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Comparison of test methods for oxygen permeability: Optical method versus carrier gas method

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ABSTRACT

The oxygen permeability of films is relevant for packaging related and technical applications. An increasingly used test method for the measurement of oxygen permeability is the optical test method, because it allows a simple and cost-efficient measurement setup. This method is based on optical chemical sensors. However, not much is known about its validity. Therefore, method validation is necessary which is subject of this study. The optical method is compared with the carrier gas method for a variety of film samples. In the tested permeability range of 0.5–2500 cm^3 (STP)·(m^2 d bar)$^{-1}$ both methods deviated less than 20% for zero and 50% relative humidity.

1. Theoretical background

1.1. Relevance of oxygen permeability

A common reason for quality reduction of packaged goods, such as foods and technical products, is either too low or too high oxygen permeation.

To measure the oxygen permeability of films in a gas phase with an optical sensor offers new opportunities. An intelligent application of such sensors allows, together with a newly designed measurement cell with improved leak tightness (zero value), the permeation measurement in the range of 10^{-1} to 10^6 cm^3 (STP)·(m^2 d bar)$^{-1}$ and therefore the analysis of barrier films with low oxygen permeability for oxygen sensitive food products as well as perforated films with high oxygen permeability, normally used for packaging of fruits and vegetables. Low oxygen permeability of down to 1 cm^3 (STP)·(m^2 d bar)$^{-1}$ is required for long duration foods and some fresh products like cured meat [1], high permeability up to 100,000 cm^3 (STP)·(m^2 d bar)$^{-1}$ is required for fresh food like fresh cut fruits [2].

1.2. Basic theory of permeation

In principle there are two different processes by which gases and vapors permeate through polymers: (a) a solubility-diffusion effect by which gases and vapors dissolve at one surface of a polymeric sample, diffuse through the polymer via a concentration gradient and evaporate on the other surface of the polymeric sample [3–6] and (b) a pore effect by which gases and vapors diffuse through microscopic pores, pinholes or cracks of polymeric materials [7]. An universal permeation measurement should be able to measure both effects adequately.

The flux J [m^3 (STP)·m^{-2}·s^{-1}] through a polymer layer is described by the following equation [5,6]:

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$$J = \frac{Q \cdot (p_1 - p_2)}{A} = D \cdot S \cdot \frac{p_1 - p_2}{l} = P \cdot \frac{p_1 - p_2}{l} \quad (1)$$

Where Q is the permeability [m^3 (STP)$\cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$], p_1 and p_2 are the upstream and downstream pressures [Pa], l is the thickness of the film [m], D is the diffusion coefficient [$m^2 \cdot s^{-1}$], S is the Henry's law solubility coefficient [m^3 (STP) $\cdot m^{-3} \cdot Pa^{-1}$] and P is the permeation coefficient [m^3 (STP) $\cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$]. It has to be stated that in literature different units are used for the same physical value. For example in data sheets of polymers the permeation coefficient of a gas is often given in the unit cm^3 (STP)$\cdot$ 100 $\mu m \cdot m^{-2} \cdot d^{-1} \cdot bar^{-1}$, where STP stands for standard temperature (273K) and pressure ($1.013 \cdot 10^5$ Pa). By using STP a certain volume of a gas corresponds to a defined mass.

The requirements of fruits and vegetables are often in a range that cannot be achieved by typically used polymers. In this case perforation is an option to increase the gas permeation. In packages with perforation the gas exchange through the package is the sum of gas diffusion through the perforation and the gas permeation through the polymeric film.

If there is no absolute pressure difference inside and outside the packaging the gas flux through the perforation is proportional to the diffusion coefficient D_{gas} in the air, the area of permeation A_h and the gas concentration difference outside and inside the packaging ($c_{o,gas}$-$c_{i,gas}$) and indirect proportional to the effective length of the pore l_h [8].

$$Q = \frac{D_{gas} \cdot A_h \cdot (c_{o,gas} - c_{i,gas})}{l_h} \quad (2)$$

The area of permeation is $A_h = N \cdot \pi \cdot r^2$, where N is the total number and r is the radius of perforation. The resistance against diffusion is non-proportional to the length of a pore. Also the ambience of the pore has a significant influence on the resistance against diffusion. Therefore, Fishman [8] has defined an effective length of a pore. In his model the effective length of a pore is the sum of film thickness l and the pore radius r: $l_h = l + r$.

