Alternative Method for Determining O_2 and CO_2 Transmission Rates Through Microperforated Films for Modified Atmosphere Packs

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Most experimental systems for measuring the permeability of microperforated polymeric films are static, mainly because in dynamic systems the small differences in pressure on both sides of the perforation may result in serious errors in the measurements. The O_2 and CO_2 transmission rate through microperforations of different sizes (from 40×30 to $350 \times 110\,\mu m$) were determined in a static and in a dynamic system. In the latter case, rather than the diffusive flow, the hydrodynamic flow generated by the difference in pressure was measured (between 5 and 90 mbar). This was determined by applying Bernouilli's theorem and an experimental equation potentially relating the area of the microperforation with the transmission rate. A comparison of the transmission rates obtained in both cases gives coefficients of determination close to one (>0.993). This means that measuring the hydrodynamic flow can be considered as an alternative for the quantification of the diffusive flow through a microperforation. This is a simple and quick methodology that does not require expensive equipment. Furthermore, this feature enables commercial leak detection equipment to be used to quantify diffusive transmission rates through microperforations. Copyright © 2012 John Wiley & Sons, Ltd.

KEY WORDS: microperforations; permeability; transmission rate; gas exchange; modified atmosphere packaging

INTRODUCTION

Microperforated films (perforation diameter $<200\,\mu m$) are an option for achieving the appropriate gaseous composition in modified atmosphere packaging of high respiration fresh food products, for example, minimally processed fruits and vegetables. They are an alternative for overcoming the limitations of conventional polymeric films. Given that the diffusion of O_2 and CO_2 through air is 8.5 and 1.5 million times greater, respectively, than through low-density polyethylene films, the perforations allow a much higher exchange of gases.[1] This difference in gas diffusion means that the gas exchange of a container occurs almost entirely through the microperforations in relatively impermeable films.

The ratio of the permeability for CO_2 and O_2, P_{CO2}/P_{O2}, in conventional polymeric films is usually between 3 and 6.[2–4] Moreover, in the new biobased polymers, the permselectivity value is higher, approximately 30.[5] Bearing in mind that the respiration coefficient of the packaged product can fluctuate between 0.7 and 1.3 [6] if there is no temperature abuse, a relatively high concentration of CO_2 is not reached in containers with nonperforated films. In microperforated films, the ratio P_{CO2}/P_{O2} is close to 1 [7] so that atmospheres with elevated CO_2 concentrations can be achieved without the quantity of O_2 in the package dropping rapidly towards detrimental anaerobic conditions.

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The design of microperforated polymeric films for modified atmosphere packaging involves predicting the permeability necessary for the gases exchanged and how to achieve this depending on factors such as the storage temperature, the type of polymeric material used, the number and size of the holes and the composition of the packaging atmosphere.[8–11] Even the movement of air caused by cooling fans can affect the exchange in this type of material.[12] Unlike conventional films for which permeability can be measured with a diffusion cell following one of the standard dynamic analysis methods (e.g. ASTMD 3985 for O_2 and ASTMD 1343 for CO_2), most experimental systems for measuring the permeability of perforated or microperforated plastics are static because in these cases the flow through the perforation only obeys diffusive mechanisms.[13–15] Ghosh and Anantheswaran [16] described a flow-through method for measuring permeability, with adequate control of the pressure at both sides of the microperforation. Nevertheless, dynamic methods are of doubtful application because of the gas convection that takes place when the pressures between the two cells are even just slightly unbalanced.[17]

In a previous work,[18] we derived an empirical equation that could potentially relate the area of a microperforation with the transmission rate of oxygen and carbon dioxide from experimental data obtained with a static measuring system. The gas exchange through microperforated films that this equation predicts was verified experimentally with packages containing minimally processed products.[19]

This work proposes an alternative way to estimate the transmission rate of the microperforations. This involves using a dynamic system, not to measure the diffusive flow through the microperforation, but rather the hydrodynamic flow caused by the differences in pressure at both sides of the perforation. The equivalent area of the microperforations is determined from the hydrodynamic flow. This area is related to the diffusive flow, which governs the gas exchange in microperforated films. The transmission rates obtained in static and dynamic systems have been compared to validate the methodology.

MATERIALS AND METHODS

Microperforated film

The Amcor P-Plus films used have a polymeric matrix made up of one layer of low-density polyethylene and another of polyester and microperforations of different sizes (Amcor Flexibles, Ledbury, UK).

