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A Simple Permeation Test Cell for Dual Application

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ABSTRACT

This study aimed to develop a simple and inexpensive permeation test cell for dual application with test samples that were either flat films or preformed articles. The two-chamber cell was designed in accordance with isostatic principles. The shallow lower chamber was equipped with a carrier-gas inlet apparatus and a sample-fixing tool. There were two different types of upper chamber; one for flat films and the other for preformed packages. The important features of this cell were the designs of chambers, the fixture tool and the gas flow configuration. The fixture tool was adjustable to fix preformed samples of different sizes and shapes. Gas flow configuration in the system was controlled by 3 three-way valves and 2 flow-control valves. The arrangement of these valves was crucial to the system. Oxygen transmission rates determined using this permeation cell were 8,732±201, 4,363±28 and 1,668±111 cm^3/m^2.day.atm for LLDPE 20 μm, CPP 25 μm and an unknown film 50 μm, respectively. A PE bottle 325 ml, thickness 1.260 mm; a PE bottle 250 cm^3, thickness 0.475 mm and a PE cup 250 cm^3, thickness 0.320 mm had values of 2.36±0.096, 1.95±0.07 and 3.20±0.18 cm^3/pk.day.atm, respectively. These values corresponded well with those measured using a commercial apparatus available in laboratories.

Key words: permeation cell, oxygen transmission rate, permeability, plastic packaging

INTRODUCTION

Gas permeation through plastic is a mass transport phenomenon. The mechanism of the transport involves solubility and diffusion of gas or permeant (Hernandez and Gavara, 1999). The nature of the plastics and permeants determines the rate of permeation; therefore, gas permeability of plastic is crucial in packaging material design, especially for food and pharmaceutical products. Ingress and egress of permeants may dramatically change physical, chemical and microbiological qualities of packaged products and subsequently affect the product shelf life.

Measurement of gas permeation is generally based on three methods: the volume-variable method, the pressure-variable method and the isostatic method (Hernandez and Gavara, 1999). In the volume-variable method, an increase in volume at constant pressure, which is a function of the permeating gas, is generally measured by the displacement of liquid in a connected capillary. At steady state, the rate of increase in volume as measured by the liquid velocity is used to calculate the gas permeability. The pressure-variable method or manometric technique employs the principle of gas diffusion from the high-pressure side of the film to the low-pressure side. The increase in

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pressure on the low-pressure side is then converted to a gas permeation rate. The isostatic or concentration increase method is probably the most widely used. The total pressure on both sides of the film is approximately equal and the partial pressure difference of the permeant across the film drives the gas permeating to the lower pressure side. The partial pressure difference across the film is maintained by continuous sweeping of one side with test gas and the other with inert gas. The quantity of test gas permeated into the inert gas is then measured by a gas analyzer or detector to calculate the permeation rate (Robertson, 1993).

A number of techniques and commercial instruments for measuring the gas permeation of plastic films have been employed. Mostly, the apparatuses are expensive, specific to a certain application, such as flat film, and have a high cost of maintenance. These pose some obstructions to academic progress. Thus, the objective of this work was to develop a prototype permeation cell for measuring gas transmission rates, which was simple, inexpensive and suitable for dual application, so that the test samples could be either flat films or preformed articles. Isostatic principles were employed and a gas chromatography system connected directly to the cell detected and measured the amount of permeated gas.

MATERIALS AND METHODS

Design of permeation cell

Based on isostatic principles, the permeation cell consisted of two chambers and was constructed of stainless steel, SUS 304, in a circular shape. The lower chamber served to mount a test sample of either film or preformed package, while the upper chamber was designed to fit the sample features. Hence, there were two different types of upper chamber, one for films and the other for performed packages. The lower chamber was equipped with a gas inlet to receive a continuous flow of inert or carrier gas from the tank. The carrier gas spontaneously swept the test gas that had been permeating through the sample from the upper chamber to a gas chromatography system (Agilent model 6820, USA). In addition, the test gas flowed continuously into the upper chamber and vented out to the atmosphere to maintain isostatic conditions. The two chambers were assembled and securely closed with the help of three bolts and an O-ring made of nitrile butadiene rubber.

