; Langowski, 2008). Often used RH gradients are 85% to 0% and 50% to 0% RH. Due to the fact that at polar polymers the water vapour permeability coefficient increases with higher RH due to swelling, the WVTR is valid there only for a defined RH on both sides of a film. An often used unit for WVTR is (g·100 μm/(m²·day), 85→0% RH).

$$\text{WVTR} = \frac{m \cdot l}{A \cdot t}; \quad T = \text{const.}; \ \varDelta\text{RH} = \text{const.} \tag{1}$$

Another possibility to determine the WVTR is a sorption experiment (non-steady-state measurement). The sorption method is only suitable for isotropic, monolayer materials (Barrer, 1941; Crank, 1975). For these tests, samples are dried and then stored at a defined RH. The samples absorb water vapour and their weight increases. This method is a non-steady state measurement, because the samples are not in equilibrium with the RH of their direct environment during the measurement.

Barrer derived from Fick's laws a time dependent description for the absorption of substances (Eq. (2)) (Barrer, 1941; Crank, 1975).

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=0}^{\infty} \cdot \frac{8}{(2n + 1)^2 \cdot \pi^2} \cdot e^{\frac{-D \cdot (2n+1)2 \cdot \pi 2 \cdot t}{l2}} \tag{2}$$

(m_t) is the amount of absorbed water vapour at the time (t), (m_∞) is the amount of absorbed water vapour at equilibrium, (D) is the diffusion coefficient, (l) is the thickness and (m_t/m_∞) is the relative mass fraction of water vapour in the film. For small times ($m_t/m_\infty < 0.5$ to 0.7) Eq. (2) simplifies to Eq. (3) (Barrie & Machin, 1971a,b; Barrie et al.,

1987; Crank, 1975; Okamoto et al., 1992; Vieth, 1991).

$$\frac{m_t}{m_\infty} = \frac{4}{\sqrt{\pi}} \cdot \sqrt{\frac{D \cdot t}{l^2}} \tag{3}$$

Eqs. (2) and (3) are only valid for the case that the absorption by a sample can be described by the solution-diffusion model (Barrer, 1941; Crank, 1975; Langowski, 2008). Therefore, strictly speaking Eqs. (2) and (3) are valid only when following boundary conditions are fulfilled (Barrer, 1941; Crank, 1975): 1.) Henry's law can be applied (Eq. (4)), i.e. the concentration ($c_{absorpt}$) of the absorpt (water) in the polymer depends linearly on the partial pressure ($p_{component\ to\ be\ absorbed}$) of the component to be absorbed (water vapour). The proportionality constant is the sorption coefficient or solubility coefficient (S) (Barrer, 1941; Henry, 1803; Langowski, 2008, van Krevelen and Nijenhuis 2009).

$$c_{absorpt} = S \cdot p_{component\ to\ be\ absorbed} \tag{4}$$

2.) The adsorption of water vapour on the surface of the film is fast. The diffusion in the polymer is the time limiting step for the absorption rate of the film.

3.) The polymer does not react with the sorbed water.

4.) The diffusion and sorption coefficients are constants.

5.) The film material is isotropic on a macroscopic scale.

However, in real-life these conditions are often not fulfilled, because the polymer can interact with sorbed water vapour. Therefore, diffusion and sorption coefficients are often dependent on the amount of sorbed water vapour (Peterlin, 1985). The water vapour sorption isotherm cannot be described by Henry's law in such case. In this case, Eqs. (2) and (3) are simplifications. To distinguish exact values from the coefficients of these simplifications, they are labelled 'effective' in this work. The effective permeation coefficient is calculated from the effective sorption coefficient ($S_{eff.}$) and the effective diffusion coefficient (Eq. (5)) (Crank, 1975).

$$P_{eff.} = S_{eff.} \cdot D_{eff} \tag{5}$$

Interestingly, the application of the sorption method causes often a paradox situation. It can be best applied for polar polymers which absorb enough water vapour to be gravimetrically measured but the water vapour sorption of these polymers cannot be (exactly) described by Henry's law (constant sorption coefficient).

2. Materials and methods

2.1. Materials

All used materials are described in the referenced literature or in the following subchapters. The films analysed for this study were extruded or they were produced as cast films using the facilities of Fraunhofer IVV (Freising, Germany). The WVTR of identical samples were determined by permeation and sorption experiments. The selected materials were chosen due to their high water vapour sorption which is necessary for the gravimetrical measurement method.

- Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a semi-crystalline thermoplastic polyester (Enmat™ Y1000 P, TianAn, China; 3% HV; T_m: 170–176 °C, density: 1.25 g/cm³, M_w: 380,000 g/mol). It was extrusion blended with 10, 20 and 30 wt.-% wheat straw and monolayer films were formed thereof.
- Polylactic acid (PLA) film samples (PLA 2002 D, NatureWorks LLC, Minnetonka, USA) was extruded to monolayer films at temperatures between 180 and 250 °C. This PLA polymer has a density of 1.24 g/cm³ and a melting temperature of 210 °C.
- Polyamide (Ultramid B36 LN, BASF, Germany) was extruded to monolayer films at temperatures between 185 and 270 °C.
- Polyethylene, low-density (PE-LD; Lupolen 1806, basell, Germany; density: 0.92 g/cm³, T_m: 108 °C) was blended with milled silica gel (Merck, Germany) and extruded to films at temperatures between

150 and 210 °C.
- Cast films of whey protein were produced according to methods described by Schmid (Schmid et al., 2016; Schmid et al., 2014). The formulation was blended with different additives such as urea, sodium sulphite (Na_2SO_3) and sodium dodecyl sulphate (SDS).

It is worth to mention that relevant polymer properties, which can influence the sorption behaviour and water vapour transmission rate, such as crystallinity, crystallite size, microscopic polymer structures and anisotropic polymer properties were not determined or data about these properties was not available. Therefore, the discussion of results of this study does not consider these specific properties.

2.2. Methods

2.2.1. Steady-state (permeation)

The WVTR was measured according to the carrier gas method (electrolytic method; DIN EN ISO 15106-3) with a permeation-testing device (AQUATRAN, Mocon Inc., Minneapolis, USA) or with the gravimetric method (DIN 53122-1). The gradients of relative humidity between both sides of the samples were set to 85%→0% or 50%→0%. Tests were done as duplicates or triplicates.

2.2.2. Non-steady-state (sorption)

For the sorption experiments all samples were dried at 0% RH in a desiccator with activated silica gel to constant weight. Water vapour absorption experiments with films were evaluated at a relative mass fraction of absorbed water of between 0 and 0.7 or 0 and 0.5. The effective diffusion coefficients were calculated using the slope of the initial absorption-time curve (according to Eq. (3)) and the thickness of the film. The effective sorption coefficients were calculated from the water vapour absorption at equilibrium (Eq. (4)). The WVTR was calculated using Eq. 5. Experiments were done as 5- or 6-fold determinations. In Fig. 1 an example for a result of a sorption experiment is shown.

3. Results and discussion

In Table 1 the results of sorption and permeation measurements are listed while in Fig. 2 the results of WVTRs from sorption and permeation experiments are compared in one figure. The results for sorption experiments report about samples with relatively high amounts of absorbed water vapour, at least (0.5 g water)/(100 g dry mass) (Table 1). It is difficult to measure mass changes gravimetrically when samples absorb much lower amounts of water vapour.

Due to the fact that all the samples had a polar nature, their sorption isotherm deviated from Henry's law, i.e. the applied equations for the
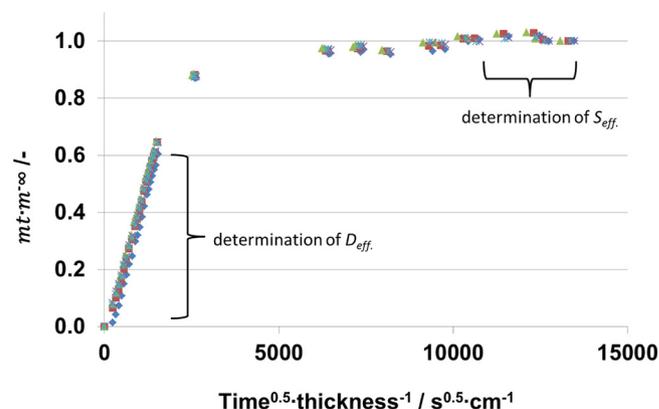
Fig. 1. Example for sorption experiment (time-dependent water vapour absorption); PLA film with 1150 μm thickness: 5-fold determination; 23 °C; stored at 85% RH.