An optical microscope (Zeiss, Thornwood, NY, USA) equipped with a calibrated ocular micrometer was used to determine the microperforation size. Many microperforations have an elliptical shape, and therefore readings were taken of the major and minor axis defining the area of the ellipse. The perforation sizes fluctuated from $40 \times 30\,\mu m$ for the smallest to $350 \times 110\,\mu m$ for the largest. The thickness of the film, L, was determined as the average of five measurements of the areas immediately adjoining the perforation taken with a Mitutoyo (Kawasaki, Japan) gauge. The films used have a thickness of between 29 and $37\,\mu m$.

Dynamic measurement system

The design of the apparatus is based on the standard test method for the oxygen gas transmission rate through plastic film and sheeting, ASTM D3985-95. The most relevant components of the equipment are shown in Figure 1a and are the following: a diffusion cell consisting of two metal halves with the test film mounted between the two components; an adjustable temperature chamber (Sanyo MIR-153; Sanyo Electric Co. Ltd, Osaka, Japan) where the diffusion cell is placed which allows the temperature to be maintained with a fluctuation of $\pm 0.2\,°C$ between $-30\,°C$ and $50\,°C$; gas streams consisting of a nitrogen current circulating in the lower half of the diffusion cell and a gas current of O_2 or CO_2, whose permeability will be determined, flowing through the upper half; mass flowmeter controllers (Brooks Instrument model 5850 TR, Hatfield, PA, USA), which have a range between 0 and $100\,ml\,min^{-1}$ and an accuracy of $\pm 1\%$ full scale; and O_2 and CO_2 analyzers. The gas that passes through the microperforation into the nitrogen carrier gas is transported to Strathkelvin 1302 microcathode oxygen electrodes attached to a Strathkelvin 928 dissolved oxygen measuring system (Strathkelvin Instruments, Glasgow, UK) connected to a computer by a 928 six-channel interface to measure the O_2 concentration. The CO_2 is analyzed by an infrared probe, Testo model 0632 1240, with a range from 0 to $10\,000\,ppm$ and an accuracy of $\pm 50\,ppm$, connected to a data logger Testo 950 (Instrumentos Testo S.A, Barcelona, Spain).
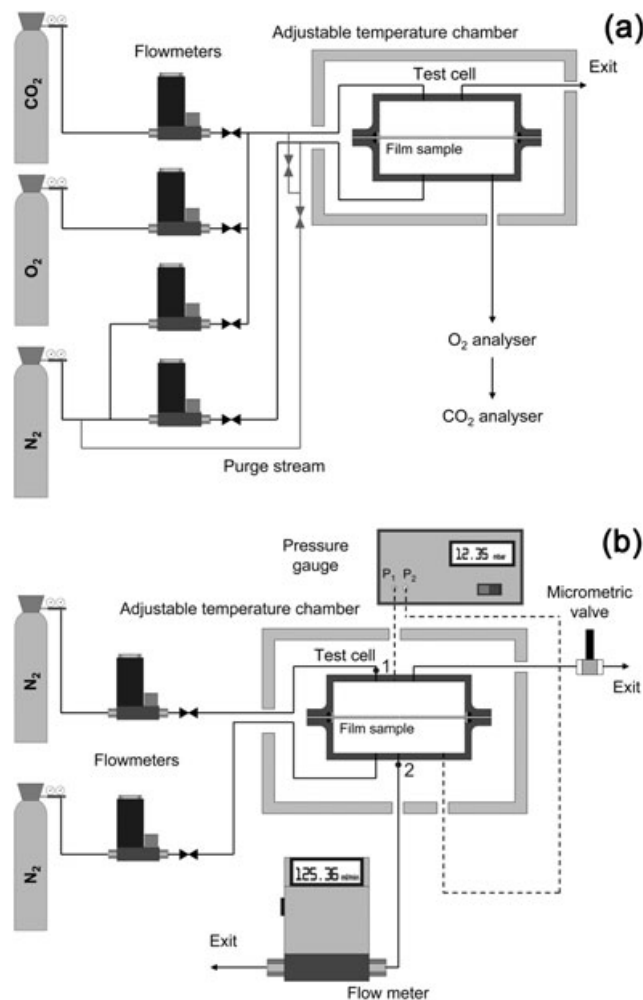
Figure 1. Schematic of the dynamic measurement system: (a) for non-microperforated films and (b) for microperforated films.

A detailed illustration of the diffusion cell is shown in Figure 2. The cell has three openings in each half: two are for the entrance and exit of the gases, and the third, situated in the centre, is for placing a PT100 probe for measuring the temperature.

