PERMEABILITY MEASUREMENT

I. INTRODUCTION

A permeability measurement consists in measuring the flow of gas or vapor through a film or a package. Low permeability values are of great interest for lifetime of numerous products in alimentation, pharmaceutical industry or electronic devices (OLED,…).

II. PERMEABILITY MEASUREMENT

II.1. Principle

Most of apparatus get a cell with the sample to test separating the cell in 2 parts : in one part the test gas is circulating ; in the other part the molecules which cross the material are quantified by a sensor.

II.2. Apparatus

At Coating Plasma Industrie we have 2 apparatus :

- a Mocon OxTran 2.61 to measure the oxygen flow through polymer films (Figure 1).
- a Systech 7001 to measure the water vapor flow through polymer films (Figure 4).

Figure 1 : Mocon OxTran 2.61 (oxygen permeability measurement)

The sensor of the 2 apparatus is an electrolytic sensor which allows high precision measurements and good reproducibility. This kind of sensors produces a current which the intensity is proportional to the quantity of molecules detected. Each sensor is specific to a molecule.

These 2 apparatus are designed to the measurement of polymer films but with some modifications of the measurement cells, it is also possible to measure a complete 3D package like bottle, tray, bag,… (Figure 2 and Figure 4).

The results are given when the equilibrium is reached. This means that several measurements are maid and when the value becomes stable, the last one is considered as the right value.

➔ **MOCON OX-TRAN 2/60 Oxygen permeameter**

- Measurement range : 0.5 $cm^3/m^2/24h$ – 1000 $cm^3/m^2/24h$ with 10 cm^2 ; 0.05 $cm^3/m^2/24h$ with 100 cm^2
- Controlled temperature range : Ambiant to 65°C
- Humidity control : films 35 à 90%, package dry or ambiant
- Number of test cells : 1 to 6
- Tested area : 10 cm^2. A specific module allows measurement on 100 cm^2 for barrier film (Figure 3)
- Sensibility : 0.01 $cm^3/m^2/24h$ on the 6 cells
- Repeatability : +/- 0.5 cm^3/m^2 on 1 cell
- Samples : Films, packages, plastic bottles,...
- Conforms to : ASTM D-3985, ASTM F-1927, ASTM F1307, ISO 15105-2, DIN 53380