Gas flow assembly

The basic approach of this study was to integrate and modify the isostatic principles described in ISO 15105-2:2003(E), which is specific to flat film samples, and ASTM 1307-02 and Loudenslagel and William (1970), which are specific to preformed packages.

As the lower chamber was adaptable for mounting films and preformed packages, the gas inlet configuration had to be designed to correspond to the sample features. For flat films, the two gas apertures were located on the rim of the chamber on opposite sides. Narrow mouth containers such as bottles and cups, which are widely used as disposable food and drink containers, were chosen to represent preformed packages in this study. The space between the two gas apertures was consequently narrowed down to allow gas to flow into the test package. These apertures were then placed at the center of the chamber. The inert gas flow directions were guided either to the apertures on the rim or to the center by means of 2 three-way valves connected to gas inlet and outlet tubes.

Both upper chambers were equipped with a gas inlet and outlet to allow test gas to pass continuously over the sample and vent out. Another three-way valve was connected to the gas inlet to select the procedure, either purging or testing. The flow rates of the test and of carrier gases were controlled by flow control valves.

Oxygen transmission rate (OTR) test

Three different films were selected according to their OTR values previously measured by commercial instrument (Illinois 8500), to test the performance of the prototype permeation cell. In addition, the OTRs of two PE bottles of 325 and 250 cm^3 and a PE cup of 250 cm^3, representing preformed packages were also measured. Oxygen gas (O_2) that permeated into the nitrogen gas (N_2) stream was detected and measured by a calibrated gas chromatograph, which had been prepared in the authors' laboratory.

RESULTS AND DISCUSSION

Permeation cell assembly

The permeation cell, consisting of two chambers, was constructed of stainless steel, SUS 304, in a circular shape (Figure 1). To achieve a film diffusive area of 100 cm^2 as recommended in ISO 15105-2:2003(E) and ASTM F-1307-02, the inside diameter of the lower chamber was made 11.28 cm. The upper chamber was identical to the lower, except it had a greater inside volume to accommodate the test gas (Figure 1 (a)). The volume inside the cell is not critical, but a smaller volume is preferable due to the sensitivity of measurement (Al-Ati *et al.*, 2003). This cell provided a total volume of 46.05 cm^3, of which 10.63 cm^3 was in the lower chamber, with 35.42 cm^3 in the upper one. The two chambers were assembled and securely closed with the help of three strand bolts and an O-ring made of nitrile butadiene rubber. The apertures for the inert gas inlet and outlet were located on the inside rim of the lower chamber on opposite sides, while the apertures for the test gas were on the outside rim and went straight to those of the upper chamber.

The lower chamber was designed for mounting preformed packages as well. Narrow-mouth bottles and cups of 250 to 325 cm^3 were chosen as test samples in this study. As their mouth width ranged from 3 to 7 cm, the gas inlet configuration was redesigned in such a way that the distance between the apertures' center was reduced to 10 mm; consequently, the outside distance was 20 mm. These two apertures were relocated at the center (Figure 1 (b)).

The upper chamber was cylindrical in shape with an outside diameter identical to that of the lower chamber. To provide adequate gas volume and good gas circulation, the chamber height and volume were 25.3 cm and 850.15 cm^3, respectively. Two gas tubes were provided to