This equipment was designed for determining the permeability coefficient of non-microperforated films, Figure 1a. The sequence of modifications made to the measurement system for use with microperforated films is now described and shown in Figure 1b. First, a PCE Ibérica-DM30 pressure gauge (Tabarra, Spain), with a range of -30 to 30 mbar, a resolution of 0.01 mbar and an accuracy of $<\pm 2.5\%$, was added to the equipment to monitor the pressure difference at both sides of the film. This pressure difference was regulated by installing a HOKE Milli-Mite 1300 Series micrometric valve (Spartanburg, SC, USA). Small pressure differences at both sides of the film, of the order of 0.1 mbar, caused sudden increases in the concentration of O$_2$ or CO$_2$ in the nitrogen carrier stream of 220 ppm; a pressure difference of 0.3 mbar resulted in an abrupt growth of 875 ppm in the O$_2$ or CO$_2$ concentrations in the analyzed stream. These measurements were made with a flow of 80 ml min^{-1} in both halves of the diffusion cell, for O$_2$ or CO$_2$ concentrations in the upper half of the cell of 10% and using a film with a microperforation of 130×120 µm. The measurement of microperforated film permeability using differences in concentrations of the gas being tested in dynamic systems is highly susceptible to changes in pressure and consequently not very accurate.[17] It was therefore decided to modify the gas streams for determining the hydrodynamic flow passing through the microperforation. In the new system (Figure 1b), only nitrogen circulates in each half of the diffusion cell (with an inlet flow of 100 ml min^{-1}). The
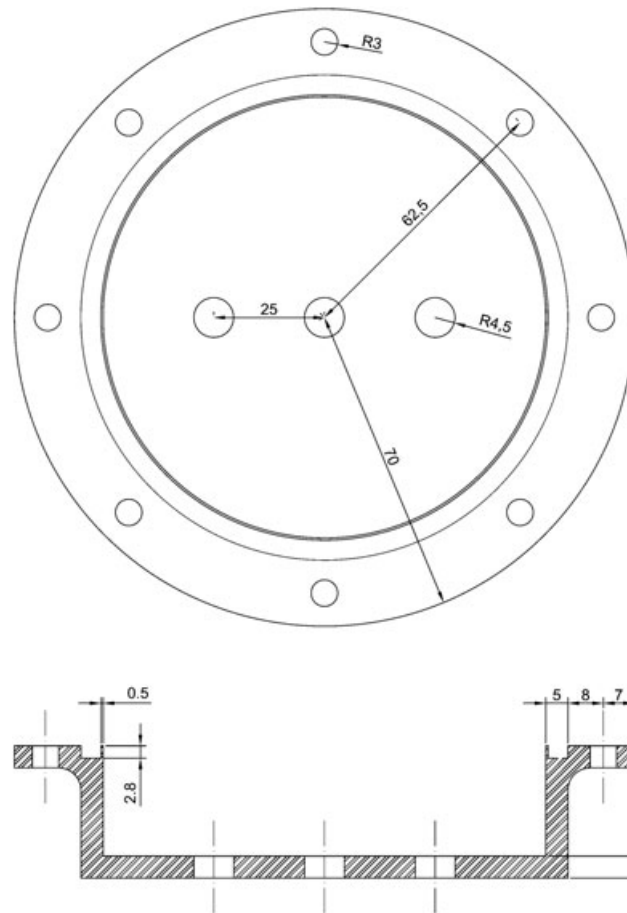
Figure 2. Diffusion cell (dimensions in millimetres).

pressure differences at both sides of the film were regulated between 5 and 90 mbar. The final change in the system was the installation of a MAS-3005 mass flowmeter supplied by Kobold Instruments (Pittsburgh, PA, USA) with a range between 0 and 200 ml min^{-1} and an accuracy of $\pm 1.5\%$ full scale (Figure 1b). The hydrodynamic flow was determined using the difference in flow at the entrance and exit of the low pressure zone, and consequently, the O_2 and CO_2 analyzers were not necessary.

Statistical analysis

All analyses were carried out in triplicate. The means and standard deviation were calculated. In fact, the data shown in the figures are the average of all repetitions, whereas the error bars are the standard deviation. The coefficients of determination, R^2, were calculated using MATLAB 7.11, R2010b (MathWorks, Natick, MA, USA).

