

Evaluation of Permeation Cell for Measuring Edible and Active Films Gas Permeability

Khaled S.A. Nagy and Manal A. Sorour
Food Technology Research Institute, Department of Food Engineering and Packaging,
Agricultural Research Center, Giza, Egypt

Abstract: Gas permeability of edible, imported and local produced smart films used in extending shelf life of fruit and vegetables were evaluated. The modified design and construction of the permeation cell was discussed. Gas permeability of edible film made of CMC and Gelatin was measured with time and for local smart film was measured and compared with the imported film. The results observed that oxygen permeability of edible CMC, gelatin films were 4.099×10^{-8} , $4.485 \times 10^{-8} \text{ m}^3/\text{m} \cdot \text{day} \cdot \text{mmHg}$, respectively while oxygen permeability of imported and local produced smart film was 5.28×10^{-5} and $4.57 \times 10^{-5} \text{ m}^3/\text{m} \cdot \text{day} \cdot \text{mmHg}$, respectively. Carbon dioxide permeability for edible CMC and gelatin were respectively while for imported and local produced smart film were 7.488×10^{-6} and $9.3 \times 10^{-6} \text{ m}^3/\text{m} \cdot \text{day} \cdot \text{mmHg}$, respectively.

Key words: Permeability, permeation cell, edible film, smart film, gas permeability, carbon dioxide

INTRODUCTION

The use of polymers as food packaging materials has strongly increased due to their advantages over the traditional materials as glass and tinplate. In fact, the large variety of plastic materials and the different compositions available make possible to adopt the most convenient packaging solution and design, focusing on the specific needs of each product. Nevertheless, the main issues of polymers in food packaging is that they are all permeable to gases and low molecular weight molecules which limit their acceptability for packing items that are sensitive to atmospheric gases. The traditional solutions to overcome this problem are the so called passive barriers. In particular, the plastic materials, suitable for food packaging are properly processed, assembled with other polymers to create multifunctional structures and/or treated by different technologies to improve their barrier properties (Lopez-Rubio *et al.*, 2004; Sugiyama *et al.*, 2006).

The active packaging technologies relate to all these systems that actively interact with the packaged food or the food surface, to extend the shelf life and to improve the quality of the products by preserving their sensorial characteristics and safety along the storage period. Besides the other traditional packaging solutions and processes, as passive barrier and modified atmosphere techniques, the active technologies allows to prolong the shelf life of sensitive foods and to guarantee their freshness, through a continuous and specific modification of the environment inside the packaging.

Permeability is the ability to skip the film of gas in a unit area of material in certain circumstances. Permeability value is strongly influenced by the chemical nature and structure of the polymer. Oxygen permeability values on packaging films useful for estimating the shelf life of packaged products. By Salman (2013) edible film is a thin layer of edible, used in food wrapping manner, dipping, brushing or spraying to provide selective detention against displacement gas, water vapor and dissolved materials as well as protection against mechanical damage. Theoretically, the material must have properties of edible films resist moisture loss product has a selective permeability to certain gases, controlling the movement of dissolved solids to maintain the natural color pigments and nutrients, as well as a host of additives like dyes, preservatives and flavor enhancer that improves the quality of foodstuffs (Gemadios and Weller, 1990).

Edible films based on polysaccharides such as alginate, cellulose ethers, chitosan, carrageenan or pectin, generally exhibit good gas barrier properties. Addition of lipids or starch to a film formulation can improve both oxygen and oil barrier properties (The gas permeability properties of such films result in desirable modified atmospheres, thereby increasing the shelf life of the product without creating anaerobic conditions (Baldwin *et al.*, 1995). Addition of a fatty acid through an emulsion with proteins can increase the O_2 and CO_2 permeability of the resulting film while addition of acetylated monoglycerides actually provides the reverse effect (Wu *et al.*, 2002).

Use of natural polymers such as proteins and polysaccharides as coating or film materials for protection of food has grown extensively in recent years. These natural polymers can prevent deterioration of food by extending shelf life of the product and maintaining sensory quality and safety of various types of foods (Robertson, 1993). Generally, film and coating systems are designed to take advantage of barrier properties of polymers and other molecules to guard against physical/mechanical impacts, chemical reactions and microbiological invasion. In addition, the use of natural

polymers presents added advantages due to their edible nature, availability, low cost and biodegradability. The objective of this study is to develop a permeation cell for measuring gas permeability of edible, imported and local produced smart films.