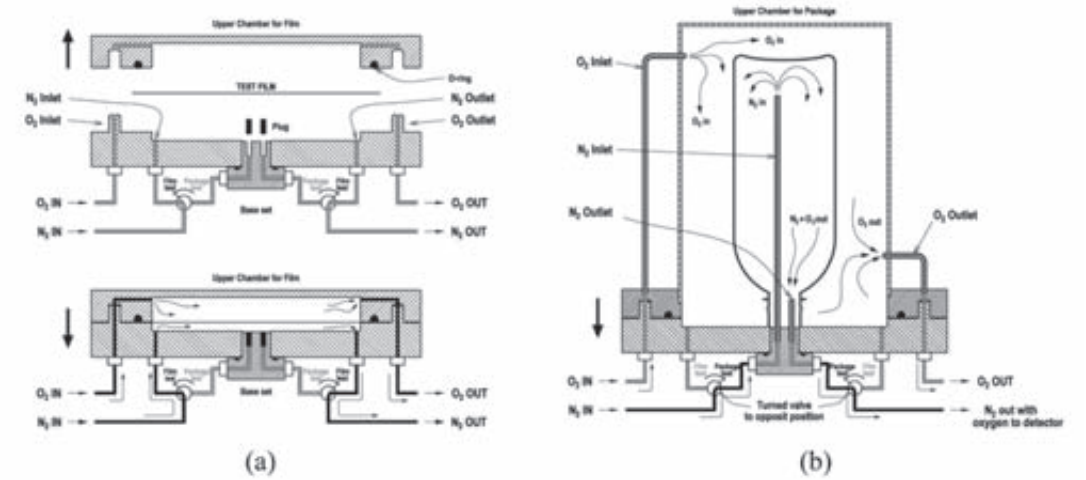

Figure 1 Permeation cell assembly with gas inlet and outlet positions: (a) for film; (b) for preformed package.

connect with the gas inlet and outlet of the lower chamber.

All components of the permeation cell and the assembly are depicted in Figure 2. In addition, one fixing tool was equipped in the lower chamber when preformed packages were tested. This tool was adjustable in accordance with the sample feature by means of a moving pad that gently pressed the sample mouth against the rubber seal to prevent gas leakage.

Gas flow assembly

Gas flow assembly for films is shown in Figure 3 and for preformed packages in Figure 4. Based on isostatic principles, two procedures, purging and testing, were performed consecutively.

The three-way valve, V1, selected the types of gas flowing into the cell by switching its position. At the "Purge system" position, N_2 was allowed to flow in and purged air from the cell (see Figure 3 (a)) while the "Test" position was set to sweep O_2 into the upper chamber (see Figure 3 (b)). V2 and V3 were switched to a position in accordance with the sample features to direct N_2 flow in and flow out of the lower chamber. Hence, they were positioned at "Film Test". The flow rates of O_2 and N_2 were controlled by two flow control valves, FC1 and FC2, respectively. Each gas was supplied from a tank at 0.1 MPa by means of regulators and its flow rate was controlled by FC1 or FC2 in the range of 35-50 cm^3/min. In this respect, the purging period of 30 minutes was adequate to fill completely the cell with N_2 before starting the test procedure. That is an important step for gas permeation measurement.

The N_2 gas exited the lower chamber and carried O_2 permeating through the sample to the sampling port before entering the gas chromatography system.

Figures 4 (a) and (b) describe the pathway of gas flow in the cell during the purge and test procedures, respectively, for measuring gas permeation of the preformed package. The gas flow pattern was similar to that explained previously, except that the N_2 gas swept through the inlet and outlet at the center of the lower

