

# GAS BARRIER PROPERTIES OF POLYMERIC FILMS WITH HYBRID ORGANIC/INORGANIC COATINGS FOR FOOD PACKAGING APPLICATIONS

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## Abstract

The permeability and diffusivity of oxygen in films of PET coated with a thin layer of a hybrid organic/inorganic (ceramer) material have been determined at 65°C. The permeability data are collected using a closed-volume permeation apparatus and the diffusivity has been calculated with the time-lag method. The addition of coating dramatically improves the oxygen barrier properties of the substrate, the apparent permeability of the multilayer film being up to 3 orders of magnitude lower than that of pure PET. The pure coating properties are opportunely calculated by taking into account the effect of the different diffusion resistances in the various layers. The effect of ageing has also been investigated, by comparing the oxygen permeability before and after immersion in water of the films that are suspected to be degraded by water.

**Keywords:** ceramers, hybrid organic/inorganic materials, nanocomposite, barrier properties.

## Introduction

In the last few years a new class of materials with nanophasic morphology, the ceramers, has been proposed and developed because of its peculiar and interesting features.

Ceramers are hybrid materials composed of organic and inorganic moieties, the inorganic fraction being generally based on silica. The peculiar properties of this kind of organic/inorganic hybrids result from the synergism between the properties of the polymer composing the organic phase, such as tenacity, flexibility, transparency, processability, low cost and good adhesion to substrates, and those of the inorganic component, mainly toughness, flame retardancy, chemical and thermal stability, gas barrier effect. With respect to conventional composite and nanocomposite materials, ceramers are characterized by a stronger network of the two components that are interconnected on a nanometric scale.

It is the main objective of this work to focus on the oxygen barrier properties, that are extremely important in food packaging industry because they affect the shelf life of packaged foods. [1-3].

## Materials and Methods

The samples tested in this work were multilayer films in which a thin layer of ceramer is coated on a common food packaging material as PET. The organic-inorganic hybrid coating was prepared through sol-gel methodology and dip-coated on the substrate in order to have 1  $\mu\text{m}$  of coating on both sides. The coating shows good homogeneity and adhesion to the substrate as well as enough transparency.

Oxygen permeability in the films was investigated by using a closed-volume manometric apparatus, especially designed to characterize ultra barrier films (Fig.1) [4]. A constant pressure difference is maintained across the sides of the sample and the amount of mass permeated is calculated measuring the pressure increase in a closed volume of known dimensions at constant temperature. The value of the Oxygen Transfer Rate,  $O.T.R.$ , which is defined in terms of the steady state gas flux,  $J_{SS}$ , and the pressure difference,  $\Delta p$ , is then calculated from the experimental data as:

$$O.T.R. \stackrel{DEF}{=} \frac{J_{SS}}{\Delta p} = \left( \frac{dp_d}{dt} \right)_{t \rightarrow \infty} \cdot \frac{V}{R \cdot T \cdot A} \cdot \frac{1}{\Delta p} \quad \text{Eq. 1}$$

where  $A$  is the area of the sample,  $V$  is the downstream volume,  $R$  is the universal gas constant, and  $p_d$  is the downstream pressure. The O.T.R. value in this work is expressed in  $\text{cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{d} \cdot \text{atm})$ .

The characteristic time of the diffusion process can be evaluated using the time lag value ( $\tau_L$ ), that is the intercept on the  $t$  axis of the  $p_d$  vs.  $t$  curve after steady state, represented by a constant value of the slope, has been reached (as shown in fig. 2). If  $p_d$  is negligible compared to the upstream pressure, as it is the case of our experiments, and the film is initially gas-free, the time lag value ( $\tau_L$ ) is related to the diffusivity,  $D$ , of the gas in the material, through the following equation [5]:

$$\tau_L = \frac{l^2}{6 \cdot D} \quad \text{Eq. 2}$$

where  $l$  is the sample thickness.

The small size of the downstream volume and the high resolution of the manometer (full scale value 10 mbar, accuracy equal to 0.15% of the reading) allows for a high sensitivity of the apparatus.

The experiments on the multilayer films were carried out only at 65°C because, at room temperature, the flux was too small to be detected in reasonable time; the upstream pressure was maintained at about 4 bar while the downstream side was initially evacuated to less than  $10^{-2}$  mbar with a vacuum pump.

