Optical Sensor Spots for Oxygen Permeation Testing

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Introduction

An oxygen permeation measurement device for food packaging applications has to have a measurement range from 10^{-1} to 10^{6} cm³(STP) m^{-2} d^{-1} bar^{-1} that is sufficient for the typical food applications. The values up to 1 cm³(STP) m^{-2} d^{-1} bar^{-1} are needed for long duration food and some fresh food products like cured meat. The high values up to 10^{6} cm³(STP) m^{-2} d^{-1} bar^{-1} are needed for fresh food like fresh cut fruits. However a measurement limit of 10^{-3} cm³(STP) m^{-2} d^{-1} bar^{-1} with a cost effective permeation measurement device would be a breakthrough for the development of LED displays, photovoltaic modules and vacuum insulating panels. The highest requirements come from OLED displays and organic solar cells with a measurement limit of 10^{-6} cm³(STP) m^{-2} d^{-1} bar^{-1}. However that measurement limits can only be achieved by high sophisticated, very expensive measuring systems that – in addition – can only be handled by experts.

Optical Oxygen Permeation Measurement

The test chamber (Figure 1) in which the test film is mounted consists of two metal parts of circular cross-section. The surface for the permeation measurement and the volume of measurement chamber may vary. The surface to volume ratio should be in the range of 0.5 cm^{-1} to 2 cm^{-1}. The temperature of the upper half of the chamber is measured using a thermometer. The lower half of the chamber is sealed against the mounted film with an O-Ring such that it presses the film against the flat edge of the lower half of the chamber, as close as possible to its inner edge.

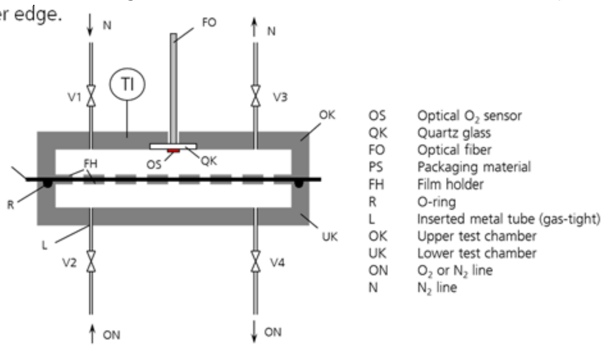

Figure 1: Schematic representation of the test chamber for testing films

The test involves two procedural steps. (1) After inserting the test specimen, the measurement system is first of all checked for tightness. To do this both sides of the test specimen are flushed with nitrogen. The valves are then closed. The oxygen increase in the upper test chamber is then recorded as the baseline (= zero value). (2) The side of the test specimen without the oxygen sensor is then flushed with oxygen or with air. The slope of the stationary increase in oxygen in the upper test chamber minus the slope of the baseline gives the permeability of the test specimen.

Evaluation

According to the ideal gas law, the following equation can be applied:

$$\dot{p}_{O_2} \cdot V_{test\ cell} = p_{std} \cdot \dot{V}_{O_2}(STP) = \dot{n}_{O_2} \cdot R \cdot T_{std}$$

When the measurement is carried out at 296K (= 23°C), instead of the standard temperature 273K (= 0°C), the permeability Q can be calculated using the following equation:

$$Q = \frac{\dot{p}_{O_2} \cdot V_{test\ cell}}{p_{std} \cdot A \cdot \Delta p_{O_2}} \cdot \frac{T_{std}}{T_{meas}}$$

Symbol	Explanation	Units
$\dot{p}_{O_2}$	Increase in oxygen partial pressure in the upper test chamber (UTC)	hPa · d^{-1}
$V_{test\ cell}$	Volume of the UTC	cm³
p_{std}	Standard pressure	1013 hPa
$\dot{V}_{O_2}(STP)$	Oxygen volume flow into the UTC under standard conditions	cm³(STP) · d^{-1}
$\dot{n}_{O_2}$	Molar mass flow into the UTC	mol · d^{-1}
R	Gas constant	8.314 J · mol^{-1} · K^{-1}
T_{std}	Standard temperature	273 K
T_{meas}	Measurement temperature	K
Q	Oxygen Transmission rate	cm³ · m^{-2} · d^{-1} · bar^{-1}
Δp_{O_2}	Difference in oxygen partial pressure between lower and upper chamber	bar

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Results and Discussion

PST6 and TAF12 sensor types

Especially, for high barrier permeation measurements, an oxygen sensor with an improved limit of detection was developed. To achieve this, different polymers with high oxygen permeation rate and several oxygen indicator dyes were tested. Sensor membrane TAF12 was the most promising sensor, resulting in a limit of detection of 0.5 ppm and a dynamic range from 0 to 1000 ppm gaseous oxygen. The technical data are shown in Table 1.

Table 1: Technical data of the new TAF12 type sensor spot in comparison to the standard PST6 type sensor spot

	PSt6 (standard)	TAF12 (new)
Dynamic range [ppm]	0 – 42000	0 – 1000
Resolution [ppm]	20 ± 7 200 ± 9 2000 ± 15 20000 ± 900	10 ± 0.5 100 ± 0.8 200 ± 1.5
Detection limit [ppm]	25	0.5

Oxygen Transmission Rate

Figure 2 shows measurement data for the example of a 100 µm PET film. Two regions can clearly be seen: the zero value measurement region and the actual permeation measurement using oxygen as the test gas.

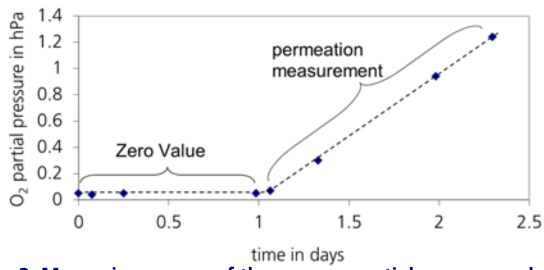

Figure 2: Measuring course of the oxygen partial pressure, when measuring the oxygen permeation through a 100 µm PET film (HOSTAPHAN ® RN 100)

The 100 µm PET film HOSTAPHAN® RN 100 is the calibration film used for reference measurement. The oxygen transmission rate of this film is well known from over hundred single measurements an is in a range of 12.26 to 14.10 cm³(STP)m^{-2} d^{-1} bar^{-1} at 23°C. All measured oxygen transmission rates with overall 15 measurement cells were in this range. Besides the cost efficiency the benefit of the optical permeation measurement is the possibility to measure barrier films as well as perforated and high permeable films. This is not possible with carrier gas permeation methods. The highest measured permeability of a film was $2 \cdot 10^{7}$ cm³(STP)m^{-2} d^{-1} bar^{-1} for a 30 µm PE film filled with $CaCO_3$.
The lowest measured oxygen permeation value was 0.01 cm³(STP)m^{-2} d^{-1} bar^{-1} for a film with the layer composition PETmet/ PETmet/ PETmet/PE-LD with a thickness of 12µm+12µm+12µm+50µm = 86 µm. These types of films are typically used for encapsulation of vacuum insulation panels.

References

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[2] Christian Huber, Sven Sängerlaub; Kajetan Müller, New Permeation Measurement Device using Optical Sensor Spots, 25th IAPRI Symposium on Packaging, 16.-18. May 2011, Berlin, Germany.

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