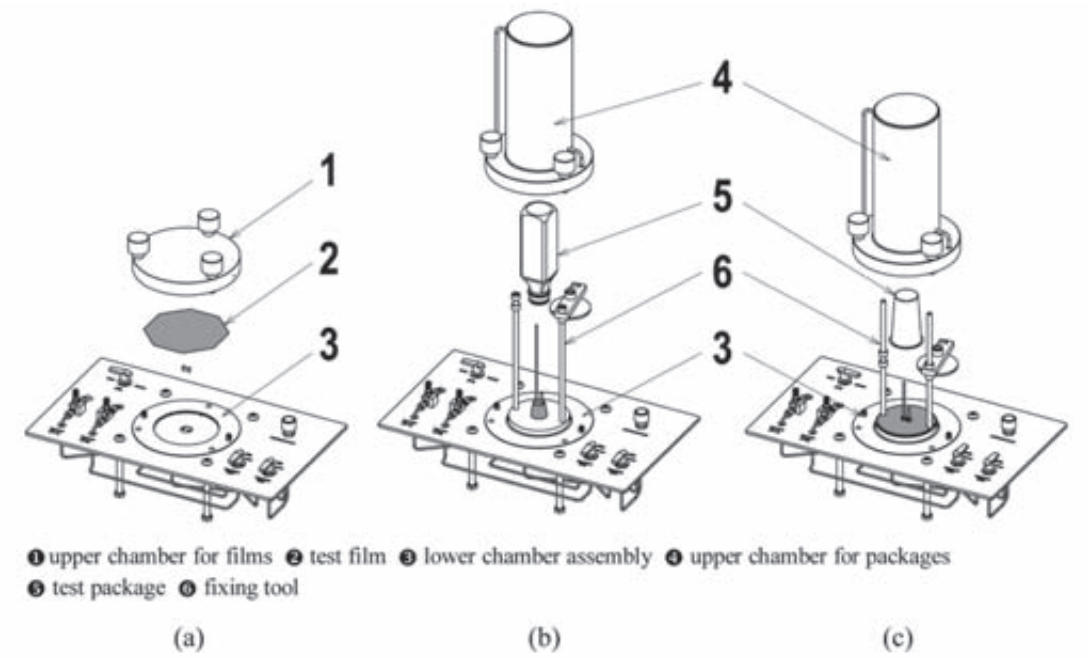

Figure 2 Permeation cell components and assembly: (a) for film; (b) for bottle; (c) for cup.

chamber by switching V2 and V3 to the "Package Test" position. The N_2 gas flowed inside the test package, while O_2 passed over the outside.

The N_2 gas containing permeating O_2 swept into the sampling port that was connected to the gas chromatography system (Agilent model

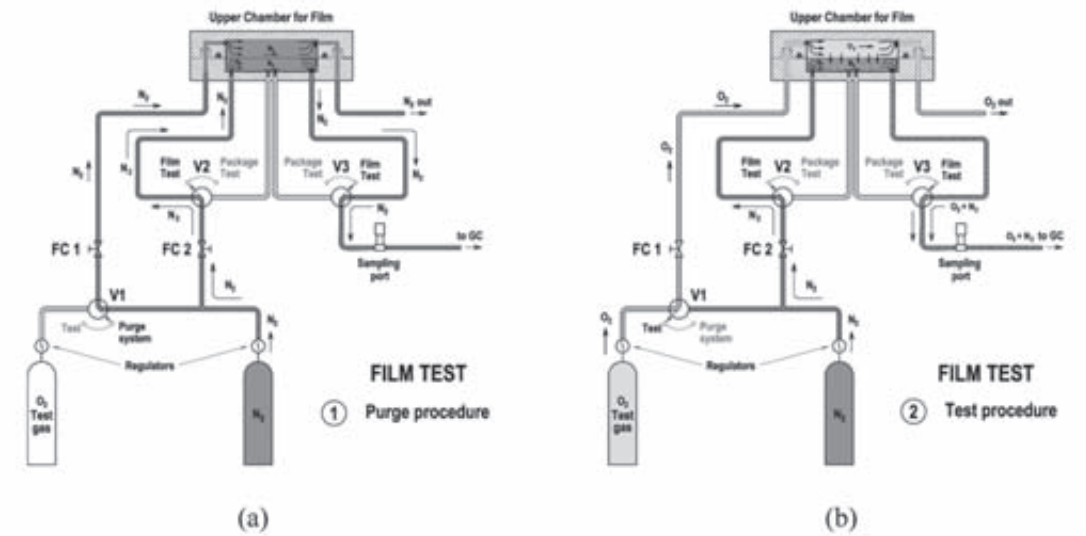

Figure 3 Diagram of gas flow assembly for permeation test of films: (a) purge procedure; (b) test procedure.