RESULTS AND DISCUSSION

Figure 3 shows hydrodynamic flows through microperforations of six different sizes in relation to different pressures on both sides of the cell. To establish the relation between the flow passing through the perforation, J_h, with its equivalent diameter, D_e, and with the difference in pressure of both sides of the plastic film, ΔP, the Bernouilli theorem can be applied between points 1 and 2. Point 1 is located in the entrance pipe to the zone with the greater pressure, whereas point 2 is placed in the exit pipe of the zone with the lower pressure. Considering laminar flow (Re < 2100) so that the Fanning friction factor,
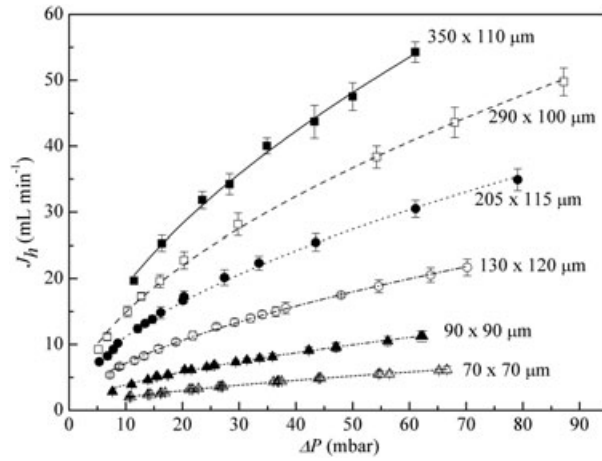
Figure 3. Experimental (symbols) and predicted (lines) data of the hydrodynamic flow as a function of the pressure difference, for various microperforation sizes.

f, can be expressed as 16/Re, and disregarding the pressure drop due to the enlargement at the entrance to the cell and the contraction at the exit (due to the widening and the narrowing of the cross section of the pipe), the following expression is obtained:

$$\frac{\Delta P}{\rho} = u_2^2 - u_1^2 + \frac{32\,\mu L}{D_e^2 \rho} u \tag{1}$$

where u_1, u_2 and u are the gas velocity at points 1 and 2 and while passing through the perforation, respectively; μ is the gas viscosity; and ρ is the gas density. If the rates are expressed in terms of the flow, and it is taken into account that the flow at the entrance to both chambers is equal, then the previous equation becomes

$$\frac{\Delta P}{\rho} = \left(\frac{Q + J_h}{\pi r^2}\right) - \left(\frac{Q}{\pi r^2}\right) + \frac{32\,\mu L}{D_e^2 \rho} \frac{4 J_h}{\pi D_e^2} \tag{2}$$

r being the radius of the entrance and exit pipes to and from the cell. Thus, the flow passing through the perforation, J_h, can be expressed as

$$J_h = \sqrt{\left(Q + \frac{64\,\mu L\,\pi r^4}{\rho D_e^4}\right)^2 + \frac{\Delta P \pi^2 r^4}{\rho}} - \left(Q + \frac{64\,\mu L\,\pi r^4}{\rho D_e^4}\right) \tag{3}$$

According to Equation (3), the flow passing through a given perforation is proportional to the square root of the difference in pressures. The fit of the hydrodynamic flow experimental data to Equation (3) is shown in Figure 3, and a good correlation can be seen for all the perforation sizes ($R^2 > 0.997$).

Experimental data were also obtained of the hydrodynamic flow for different equivalent diameters of the microperforations, maintaining the same difference in pressure in all cases. As an example, Figure 4 shows the results for $\Delta P = 10$ mbar, in addition to showing the fit of these data to Equation (3). It can be seen that the dependence of the flow on the diameter is consistent with the theoretical predictions given by the equation ($R^2 > 0.970$).

In a previous work using similar microperforated films,[18] static techniques were used to experimentally measure the oxygen and carbon dioxide transmission rates of microperforated film, TR_{O2} and TR_{CO2}. A potential equation was found to provide a good prediction of the dependence of the O_2 and CO_2 transmission rates on the perforation area, A_h:
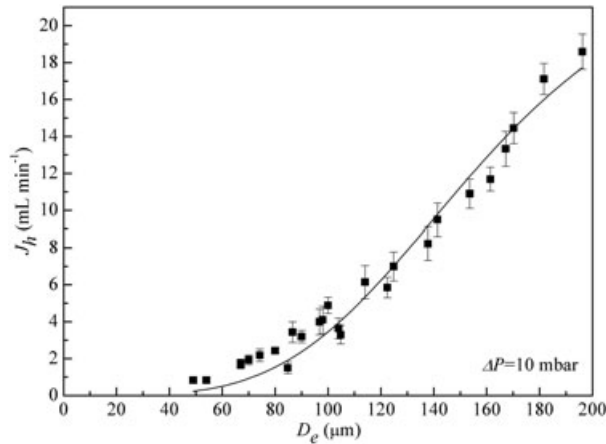
Figure 4. Effect of the equivalent diameter on the hydrodynamic flow. Experimental (symbol) and predicted (solid line) data.