1.3. Classification of test methods

The test methods for gas permeation measurement can be divided into three methods: total pressure methods, isostatic methods and the quasi-isostatic methods. Additionally, at some permeants like water vapour the transmission rate is measured gravimetrically [9].

A manometric and a volumetric method for measuring the gas permeability of flat films are specified in ASTM D 1434. The test gas is permeating through the sample from the high-pressure site to the low-pressure site and the pressure on the low-pressure site increases. In steady state, the pressure increases linearly with time. For long times, the temporal slope of pressure slows down since the driving pressure gradient decreases. As a pressure sensor is used, all gases can only be measured not specifically. The method can be applied only at 0% relative humidity.

The measurement via the isostatic method is similar to the above mentioned total pressure method. The difference is that only a partial pressure difference between both sides of the sample is maintained whereas the total pressure on both sides is the same. The partial pressure increases until a constant partial pressure of the permeating gas in the carrier gas signal is achieved. This partial pressure of permeating gas is proportional to the gas permeability. Electrochemical sensors are often used for oxygen detection [10,11], infrared sensors for carbon dioxide or water vapour detection [12] and electrolytic sensors for detection of water vapour [13].

The quasi-isostatic method is a modification of the isostatic method. E.g. aliquots of the permeant gas can be removed at predetermined time intervals for gas chromatography [14]. The optical permeation measurement [15], belongs to the quasi-isostatic methods. There are already a couple of publications describing this method: In principle, the oxygen permeation measurement with optical sensors is an ambient oxygen ingress rate method. This is well described by Larsen [17,18]. Optical oxygen measurement uses optical chemical sensors. The measuring principle is based on the effect of dynamic luminescence quenching of an activated state by molecular oxygen. The principle of quenching of fluorescent/luminescent materials was already described in 1919 [19]. In the 1990s first approaches for optical oxygen sensors were published [20,21] and first clinical applications were described [22]. The potential of oxygen permeation measurement based on optical chemical oxygen sensor dyes has been demonstrated on a laboratory scale by Rharbi et al. [23]. Several publications describe the application of optical chemical oxygen sensors for the permeation measurement at films [24–27], bottles closures [28], coffee capsules [29], bottles [30–32] or other forms of food packaging [33].

However, in few publications for few exemplary samples results for oxygen permeability of films derived from the optical method are compared with results from other methods [34–36]. It is the scope of this study to validate the optical method on a broader basis to establish a new standard method.

2. Material and methods

2.1. Materials

Following equipment and materials were used for the optical permeation measurement (see Table 1):

The measuring principle is described by Huber et al. [38,39]. The PSt3-type sensor spot has a limit of detection of 0.03% gaseous and 15 ppb dissolved oxygen. This system using a PSt6-type sensor spot has a limit of detection of 0.002% gaseous, 1 ppb dissolved oxygen and 3% accuracy of the respective concentration [38,39].

Table 1
Equipment and materials for the optical permeation measurement.

Component	Description	Vendor
Measuring cell	permeation measurement cell for optical oxygen permeation measurement	PreSens Precision Sensing GmbH, Regensburg, Germany
Calibration film	PET-BO Hostaphan® RN 100, thickness: 100 μm	Mitsubishi Polyester Films GmbH, Wiesbaden, Germany [37]
Film samples	various film samples from different projects of Fraunhofer IVV	–
Tissue paper	tissue paper 0.33 × 100 m, 24 g/m^2, diameter ≤9 cm	Hahnemühle FineArt Papier, Dassel, Germany
Vacuum grease	DOW CORNING® high vacuum grease	Dow Corning GmbH, Wiesbaden, Germany
Optical sensors for oxygen measurement	PSt3, PSt6	PreSens Precision Sensing GmbH, Regensburg, Germany
Measurement device	Fibox 4 trace	PreSens Precision Sensing GmbH, Regensburg, Germany