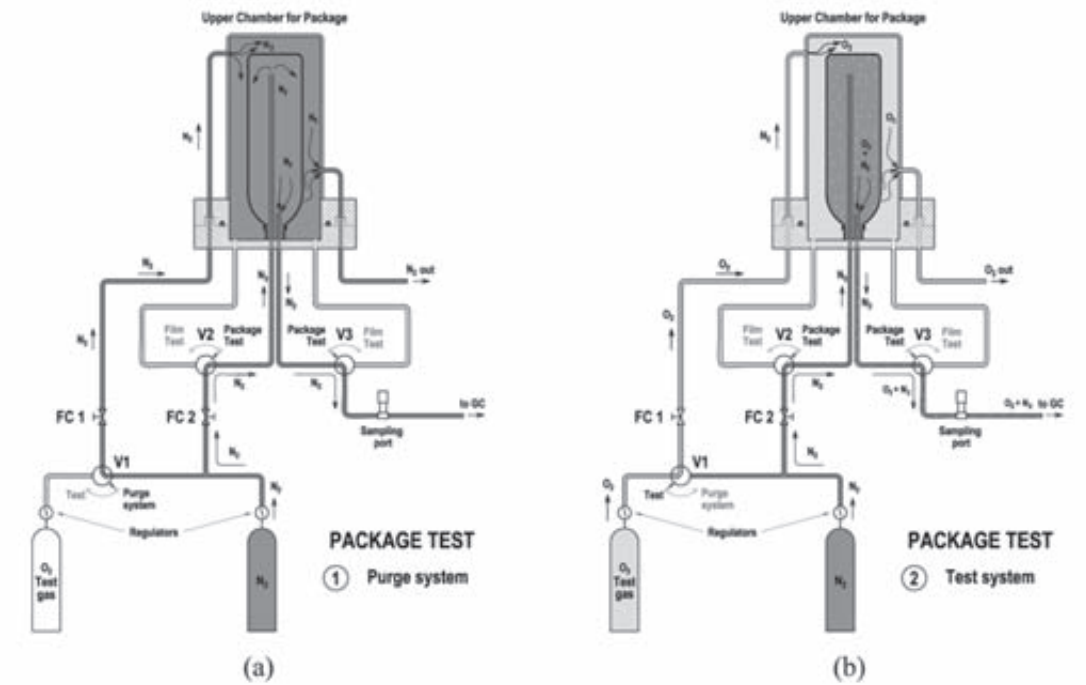

Figure 4 Diagram of gas flow assembly for permeation test of preformed packages: (a) purge procedure; (b) test procedure.

6820, USA) (Figure 5). The permeating O_2 was detected and measured by the calibrated gas chromatograph, which had been prepared. More details of the whole assembly are shown in Figure 6.

The gas chromatograph used in this study was an Agilent model 6820 in combination with a thermal conductivity detector (TCD) and a molecular sieve column (Agilent GS-Molesieve ID 0.53 μm, length 30 m). The operating conditions were set as follows: carrier gas (He) flow 6 cm^3/min, auxiliary gas (He) flow 10 cm^3/min, reference gas (He) flow 22.5 cm^3/min, split ratio 1:15, injection volume 2 cm^3, injection temperature 100°C, oven temperature 50°C and detector temperature 150°C. To control a constant

