Comparison of New Dynamic Accumulation Method for Measuring Oxygen Transmission Rate of Packaging against the Steady-State Method Described by ASTM D3985

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A new dynamic accumulation method for measuring the oxygen transmission rate (OTR) of packages and packaging films using robust and inexpensive fluorescence oxygen sensing technology has been developed. The method allows for oxygen to transfer through a given area of packaging or sample film and accumulate over time. The test volume incorporates a fluorescence-based oxygen sensor that does not consume oxygen and therefore does not interfere with the real-time measurement of oxygen concentration. The new method was tested against a widely used, commercially available instrument (Mocon Oxtran 2/20; Mocon, Inc., Minneapolis, MN, USA) designed around the steady-state gas permeation measurement approach described by ASTM D3985. Sample films were chosen to provide comparison over several orders of magnitude of OTR. Specifically, sample films with OTR values in the range of 10^1, 10^3 and 10^4 ml O_2/m^2/day were measured, and results using the two methods were compared. Results showed that the new dynamic accumulation method provides comparable results with the steady-state method (ASTM D3985). Copyright © 2012 John Wiley & Sons, Ltd.

INTRODUCTION

Knowledge of the gas transmission properties of packaging materials is critical for a successful package design. Oxygen transmission rate (OTR) is one of the most important of the gas transmission properties. OTR is often quoted as a material specification and is provided as a relative value on the basis of standard test conditions of 23 °C normalized to 1 atm partial pressure difference. A method to measure OTR is described by ASTM D1434,[1] in which a sample forms a sealed barrier between two chambers, a chamber initially containing pure oxygen and an oxygen-free chamber. The pressure or volume of the oxygen receiving chamber is monitored over time, and the OTR is determined from the change in volume or pressure. This method has been used by several researchers, including George *et al*.,[2] Laohakunjit and Noomhorm[3] and Raj *et al*.,[4] but is experimentally difficult and not considered as accurate as other methods. One of the most popular methods for measuring OTR is ASTM D3985,[5] which is used by many researchers, including Brennan *et al*.,[6] Dufrense *et al*.,[7] Kim *et al*.[8] and Mexis *et al*.[9] ASTM D3985 is considered to be a steady-state, isostatic method using a coulometric sensor. Commercially available instruments have been developed around ASTM D3985 and are available from several vendors, including Illinois Instruments (Johnsburg, IL, USA) and Mocon, Inc. (Minneapolis,

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MN, USA). The steady-state method involves the measurement of trace amounts of oxygen in a steady stream of oxygen-free carrier gas, which requires an extremely sensitive oxygen sensor capable of providing a sufficient signal-to-noise ratio.

Measuring OTR using the isostatic, steady-state method involves a permeation cell in which the sample material separates two chambers. Gases at similar absolute pressures and flow rates pass on either side of the sample film. An oxygen-rich gas, typically air or pure oxygen, passes on one side of the sample, while an oxygen-deficient carrier gas, such as nitrogen, passes on the opposite side. Oxygen permeates from the side with high concentration, through the film and into the oxygen-deficient carrier gas stream. After leaving the sample chamber, the carrier gas passes through a coulometric oxygen sensor to measure the oxygen concentration in the carrier gas. OTR is estimated using the carrier gas flow rate, the concentration of oxygen in the carrier gas and the sample permeation area. Because the absolute pressure is the same on both sides, the method is called *isostatic*, and because the oxygen concentration gradient is always constant, the method is called *steady state*. This isostatic, steady-state process is depicted in Figure 1.

Another method, called *dynamic accumulation* (DA), was recently described by Abdellatief and Welt.[10] Other attempts at using DA have been described by Ghosh and Anantheswaran,[11] Kim et al.[12] and Moyls et al.,[13,14] but these methods differed in that gas samples were removed from the permeation chamber for analysis, which can be detrimental to the measurement. Siro et al.[15] recently described a method similar to Abdellatief and Welt,[10] but with a linear approximation to the exponentially asymptotic behaviour displayed in the accumulation chamber.