In order to estimate the permeability of each layer of the composite sample the series resistance formula was used:

$$\frac{l_{TOT}}{P_{TOT}} = \sum_i \frac{l_i}{P_i} \quad \text{Eq. 3}$$

where  $l_i$  and  $P_i$  are the thickness and the permeability of layer  $i$ . The permeability  $P_i$  can be defined through the following relationship and the first part of Eq. 1:

$$P_i \equiv O.T.R._i \cdot l_i \quad \text{Eq. 4}$$

One can also evaluate the kinetics of the diffusion of each layer, with the following formula that is derived in the limit of infinite times using the appropriate boundary and initial conditions and Laplace's transform [6-7]:

$$\tau_{12} = \frac{\frac{l_1^2}{D_1} \left( \frac{3l_1}{4D_1S_1} + \frac{l_2}{2D_2S_2} \right) + \frac{l_2^2}{D_2} \left( \frac{l_1}{D_1S_1} + \frac{l_2}{6D_2S_2} \right) + \frac{S_2 l_1^2 l_2}{(D_1 S_1)^2}}{\frac{2l_1}{D_1 S_1} + \frac{l_1}{D_2 S_2}} \quad \text{Eq. 5}$$

where  $\tau_{12}$  is the time lag for the multilayer permeation test, and  $S_i$  is the gas solubility in each layer  $i$ , that is related to diffusivity and permeability by:

$$P_i = D_i \cdot S_i \quad \text{Eq. 6}$$

It must be noticed that, when evaluated for multilayer materials, the values of  $P$  and  $D$  obtained from equations 4 and 2, as well as the solubility coefficient evaluated from equation 6, are not material properties, but rather effective quantities depending also on the sample geometry.

## Results

In Table 1, the oxygen transport properties in the materials studied are reported, in terms of oxygen transfer rate, time lag, permeability and diffusivity, at 65°C. The data presented are the average values obtained from at least two permeation experiments, and the permeability of the hybrid coating has been calculated with eq.(3): the error bar on  $P_c$  represents the effect of a  $\pm 0.1 \mu\text{m}$  uncertainty on the value of the coating thickness.

As one can see, the permeance of PET is reduced by more than 2 orders of magnitude after addition of the hybrid coating, from 18.3 to 0.12  $\text{cm}^3(\text{STP})/(\text{cm}^2 \text{ d atm})$ . Also the permeation kinetics is considerably slowed down by the coating, the time-lag value of the coated material being almost 500 times higher than that of pure PET at 65°C. The effective permeability of the multilayer material is less than 1/100 of that of pure PET: from Eq. 3 the permeability of the hybrid coating can be evaluated, leading to a value that is 3 orders of magnitude lower than that of pure PET ( $4 \times 10^{-5}$  vs. 0.1 Barrer). The effective diffusivity of the multilayer material, calculated with Eq. 2, is equal to  $5.2 \times 10^{-11} \text{ cm}^2/\text{s}$ , while that of pure PET is  $2.3 \times 10^{-8} \text{ cm}^2/\text{s}$ .

Due to the hydrophilic nature of the organic phase composing the hybrid coating, exposure to humidity or water can degrade the material and/or modify its properties: the effect of ageing on the gas transport properties was therefore studied, by comparing the transport properties of the samples “as received” and those of samples “aged” through immersion in liquid water and saturated water vapour for 4 days. The data for the treated materials are also listed in Table 1: the oxygen permeability increases with respect to untreated samples after immersion in liquid water, but not dramatically. The permeability also increases after exposure to water vapor, but to a lower extent than in the case of liquid. The effective diffusivity, which could be evaluated only for the sample treated in liquid water, also shows an increased value with respect to the untreated material, but is still ten times lower than that of pure PET. The results show that, as it could be expected, the materials loose part of their barrier capacity after treatment in water, in particular when they are kept in liquid water. However, the transport behaviour, especially if evaluated in terms of permeability, is still excellent for packaging applications: the satisfactory stability of the hybrid coating with respect to water is believed to be due to presence of the inorganic phase that hinders the mobility of the hydrophilic polymeric chains.

## Acknowledgements

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## References

1. Schottner, Gerhard (2001), "Hybrid Sol-Gel-Derived Polymers: Applications of Multifunctional Materials", *Chem Mater.* 2001, 13, pp. 3422-3435.
2. Wen J. and Wilkes G. L. (1996), "Organic/Inorganic Hybrid Network Materials by the Sol-Gel Approach" *Chem. Mater.*, 8, 1667-1681
3. Messori M., Toselli M., Pilati F., Fabbri E., Fabbri P., Pasquali L. and Nannarone S. (2004), "Prevention of plasticizer leaching from PVC medical devices by using organic-inorganic hybrid coatings", *Polymer* 45, 805–813.
4. Pizzi Diego, De Angelis M. Grazia, Doghieri Ferruccio, Giacinti Baschetti Marco, Sarti G. Cesare (2005), *Chemical Engineering Transactions*, AIDIC, S. Pierucci Ed. 6, pp. 515-520.
5. Crank J.(1956), "The mathematics of diffusion", Oxford at the Clarendon press.
6. Barrie J.A., Levine J.D., Michaels A.S. and Wong P. (1963), "Diffusion and solution of gases in composite rubber membranes", *Trans. Faraday Soc. Trans*, 59, pp 869.
7. Jaeger J.C. (1955), "Conduction of heat in a solid in contact with a thin layer of a good conductor", *Quart. J. Appl. Math.* 8, 1, pp101-106