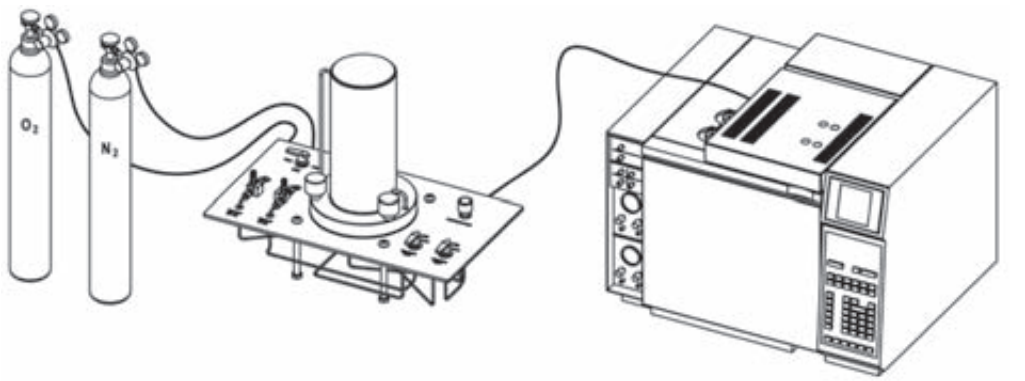

Figure 5 Diagram of oxygen permeation measurement assembly.

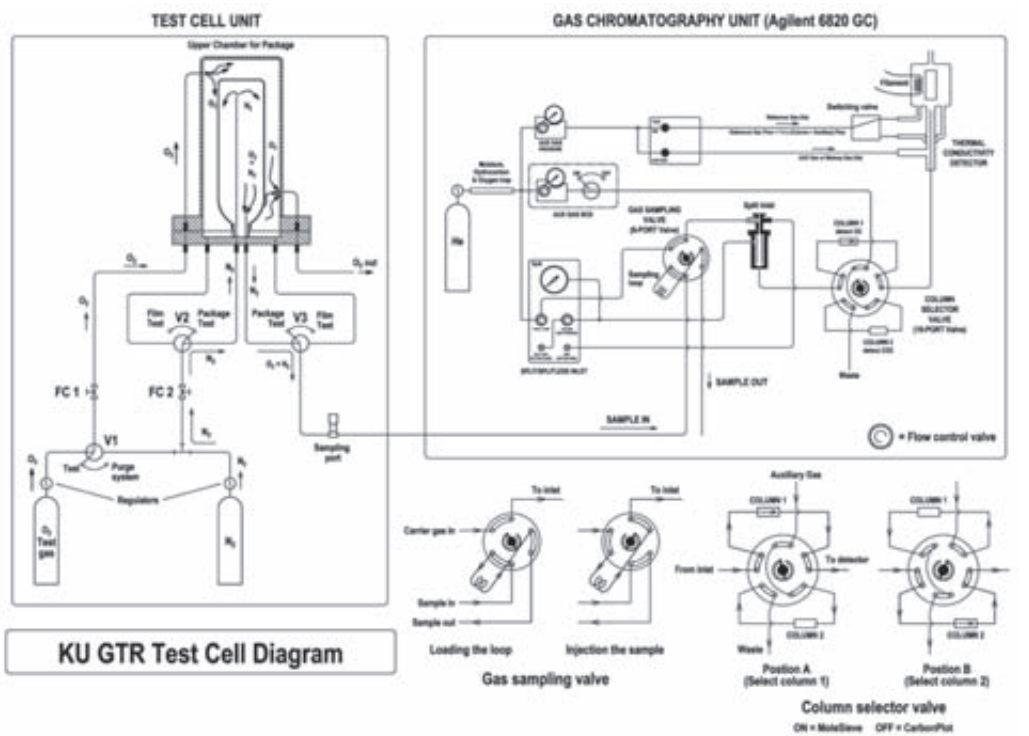

Figure 6 Diagram of permeation cell connected to sampling loop of the gas chromatography system, Agilent model 6820.

volume of gas injection of 2 cm^3, the sampling loop 2 cm^3 (Valco Instruments Co.,Ltd, USA) and the sampling valve (model 6UWE, Valco Instruments Co.,Ltd., USA) were connected to the sampling port at one end and to a split inlet at the other end. Gas sampling was done every five minutes until the steady state had been achieved. It was observed that the retention time of oxygen and nitrogen was 2.343 and 3.102 minutes, respectively. The amount of oxygen was calculated based on its peak area using the Agilent Cerity Networked Data System for Chemical QA/QC Revision - A.04.05.

Oxygen transmission rate (OTR) test

Film test

Three different films were selected according to their OTR values, which had been measured by a commercial instrument, Illinois 8500, namely LLDPE 20 μm, CPP 25 μm and an unknown film 50 μm. They were obtained from Alcan Packaging Strongpack Public Company Limited, Thailand.