Briefly, DA involves the measurement of the rate of change of oxygen concentration in the chamber or package. In previous applications of DA, researchers periodically withdrew gas from the accumulation chamber and measured oxygen via gas chromatograph. Withdrawing gas from the accumulation chamber is not desirable because each sample collected changes the conditions of the experiment. Moyls et al.[13] withdrew few and small samples in an attempt to minimize errors due to sampling. Ghosh and Anantheswaran[11] restarted tests after each sample was collected, resulting in very long test times.

Recent advances in fluorescence-based oxygen measurement have created an opportunity for improving the DA method for measuring OTR.[16] Fluorescence oxygen measurement combined with optical fibre probes provides the ability to measure oxygen nondestructively. Therefore, oxygen measurements may be made *in situ* throughout an experiment.

A DA permeation cell is depicted in Figure 2. We use air or oxygen on the opposite side of the accumulation chamber at a flow rate of approximately one chamber volume per minute (~5–10 ml/min) to maintain a constant concentration on the oxygen-rich side of the sample. In some instances, a small air pump may be used, or the bottom chamber may be removed to expose the sample to air. Commercially available DA permeation cells are available (e.g. Oxysense, Inc., Dallas, TX, USA).
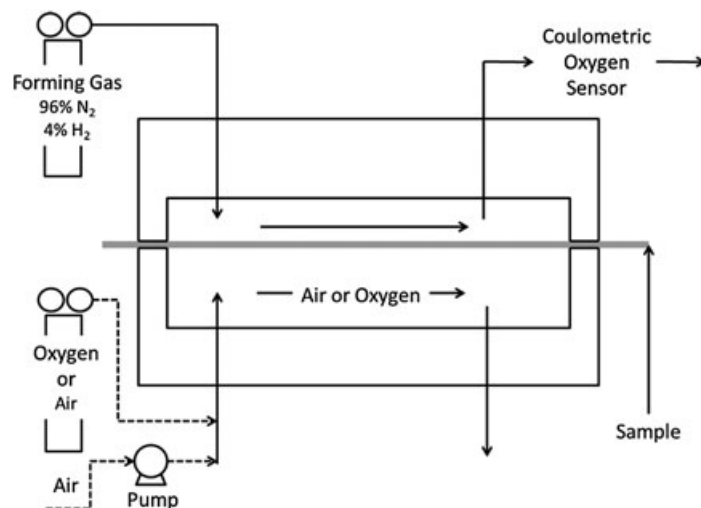

Figure 1. Isostatic, steady-state method for measuring OTR as described by ASTM D3985.
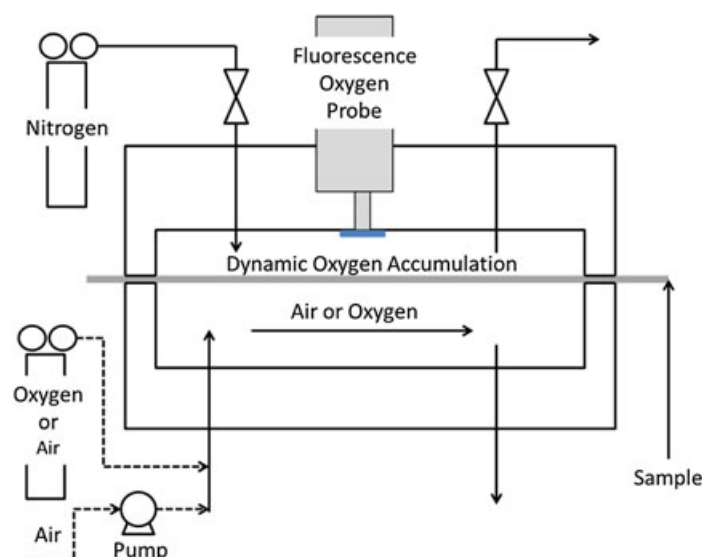
Figure 2. DA permeation cell.