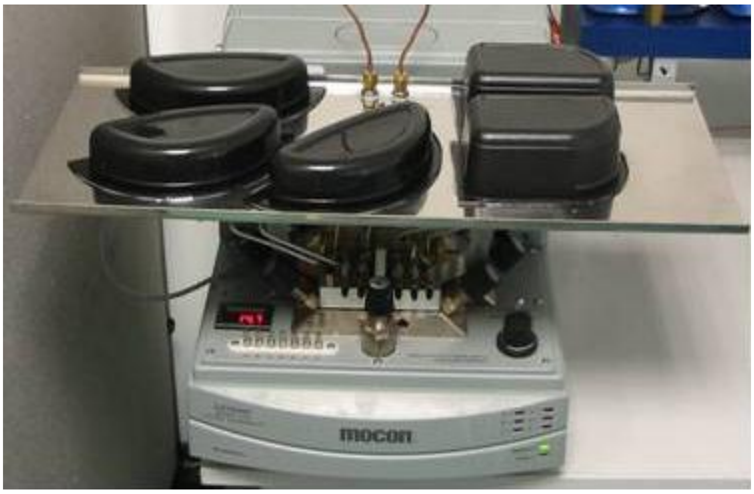

Figure 2 : Package measurement device

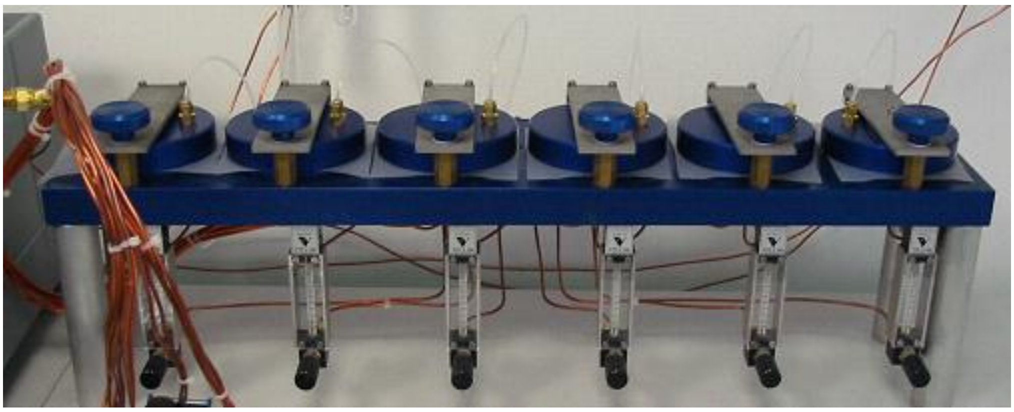

Figure 3 : Weak permeability film device

Figure 4 : Systech 7001 Water permeability measurement

➔ **SYSTECH 7001 Water Vapour permeameter**

- Measurement range : 0.002 - 7 g/m^2/24h
- Humidity control : 20 to 95%
- Controlled temperature range : 5 à 50°C
- Number of test cells : 2
- Tested area : 50 cm^2
- Sensor P_2O_5
- Thickness of samples : <1.2 mm
- Tested samples : Films, packages
- Conforms to : ASTM F-1249, ISO 15106-3, ISO15105-2, DIN53122-2

III. THEORY OFGAZEOUS TRANSPORT IN POLYMERS

A dissolution-diffusion mechanism is generally considered to describe a gas passing through a polymer.

- Gas absorption at the above surface,
- Dissolution and molecular diffusion of gases molecules inside the material
- Desorption of gas at the downstream surface

Most of the time the dissolution-diffusion step is the slowest step and so the determine the kinetic. It is considered that there is an equilibrium state at the both interfaces of film. So the gqs permeation process depends of solubilization, diffusion and concentration gradient of gas in the material.

III.1. Permeability definition

III.1.a Définitions

The polymer ability to transport a gas is describes by the permeability coefficient Pe :

$$Pe = D \cdot S = \frac{Qty_{gas} \times Thickness_{film}}{Area_{film} \times Time \times \Delta P_{gas}^{upstream/downstream}}$$

Pe unit is mol.m^{-1}.s^{-1}.Pa^{-1} in USI, however depending on applications lot of common units are also used. Pe is an intrinsic characteristic of the couple polymer/gas. Pe is independent of thickness and ΔP.

The diffusion coefficient D ($m^2.s^{-1}$) is the kinetic parameter of the global transport. It describe the gas mobility in the material and mainly depends on the molecule size, on the mobility of polymer chain fragments and on the polymer free volume.
The solubility coefficient S
The solubility coefficient S ($mol.m^{-3}.Pa^{-1}$) is the thermodynamic part of the global transport. It represents the amount of gas molecules dissolved in the material in equilibrium conditions. It is related to the gas/polymer interactions and to the polymer free volume.
An Arrhenius law describes the behavior of Pe with temperature :

$$Pe = P_0 \cdot \exp\left(-E_P / RT\right)$$

avec $P_0 = D_0.S_0$ ($mol.m^{-1}.s^{-1}.Pa^{-1}$)
E_p : activation energy ($J.mol^{-1}$)

Several quantities are also used in literature instead of permeability coefficient :

➔ **Permeation rate** : ΔP is not expressed (because ΔP=1)

$$Permeation\_rate = \frac{Quantity_{Gas} \times Thickness_{film}}{Area \times Time}$$

➔ **Permeance** : The thickness is not considered .

$$Permeance = \frac{Quantity_{Gas}}{Area \times Time \times \Delta P_{Gas}}$$

➔ **Gas flow :** when oxygen is mesured the flow is OTR (Oxygen Transmission Rate)

$$TR = \frac{Quantity_{Gas}}{Area \times Time}$$

III.2. Solubilization phenomenon

Solubilization is the therm used to describe the penetration and the dispersion of gas molecules in a polymer matrix. Several solubilization modes are distinguished depending on experimental conditions (temperature, pressure) and on material nature. The Henry mode and Double-sorption mode are the most common dissolution modes.

i. Henry dissolution

This model is defined by the Henry equation which described a linear isotherm:

$$C_D = K_D \cdot P$$

with C_D : dissolved molecule concentration in the polymer ($mol.m^{-3}$)
K_D : Henry constant de ($mol.m^{-3}.Pa^{-1}$)
P : upstream pressure (Pa)