MATERIALS AND METHODS

Design of permeation cell: The design of permeation cell used for the measurement of gas permeability of different edible films was as shown in Fig. 1. A cylindrical

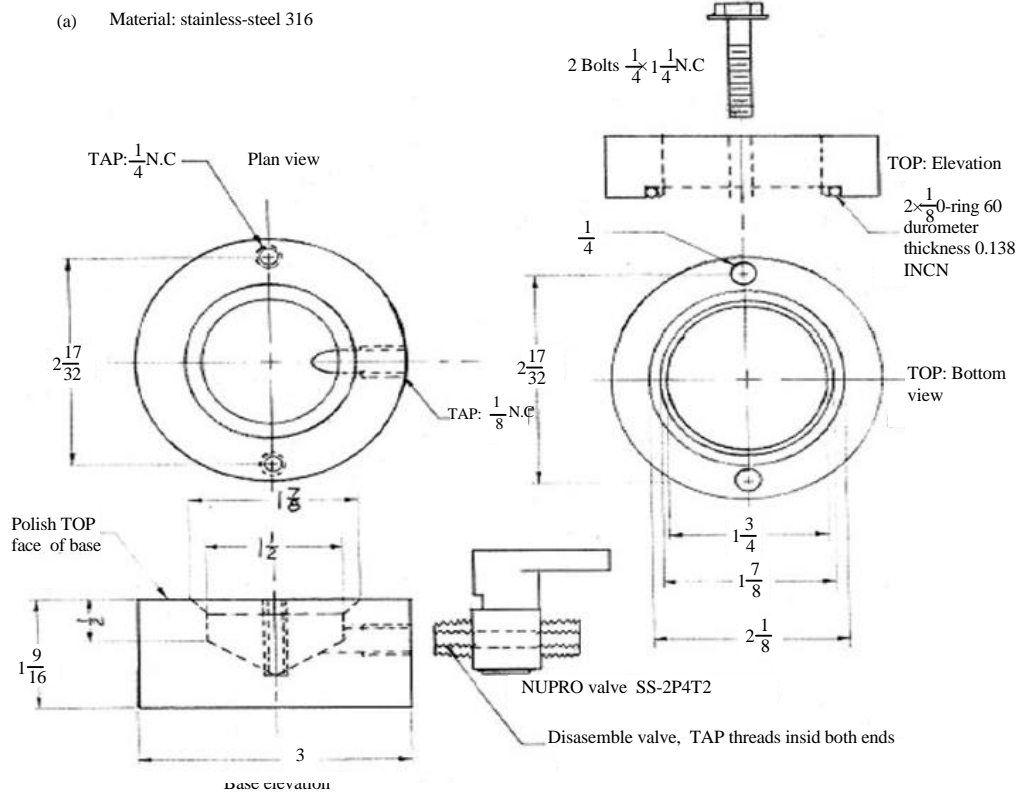


Fig. 1: a, b) The chamber filled

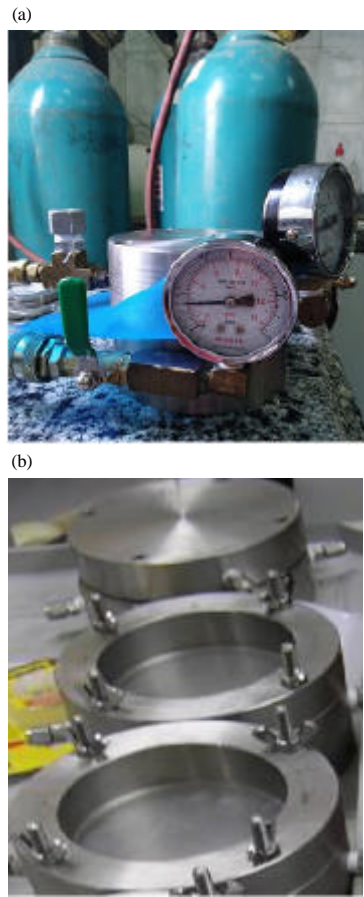


Fig. 2: a, b) Permeation cell

stainless-steel cell was divided by the test-film sample into two chambers, each one with a self-sealing septum. The volume of each chamber was 0.00023 m³ and it was modified by constructing a pressure meter with the two chambers. Permeability determination were done by placing the test film between the two chambers and closing the cell tightly. A stream of test gas passed through the first chamber and the test gas concentration was measured using model Witt Oxybaby headspace gas analyser (O₂/CO₂) following the method described by (Garcia *et al.*, 2000), nitrogen gas was passed through the second chamber. Basis of the test method is the determination of the concentration of the tested gas which diffused through the tested material (edible film) from the chamber filled with pure testing gas to the chamber with nitrogen (Fig. 1 and 2).

Preparation of edible film

Preparation of CMC edible film: A certain concentration (3%) of Carboxy Methyl Cellulose (CMC), was prepared by dissolving CMC in distilled water with stirring.

Glycerol was added as Plasticizer (1%). The prepared solutions were poured into a petri dish and dried in laboratory oven at 50°C for 24 h after which CMC films were peeled off manually.