$$TR = a_1 \cdot A_h^{a_2} \tag{4}$$

where if TR is expressed in millilitres per day and A_h in square micrometre, the values of the constants are $a_1 = 0.880 \pm 0.111$ and $a_2 = 0.577 \pm 0.0132$ for O_2 and $a_1 = 0.830 \pm 0.111$ and $a_2 = 0.569 \pm 0.0140$ for CO_2. The practical interest of using a combination of Equations (3) and (4) is that the transmission rate for O_2 and CO_2 through microperforated plastic can be determined with only one measurement of the flow, which passes through the perforation when a given difference in pressures is established. Knowing J_h and ΔP, through Equation (3), it is possible to obtain the equivalent diameter of the microperforation, which substituted in Equation (4) enables TR to be calculated.

To check the goodness of the method, the transmission rates determined experimentally in the static system [18] for microperforations of equivalent diameters between 50 and 200 μm were compared with those obtained using the dynamic experimental system and Equations (3) and (4). The transmission rates using the dynamic system were determined as follows. For each perforation, the hydrodynamic flow through it, J_h, was measured in the experimental dynamic system (Figure 1b); these data were obtained at three pressure differences at both sides of the film (15, 35 and 55 mbar) and with a N_2 flow, Q, of 90 ml min^{-1}; the equivalent diameter, D_e, was calculated using Equation (3) for the three experimental data; the perforation area, A_h, was obtained using the mean value of D_e, and using Equation (4) the transmission rate was determined. As Figure 5 shows, for O_2 (the less favourable case), the coefficient of determination ($R^2 = 0.993$) is sufficiently close to one to be able to consider the method suggested here as a possible alternative for the determination of transmission rates through microperforated films.

The application of this method to packaging when multiple perforations are present is possible if multiple small perforations are considered equivalent to a single large perforation with the same area, as other authors have proposed.[9,14,15] Renault *et al.* [20] tested a model describing gas transport through multi-microperforated films using Stephan–Maxwell laws and concluded that it is possible to compare experimental data with the model by fitting only a sum of equivalent microperforation cross-sectional areas, which is always smaller than the sum of real cross-sectional areas. The reason for this is that the model does not consider the resistance of air to gas diffusion at the two ends of each microperforation. The method here proposed considers this resistance because the transmission rates predicted by the empirical Equation (4) are very close to those obtained with the modified Fick's equation in which the total diffusive pass length of a perforation is considered as the sum of the perforation length and a correction factor. The value of this factor is half of the equivalent diameter of the perforation.[18]

The proposed methodology could be very useful and practical in cases where nondestructive leak detectors are used such as those based on Poiseuille's Law available on the market (for example: LeakPointer E2 from PBI-Dansensor A/S, Ringsted, Denmark; Pack check from Topac, Cohasset, MA,USA; or the PAC Guard Model 400 from Mocon, Minneapolis, MN, USA). In these detection
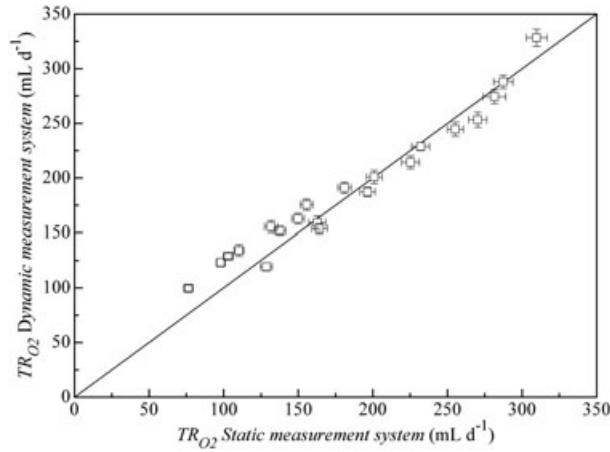
Figure 5. Comparison between the transmission rates through a microperforation measured with the dynamic and the static system for $50 < D_e < 200\,\mu m$.