**Table 1:** Transport properties of pure O<sub>2</sub> at 65°C

65°C	O. T.R.×10 <sup>3</sup> [cm <sup>3</sup> (STP)/(cm <sup>2</sup> d atm)]	Permeability ×10 <sup>3</sup> (Barrer <sup>a</sup> )	Diffusivity ×10 <sup>9</sup> (cm <sup>2</sup> /s)	Time Lag (s)
PET (36 μm)	18.3	100	23	95
PET+ hybrid coating (38 μm)	0.12	0.7	0.052	4.6 E+04
Hybrid coating (2 μm)	-	0.04±0.005	0.0003 ±0.00005	-
PET+ hybrid coating (treated in liquid water for 4 days at 65°C)	0.83	4.82	0.2	1.2 E+03
PET+ hybrid coating (treated in water vapor for 4 days at 25°C)	0.77	4.46	-	-

<sup>a</sup> 1 Barrer= 10<sup>-10</sup> (cm<sup>3</sup>(STP)·cm)/(cm<sup>2</sup>·s·cm Hg)

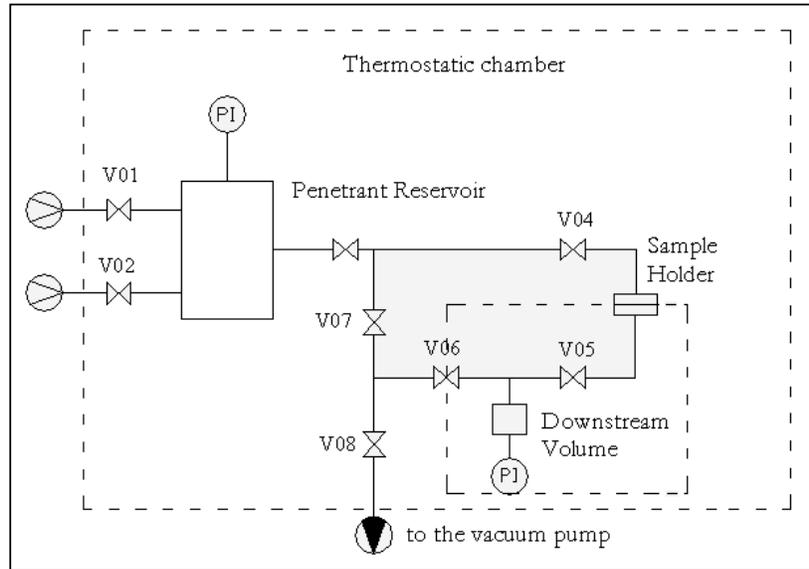


Fig. 1: Closed volume permeometer

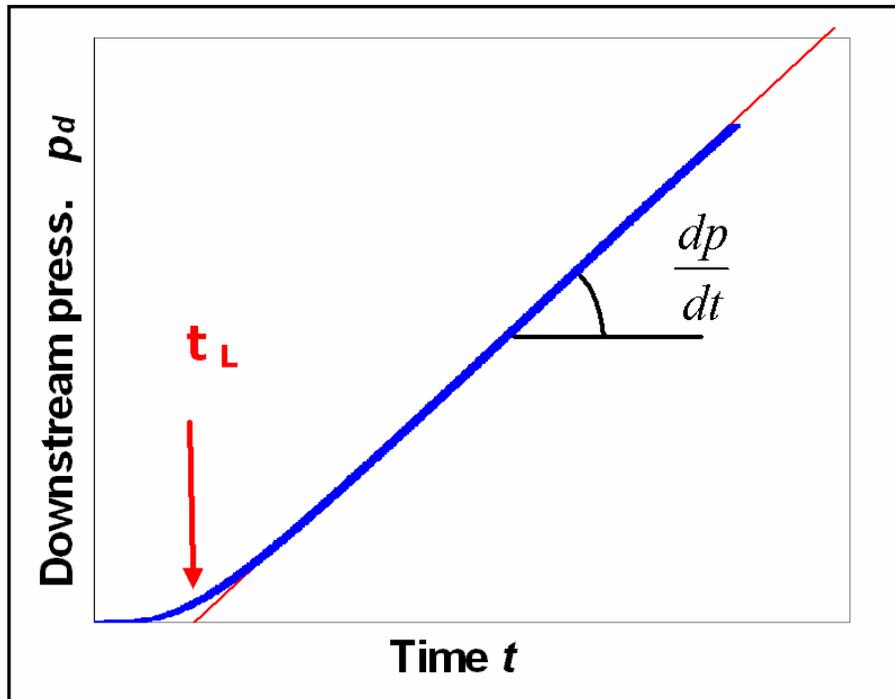


Fig. 2: Output plot, pressure  $p_d$  vs. time