Nitrogen is used to purge the sensor side of the DA permeation cell. Although the cell need not be completely purged of oxygen to run a test, complete purging provides an opportunity to calibrate the fluorescent oxygen probe at two known levels, namely, in air before purging (~20.9% oxygen) and at 0% oxygen after purging. During purging, nitrogen flow rate is typically raised to a level that is sufficiently high to purge quickly, but not so high that excessive pressure might stretch and damage the sample. In our permeation cell, 50 to 100 ml/min for approximately 3 to 5 min has been found to be convenient and to provide good purge performance. In contrast to the steady-state method, once purged, chamber valves are closed and nitrogen is shut off for the duration of the test. If sensor calibration is not required before a test, a successful test may be run even if the chamber is only partially purged before starting. Our DA chamber volume is approximately 8.3 ml, so very little gas is required to achieve a complete purge; hence, complete purging is our common practice. However, the DA method may also be applied to the case of actual packages in which the package itself becomes the accumulation chamber. When package volume is large, partial purging and/or inert void filling may be justified.

Fluorescence oxygen measurement is a nondestructive optical method for measuring oxygen. Any fluorophore that is quenched by oxygen may be used as the oxygen measurement probe. Typically, fluorophore is dissolved in a polymer matrix and either attached or presented to an optical fibre connected to both a light source and a detector. A light source excites the fluorophore, which emits a fluorescent response at another wavelength. Because of their simplicity, stability, light purity, ruggedness, longevity and relatively low cost, LED light sources are most commonly found in commercial instruments. Because oxygen quenches the fluorescent response, fluorescence intensity or decay constant may be reliably calibrated to oxygen concentration. When intensity is used, attenuation through the entire light path is important to the measurement (Figure 3A). The use of decay constant provides a more robust means of measurement and permits the separation of the fluorescent compound from the light source, which allows for measurement through an optically clear window for the case of a permeation chamber or nondestructively through the wall of an optically clear package (Figure 3B). Otherwise, an optical fibre tip may be coated with the fluorescent compound and mounted in a permeation chamber or package through a gas-tight fitting (Figure 3A).

Comparison of DA and steady-state (ASTM D3985) methods

For the steady-state approach (ASTM D3985), each reading represents an independent observation of the final result so long as the system has reached a steady-state condition. Because there is no convenient
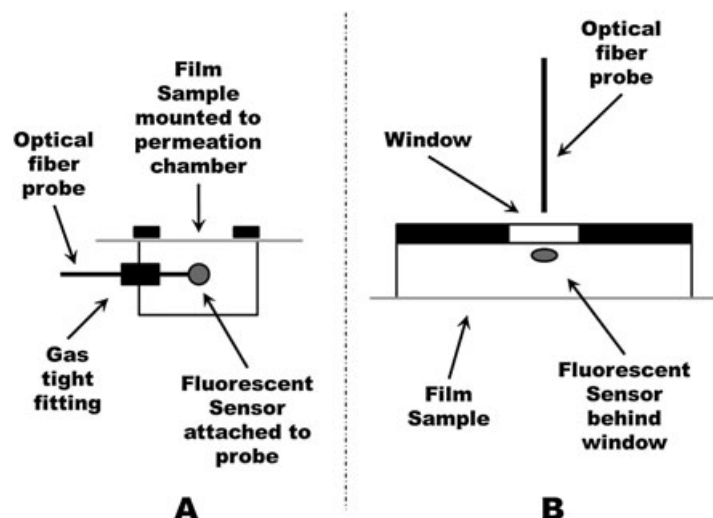
Figure 3. Fluorescent probes based on intensity (A) and decay constant (A or B).

