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A shortcut method for faster determination of permeability coefficient from time lag experiments

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Time lag permeation experiments are a well-known method for the determination of permeability and diffusion coefficients of gases in polymer films. In these experiments pressurized gas is brought in contact with one side of the film and the amount of gas evolving from the opposite, low pressure, side of the film is measured as a function of time. The permeability coefficient is obtained from the steady-state permeation flux and the diffusion coefficient is obtained from the permeation flux versus time behavior through an extrapolation method [1]. The time required to reach steady-state permeation is of the order of several hours or less for most polymers, but can be of the order of weeks or even months for films prepared from low-permeability barrier polymers. In terms of a dimensionless time – Fourier number (*Fo*) – steady state permeation is attained at $Fo \simeq 1.0$. In this paper, a novel method is described for the early determination of the permeability coefficient, which yields good estimates at 1/10th the time it normally takes with the conventional time lag methods. This new shortcut method is based upon (i) using a known, but little-used, short-time approximation of the diffusivity of the membrane, following the work of Rogers [2], and (ii) using an upstream flux or an averaged flux calculated from both upstream and downstream pressure measurements.

The Rogers short-time approximation allows manipulating the early pressure response in the outflow volume, $p(l,t)$, to the following form [3]:

$$\ln\left[\frac{p(l,t)}{\sqrt{t}}\right] = \ln\left[\frac{4p_0 SRTA\sqrt{D}}{V\sqrt{\pi}}\right] - \frac{l^2}{4D}\frac{1}{t} \qquad (1)$$

where A and l are the area and thickness of the membrane, p_0 is the upstream pressure, V is the volume of the outflow receiver, T is the temperature, and R is the gas constant. If the plot of $\ln\left(p(l,t)/\sqrt{t}\right)$ versus t^{-1} yields a straight line, the diffusivity (D) can be evaluated from the slope, while the solubility (S) from the intercept; in turn, the permeability, $P = D \times S$. The diffusivity evaluated from the Rogers approximation is in good agreement with the diffusivity determined from the classical time lag method. On the other hand, the solubility estimated from the intercept may greatly differ from the solubility determined from the classical time lag method. This is because the intercept in the Rogers approximation is the natural logarithm of a term which contains S. Thus, even small variations in the slope, which are inconsequential for the estimation of D, will magnify exponentially the error in S [3].

In the new shortcut method, the membrane diffusivity estimated from Eq. (1), is used to manipulate the transient flux (J) into the steady state flux (J_∞). In turn, the latter is used to calculate P. While J_∞ can be estimated from the gas flux entering the membrane (J_{in}), or the gas leaving the membrane (J_{out}), the former can be monitored immediately after initiation of the gas permeation experiment. On the other hand, until $Fo \simeq 0.06$, the gas does not emerge from the membrane downstream. Moreover, when the gas starts emerging from the membrane, J_{out} is relatively small, making its accurate monitoring difficult. Fig. 1 illustrates the application of the new method for the early determination of the membrane permeability based on J_{AVG}, the arithmetic average of J_{in} and J_{out}, which at $Fo < 0.06$ is essentially equal to 0.5 J_{in}. It is evident

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that right after initiation of the gas permeation experiment, the corrected permeability values are randomly distributed around the average permeability. Consequently, the average permeability could be evaluated from a time frame much shorter than the one in Fig. 1. However, the time frame up to *Fo* = 0.1 is required to collect the downstream pressure data for estimation of *D* from Eq.(1). It is important to emphasize that at *Fo* = 0.1 gas permeation is still at a highly transient state.

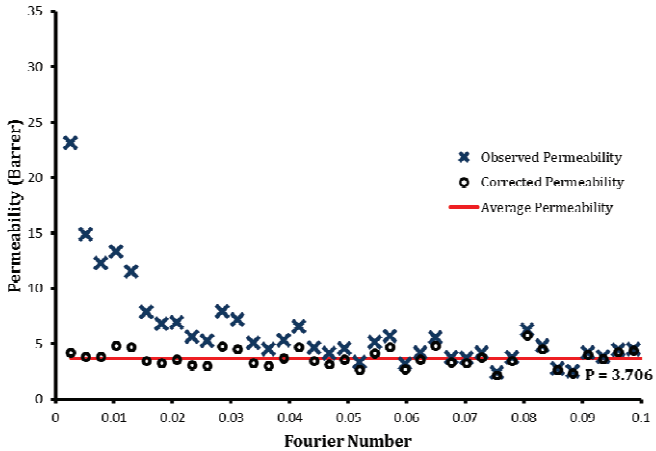

Figure 1. Plot revealing the method behind estimating the permeability in the new short-cut method. Gas permeation experiment was performed using nitrogen and a polyphenyelene oxide (PPO) membrane. The observed permeability values are determined from the experimental average flux (J_{AVG}) data, while the corrected permeability values are determined from the steady state flux (J_{∞}) obtained by correcting J_{AVG} using the Fourier number-dependent correction factors. The average permeability of 3.706 Barrer, which is denoted by a horizontal line, is obtained from the arithmetic average of the corrected permeability values for Fo < 0.1.

The new method presented in this paper is enabled by the accurate monitoring of the pressure decay at the upstream side of the membrane. This is accomplished by using the concept of a two-tank volume [4]. Essentially, the upstream part of the system consists of two volumes, the working volume and the reference volume, which can be separated by a valve. Using a high precision differential pressure transducer allows very accurate monitoring of the pressure decay in the working volume (and hence J_{in}) by comparing the pressure in the working volume connected to the membrane, with the constant pressure in the reference volume.

In this presentation, the details of the new short-cut method will be discussed. A special emphasis will be given to new opportunities in membrane characterization enabled by accurate monitoring of the pressure decay upstream from the membrane. The challenges associated with the new testing system will alos be discussed.

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