Figure 7 shows both the transient and the steady state region of O_2 flow through the test films. Moreover, the steady state of O_2 permeation was established rapidly only five minutes after the test. This graph was also useful to determine the diffusion coefficient (D) and further to calculate the solubility coefficient (S) (Hernandez and Gavara, 1999; Piringer, 2000). By using a calibrated chromatograph, with the help of the software mentioned above, the OTR value of each of the three films was calculated and is presented in Table 1. It was noted that the values were relatively consistent with those measured by the commercial instrument, Illinois model 8500, even though some deviations were observed.

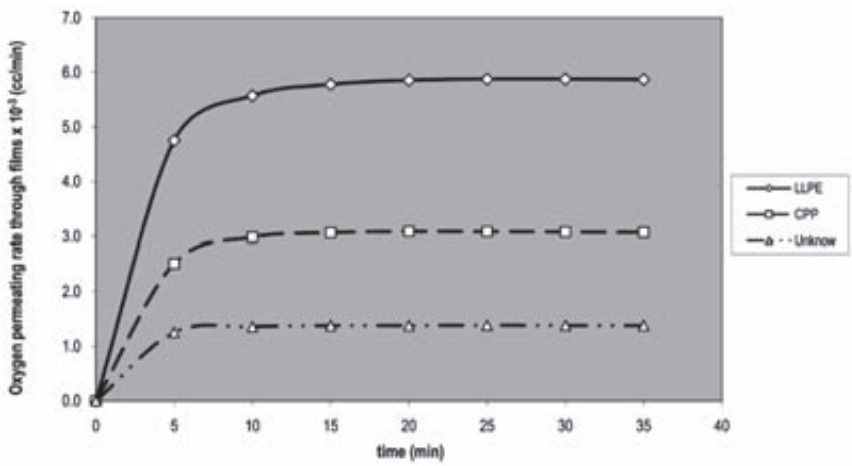

Figure 7 Rate of oxygen permeating through test films over time.

Table 1 OTR of the test films measured using the prototype permeation cell and the commercial instrument.

Films	OTR (cm^3 /m^2.day.atm)			
	Prototype permeation cell		Commercial instrument	
	Mean[1]	SD	Mean[1]	SD
LLDPE (20 μm)	8,732	201	9,533	291.55
CPP (25 μm)	4,363	28	4,599	94.22
Unknown (50 μm)	1,668	111	1,570	9.61

[1] n = 5

At this stage, the principal aim was to test the performance of the whole assembly, not to assess its accuracy. Thus, the calibration of the chromatograph had been performed with gas mixtures prepared in the authors' laboratory, instead of using standard ones. Not surprisingly, small deviations were noticed. However, the assembly showed satisfactory results and possessed many advantages, for instance, simple design, uncomplicated operation and low cost. To improve the measurement accuracy and precision, it is necessary to prepare calibration chromatographs with standard gas mixtures.

Package test

The three test packages were: 1) a PE bottle 325 cm^3, average thickness 1.260 mm; 2) a PE bottle 250 cm^3, average thickness 0.475 mm; and 3) a PE cup 250 cm^3, average thickness 0.320 mm (Figure 8). They were purchased from local markets in Bangkok, Thailand. Each sample was measured three times and the results are summarized in Table 2.

The results in Table 2 reveal that the measurements were repeatable with precision. Though the reference values were not available to compare with the data from the experiment, it was observed that the ranges of OTR were consistent with sample thickness and volume, which corresponded directly to surface area. The thicker the wall and the smaller the area was, the less amount of gas permeated.

It is important to note that the fixing tool specially designed for this study was the crucial element for the success of the measurements. The tool was adjustable in accordance with the sizes and shapes of test packages and the sample was securely mounted on the lower chamber without leakage with the help of rubber seal.