Preparation of gelatin edible film: Gelatin films were prepared by first dissolving 2% (w/w) gelatin in distilled water at 60°C for 1 h. Glycerol was added as Plasticizer (1%). The prepared solutions were poured into a petri dish and dried in laboratory oven at 50°C for 24 h after which CMC films were peeled off manually.

Preparation of smart film: Low density poly ethylene in-cooperated with (linear low density polyethylene, medium density polyethylene, Antifug, ethylene absorber (nanoparticle size) and barrier modifier was prepared as Poly ethylene pellets using twin screw extruder in cooperation with El Qadesya company and compared with imported smart film.

Thickness measurements: Film thickness was determined using a hand-held digital micrometer (Mitutoyo, Model MDC-25S, resolution 0.001 mm, USA). Measurements were carried out at 8 different film locations and the mean thickness value was used to calculate the permeability of the films.

RESULTS AND DISCUSSION

The procedure of the Test was done as follows: The upper chamber was perfused with nitrogen gas and the bottom chamber was perfused with the testing gas (O₂/CO₂) before the measurement. The time of the perfusion has to be at least 15-30 min and it prolong if the material is less permeable. The supply of the testing gas is stopped after the perfusion and all valves of the both chamber are closed. The diffusion of the gas between both chambers is in progress for 15-30 min till equilibrium. The permeation process can be described mathematically by Fick 's first law. The flux (J):

$$J = D \frac{\delta C}{\delta X} \tag{1}$$

Where

- J = The flux, the net amount of solute that diffuses through unit area per unit time (g/m².sec)
- D = The diffusivity (m²/sec)
- C = The concentration of the diffusing substance (%) and
- X = The thickness of the film (m) (Larsen *et al.*, 2000)

With the two assumptions that Eq. 1 the diffusion is in a steady state and Eq. 2 the diffusivity is constant, the flux (J) is given by:

Table 1: Conditions of measurement using permeation cell

Symbols	Units	Quantity	Description
V_c	m^3	0.00023	Volume of bottom and top chamber
d	m	0.08	Diameter of film sample
A	m^2	0.005	Area of film sample

$$J = D(C_1 - C_2)/X = Q/(A.T) \quad (2)$$

Where:

Q = The Quantity of gas diffused through the film (m^3)

A = Area of the film (m^2) and t is the time (day)

Therefore gas permeability is determined on the base of the following Eq. 3 (Garcia *et al.*, 2000):

$$GP = \frac{d}{A} \times \frac{\Delta V}{\Delta t} \times \frac{1}{\Delta P} \quad (3)$$

Where:

GP = The permeability of gas ($m^3/m.day.mmHg$)

ΔP = The pressure difference between the two sides of the film (mmHg)

$\Delta V/t$ = The constant rate of the gas diffusing through the film

A = The permeability area

d = The average thickness of the film

Permeability was obtained from the increasing of concentration of the gas permeated through the film to the calibrated volume (v) in a time (t):

$$V_c = \pi r_c^2 h \quad (4)$$

$$V_g = C.V_c \quad (5)$$

$$A_f = \pi r_f^2 \quad (6)$$

$$P_g = C \times P_i \quad (7)$$

Where:

V_c = Volume of permeation cell (m^3)

r_c = Radius of permeation cell (m)

h = Height of permeation cell (m)

C = Concentration of gas (%)

P_g = Partial pressure of gas (mmHg)

P_i = Pressure inside the cell (mmHg)

Conditions of measuring gas permeability: The conditions of measuring gas permeability (volume of stainless steel chambers, diameter of each cell and area for the required film) using permeation cell were shown in Table 1 (Larsen *et al.*, 2000).

Gas permeability of different Edible Films: The dependence of the oxygen and carbon dioxide volume

Table 2: Gas permeability of edible films

Samples	CMC	Gelatin
Thickness (μm)	11.2	14.7
O_2 permeability ($m^3.mm/m^2.day.mmHg$)	9.034×10^{-8}	1.036×10^{-8}
CO_2 permeability ($m^3.mm/m^2.day.mmHg$)	1.001×10^{-9}	4.25×10^{-10}

Table 3: Gas permeability of smart films

Sample	Imported smart film	Local smart film
Thickness (μm)	150	130
O_2 permeability ($m^3.mm/m^2.day.mmHg$)	5.28×10^{-5}	4.57×10^{-5}
CO_2 permeability ($m^3.mm/m^2.day.mmHg$)	7.488×10^{-6}	9.3×10^{-6}