systems, the package to be tested is placed in a test chamber in vacuum conditions. If the package has a leak, the pressure difference causes a hydrodynamic gas flow from the interior of the package towards the chamber. The gas usually analyzed in the chamber is CO_2. If a microperforated bag containing a gas at atmospheric pressure combined with a certain proportion of CO_2 is placed in the chamber and the given vacuum is applied, it is possible to determine the hydrodynamic flow, J_h, through the microperforation knowing the time of the experiment and the concentration of CO_2 reached in the test chamber. Therefore, using Poiseuille's Law, Equation (5), it is possible to calculate A_h, and subsequently TR through Equation (4).

$$A_h = \left(\frac{J_h 8\,\mu L \pi}{\Delta P} \right)^{1/2} \tag{5}$$

The test vacuum in these leak detectors is normally adjustable within a scale that depends of the model, but common values are between 6 and 60 cm Hg. This implies a pressure difference at both sides of the microperforation between 900 and 200 mbar. On the other hand, the minimum detection level of CO_2 is in the interval 0.35 to 1 ml s^{-1}, so these systems provide the appropriate CO_2 hydrodynamic flow through the microperforation to calculate A_h.
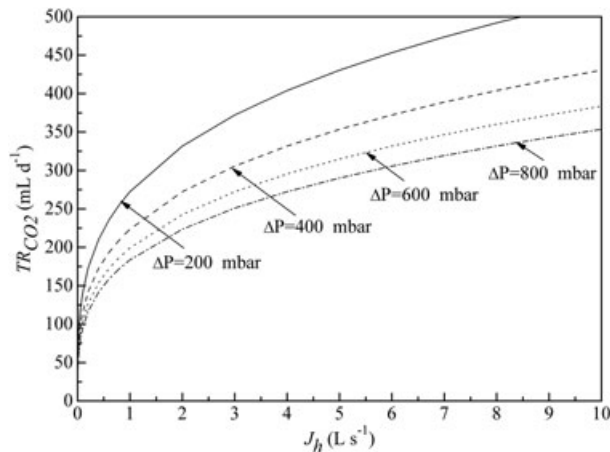

Figure 6. CO$_2$ transmission rates that can be obtained from Equations (4) and (5) for various pressure differences, $L = 35\,\mu m$ and $\mu = 1.585 \times 10^{-5}\,Pa\,s^{-1}$.

Knowing the thickness of the film and the vacuum pressure during the test, it is possible to generate graphs as the example shown in Figure 6 (for a package of 35 μm thickness containing 20% CO_2 and 80% N_2). These graphs were elaborated from a table: the first column contains a scanning of J_h values. Once the viscosity, thickness and pressure difference values were fitted and using the hydrodynamic flow of the first column, the second column gives the perforation area values calculated from Equation (5). The third column was assigned to the CO_2 transmission rates determined from Equation (4) and A_h values. The representation of CO_2 transmission rates versus hydrodynamic flow (third and first columns) allows quick reference graphs to be drawn. Obviously, the use of these graphs is limited by the minimum and maximum CO_2 flow that the detection system can measure and restricted to transmission rates included in the interval 50–500 ml d^{-1}, for which Equation (4) has been tested.[18]

CONCLUSION

An alternative methodology for measuring O_2 and CO_2 transmission rates in a static system is proposed for microperforated films whose polymeric matrix is sufficiently impermeable so as to disregard the gas exchange passing through it compared with the exchange passing through the microperforations. Although the hydrodynamic flow is not usually used to determine the gas exchange in microperforated films, these measurements could be useful for a quick estimation of the total area of the microperforations in the package. This can in turn be used to estimate the diffusive flow established both for O_2 and for CO_2. The goodness of this alternative has been evaluated by comparing the transmission rate obtained by this method and those determined using a static system. The coefficients of determination were >0.993.

Furthermore, the proposed methodology is not expensive because no sophisticated equipment is needed.

ACKNOWLEDGEMENTS

Nomenclature

a_1, a_2	constants
A_h	microperforation area (μm^2)
D_e	equivalent diameter of the microperforation (μm or m)
f	Fanning friction factor
J_h	hydrodynamic flow of gas through the microperforation (m^3 s^{-1} or ml min^{-1})
L	thickness of the film (m)
ΔP	pressure difference (Pa)
Q	flow rate (m^3 s^{-1})
r	pipe radius (m)
Re	Reynolds number
TR	gas transmission rate (m^3 s^{-1} or ml d^{-1})
u	gas velocity (m s^{-1})
μ	gas viscosity (Pa s^{-1})
ρ	gas density (kg m^{-3})

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