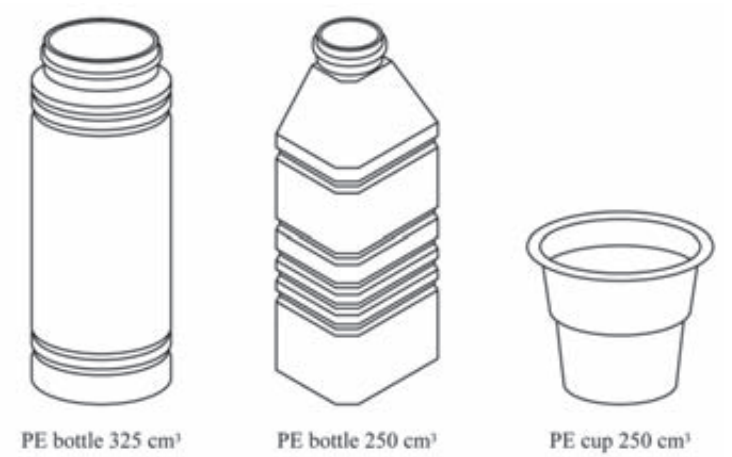

Figure 8 Bottles and cup for gas permeation test.

Table 2 OTR of the test packages measured by the prototype permeation cell.

Replication No	OTR through package (cm^3 /pk.day. atm)		
	PE bottle 325 cm^3	PE bottle 250 cm^3	PE cup 250 cm^3
1	2.29	1.93	3.39
2	2.32	2.03	3.20
3	2.47	1.89	3.03
Mean	2.36	1.95	3.20
SD	0.096	0.072	0.180

CONCLUSIONS

The prototype of the permeation test cell was successfully developed as a single apparatus for measuring the gas permeation rate through both films and preformed packages. The design was based on the principles of the isostatic method in combination with the essential concepts described in ISO 15105-2:2003(E), ASTM 1307-02 and Loudenslagel and William (1970). The whole assembly consisted of: a permeation cell, involving two chambers constructed of stainless steel in a circular shape; a package fixing tool; a gas flow assembly and a gas chromatography system.

The gas flow configuration in the system was controlled by 3 three-way valves and two flow control valves. It was found that the arrangement and positions of these valves were crucial points of the system. The three-way valves controlled the operational modes of the assembly, such as purge or test procedure, films or package test.

The OTR measurement of three different films showed good results that were relatively consistent with the values determined by a commercial instrument. Moreover, the OTR of the test bottles and cup agreed well with their features, namely the thickness and volume.

It is important to note that the performance of the prototype was very satisfactory. In addition, it had several advantages, such as simple operation, affordable cost for most research institutes or universities and adaptability to other gas measurements. It is necessary to improve its accuracy by using standard gas mixtures for preparing calibrated chromatography.

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LITERATURE CITED

Al-Ati T., J. Garza and J.H. Hotchkiss. 2003. Simple universal permeation apparatus. **Packaging Technology and Science** 16(6): 249-257.

American Society for Testing and Materials (ASTM). 2002. **Standard Test Method for Oxygen Transmission Rate Through Dry Packages Using a Coulometric Sensor.** ASTM F-1307-02.

Hernandez, R.J. and R.Gavara. 1999. **Plastic Packaging: Methods for Studying Mass Transfer Interactions.** Pira International. UK. 38 p.

International Organization for Standardization (ISO). 2003. **Plastics - Film and Sheeting - Determination of Gas-transmission Rate. Part 2: Equal-pressure Method.** ISO 15105-2: 2003(E).

Loudenslagel, K.D. and F. William. 1970. Whole-package transmission test. **Modern Packaging** 43(9): 78-82.

Piringer, O.G. 2000. Permeation of gases, water vapor and volatile organic compounds, chap. 9. *In* O.G. Piringer and A.L. Baner (eds.). **Plastic Packaging Materials for Food.** Wiley-VCH. Weinheim.

Robertson, G.L. 1993. **Food Packaging: Principles and Practice.** Marcel Decker. New York. 676 p.