The solubility coefficient is independent with the pressure and defined by a constant :

$$S = K_D$$

ii. Double-sorption model

The gas dissolution isotherm is described by the sum of 2 sorption modes : the Henry dissolution and the dissolution in microvoid following a Langmuir isotherm :

$$C = C_D + C_H P$$

The solubility coefficient is dependent of the pressure:

$$S(P) = \left(K_D + C'_H \cdot \frac{b}{1+b}\right)$$

with C'_H : microvoid saturating concentration ($mol.m^{-3}$)
b : microvoid affinity constant

The main parameters influencing the solubilization are:
- The gas molecule size
- The gas condensability
- The cohesion energy density of gas/polymer system

III.3.Diffusion phenomenon

Three transport types are distinguished :

i. "Fickian" Transport

The fickian diffusion occurs when the gas diffusion time is largely greater than the relaxation time of gas/polymer system. The 2 Fick laws describes this diffusion process :

$$J = -D \cdot \left(\frac{\partial C}{\partial x}\right) \text{ and } \qquad \frac{\partial C}{\partial t} = D \cdot \left(\frac{\partial^2 C}{\partial^2 t}\right)$$

with J : specific flow of gas through the polymer film ($mol.m^{-2}.s^{-1}$)
D : permeant diffusion coefficient ($m^2.s^{-1}$) (could depend on concentration)
C : gas concentration in the polymer in a position x and at a time t ($mol.m^{-3}$)

ii. "Non fickian" transport and anormal diffusion

These transports occur when the diffusion time is comparable to the relaxation time, anormal diffusion, and when the diffusion time is greater than the relaxation time, non-fickian transport. In these cases the diffusion coefficient variation with time can be described by the following equation :

$$\frac{\partial D(C,t)}{\partial t} = \frac{\partial D}{\partial C} \cdot \frac{\partial C}{\partial t} + \alpha' \cdot (D_e - D)$$

with D_e : diffusion coefficient at equilibrium when the polymer matrix is totally relaxed ($m^2.s^{-1}$)
α' : relaxation speed coefficient (s^{-1})

The main parameters influencing the diffusion are:
- The gas molecule size
- The gas plasticizing effect
- The gas concentration
- The glass transition temperature of the polymer Tg
- The polymer reticulation and cristallinity
- The add of plasticizing agent and the relative humidity

IV. EXEMPLE : OXYGEN PERMEABILITY MEASUREMENT OF PET FILMS

IV.1. Permeability measurement of PET

PET films with various thicknesses where measured in the same conditions. The results are shown in Table 1.

Sample	OTR	Permeability	Permeation rate	Permeance
	cm^3(STP)/ (m^2.24h)	cm^3(STP).cm/ (m^2. 24h.mmHg)	cm^3(STP).cm/ (m^2. 24h)	cm^3(STP)/ (m^2. 24h.mmHg)
PET 100 µm	11.35	1.13E-01	1.54E-04	1.54E-02
PET 23 µm	55.84	1.28E-01	1.75E-04	7.59E-02
PET 12 µm	104.95	1.26E-01	1.71E-04	1.43E-01

Table 1 : Permeability of PET films with various thicknesses

IV.2. Permeability and temperature

As said before the polymer permeability varies with temperature following an Arrhenius law. On Figure 5, the evolution of oxygen transmission rate with the temperature is shown for 23 µm PET film.

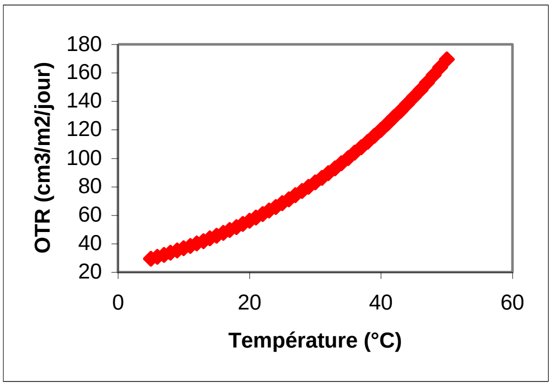

Figure 5 : Variation of a 23µm PET film permeability with temperature

V. CONCLUSIONS

The transmission rate of gases through a polymer is a critical parameter for the lifetime of numerous products in alimentation, pharmaceutical industry or electronic devices. Permeability is the quantity which characterizes the ability of a material to retain or not a gas or a vapor. Its knowledge allows selecting the most competitive materials to the required performances. The measurement is usually performed on flat films but with adaptation of the test cell it is also possible to measure the final package.

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