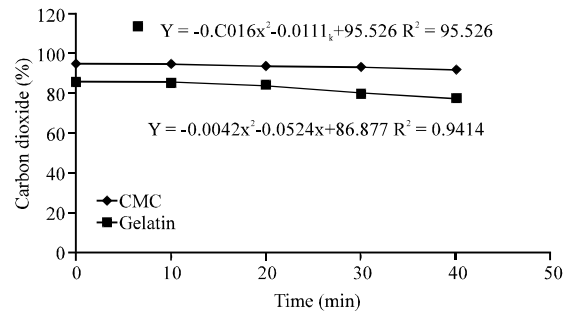


Fig. 3: Carbon dioxide evolution of CMC and gelatin film as a function of time

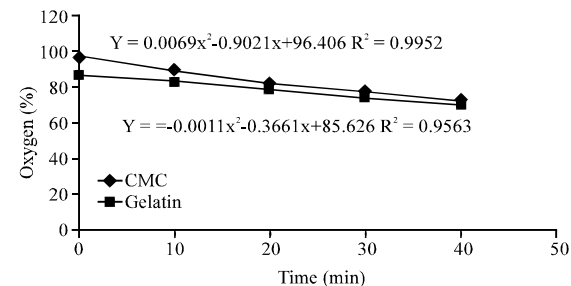


Fig. 4: Oxygen evolution of CMC and gelatin film as a function of time

concentration on time in the bottom chamber during the test as shown in Fig. 3 and 4, Gas permeability was calculated using Eq. 3, the values of permeability were compared with the data obtained from OTR instrument and the data from the literature. The accuracy of the developed method depends on the accuracy of measurement of oxygen and carbon dioxide concentrations, also, depends on the applied theoretical method. Gas permeability for edible film was shown in Table 2.

Gas permeability of smart films: Table 3 shows the gas permeability of imported and local smart film. The results observed that thickness of imported smart film was higher

than that of local produced film, also, the Oxygen permeability of imported smart film was higher than local film while carbon dioxide permeability local smart film was higher than imported one as gas permeability strongly depends on the interaction between the polymer matrix and the permeating gas (Garcia *et al.*, 2000).

CONCLUSION

The design of permeation cell was modified to measure the gas permeability of edible and smart films. The measurements and the calculations of the permeability were modified and personal access was applied. The results observed that the designed equipment is suitable of measurement of gas permeability but the measurement of the gas concentration will be needed. Oxygen and carbon dioxide measurements were compared with the OTR instrument and other researches. The accuracy of the developed method depends on the accuracy of measurement of oxygen and carbon dioxide concentrations, also depends on the applied theoretical method. Also, the oxygen permeability of imported smart film was higher than local film while carbon dioxide permeability local smart film was higher than imported one as gas permeability strongly depends on the interaction between the polymer matrix and the permeating gas.

ACKNOWLEDGEMENTS

This research was supported by STDF (10489) for the production and evaluation of the first smart film produced in Egypt with the cooperation of El-Kadysia company to enhance shelf life of fruit and vegetables during exporting. Also, the developed permeation cell was manufactured with the support of STDF and under supervision of Food Engineering and Packaging Department.

REFERENCES

- Baldwin, E.A., M.O. Nisperos-Carriedo and R.A. Baker, 1995. Use of edible coating to preserve quality of lightly (and slightly) processed products. *Critical Rev. Food Sci. Nutr.*, 35: 509-524.
- Garcia, M.A., M.N. Martino and N.E. Zaritzky, 2000. Lipid addition to improve barrier properties of edible starch-based films and coatings. *J. Food Sci.*, 65: 941-944.
- Gennadios, A. and C.L. Weller, 1990. Edible films and coatings from wheat and corn proteins. *Food Technol.*, 44: 63-69.
- Larsen, H., A. Kohler and E.M. Magnus, 2000. Ambient oxygen ingress rate method-an alternative method to Ox-Tran for measuring oxygen transmission rate of whole packages. *Packag. Technol. Sci. Intl. J.*, 13: 233-241.
- Lopez-Rubio, A., E. Almenar, P. Hernandez-Munoz, J.M. Lagaron and R. Catala *et al.*, 2004. Overview of active polymer-based packaging technologies for food applications. *Food Rev. Intl.*, 20: 357-387.
- Robertson, G.L., 1993. *Food Packaging Principles and Practice*. Marcel Dekker, New York, USA., Pages: 676.
- Salman, S.S.S., 2013. Preparation and characterization edible film packaging from carrageenan. *Proceedings of the Conjunction 3rd and 2nd Annual International Conference on Syiah Kuala University (AIC Unsyiah) and Multidisciplinary Research (ICMR)*, October 2-4, 2013, AICS, Banda Aceh, Indonesia, pp: 44-50.
- Sugiyama, N., Y. Kakuda, Y. Kimura and K. Takeuchi, 2006. Study on influence of residual oxygen on food deterioration. *J. Eng. Sci.*, 5: 134-137.
- Wu, Y., C.L. Weller, F. Hamouz, S.L. Cuppett and M. Schnepf, 2002. Development and application of multicomponent edible coatings and films: A review. *Adv. Food Nutr. Res.*, 44: 347-394.