way to know when the system reaches steady state, researchers typically make many observations and arbitrarily stop experiments when consecutive results seem to be sufficiently similar. For the DA approach, each experimental result relies on multiple observations that describe the trend of dynamically changing oxygen concentration, which is also inherently proportional to OTR. The method is robust because random measurement errors or noise cancels itself on the trend line, and each observation adds confirmation and statistical confidence in the final result. These fundamental differences lead to very different sensor performance requirements between the two approaches. Very sensitive sensors are required for the steady-state approach because it relies on instantaneous measurements of trace concentrations of oxygen in the carrier gas. Because the DA approach relies on the rate of change of oxygen concentration rather than one extremely low concentration, sensors with much less sensitivity may be used. In this work, fluorescence sensors capable of resolving 0.05% oxygen were used for DA OTR measurements (Oxysense Inc.). As barrier properties of samples increase, the steady-state method requires increasingly sensitive sensors to achieve sufficient signal-to-noise performance. In practice, measurement noise increases substantially for the steady-state method as sample OTR decreases, reducing confidence in results. There is no such issue with the DA method; however, for DA-based measurements, experimental time increases as OTR decreases. Experimental time also tends to increase with decreasing OTR for the steady-state approach, but only because it takes longer to reach steady state in materials with greater barrier properties, and it also tends to take longer to more thoroughly purge instruments after samples are mounted to protect coulometric sensors from excessive oxygen exposure. Therefore, robust low-cost sensors may be successfully used for the DA method, whereas relatively expensive and sensitive sensors are generally required for the steady-state method.

Another important operational comparison between the steady-state method and the DA method is in the consumption of gas and sensors. The steady-state method requires flowing gas throughout experiments. When not in use, instruments designed around the steady-state principle typically require a constant flow of purge gas to protect sensitive sensors from atmospheric oxygen. For steady-state instruments designed for high-barrier films with extremely sensitive sensors, special mixtures of purge gas that contain a few percent hydrogen are recommended to catalytically remove trace amounts of oxygen in the purge gas itself (Figure 1). As these sensors are continuously consumed by exposure to oxygen, performance declines until sensor replacement is required. Replacing coulometric sensors typically requires specially trained service technicians or service at the manufacturer. For the DA method using fluorescence-based sensors, sensor cost is extremely low, sensor life is very long and sensors do not need to be constantly protected from oxygen with an oxygen-free purge gas when not in use. Fluorescence sensors are easily replaced in the field often by applying a premade fluorescence sensor 'dot' (OxyDot; Oxysense, Inc.) to the glass window of the permeation chamber using

optically clear, two-sided tape (e.g. 3M 665, Scotch Double Sided Tape; 3M, St Paul, MN, USA). The DA method does not require expensive gas blends and can be performed with industrial-grade nitrogen available from any commercial gas. The DA method consumes very little gas as compared with the steady-state method. Purge gas is needed to start an experiment by purging the oxygen accumulation chamber, but once purged, the chamber is sealed, and no additional gas is required. However, for the oxygen-rich side of the film sample, researchers may choose to use industrial-grade compressed air, pump air or oxygen. Flow rates need only be barely positive to maintain oxygen concentration when applying gas to the oxygen-rich side of the film sample (Figure 2).

Because the DA method does not require flowing gasses to make a measurement, the method is also useful for measuring samples with perforations, such as microperforated films. The steady-state method (ASTM D3985) is not suitable for measuring OTR of perforated films.

Coulometric sensors used in the steady-state method may be damaged by condensation when operated at temperature lower than $10\,^{\circ}C$ and then brought back to warmer temperatures. This is particularly problematic for many refrigerated or frozen food and pharmaceutical packaging applications.[10] Fluorescent-based oxygen sensors are capable of measuring oxygen in gas and liquid phases, so there is no risk from damage due to condensation when exposed to changing temperatures. In fact, fluorescence-based oxygen sensors are routinely used by environmental scientists to measure dissolved oxygen concentrations in lake and sea floor sediments.

The purpose of this work was to compare OTR measurements made using both steady-state and DA methods. For this study, films were selected from our laboratory stock to provide OTR values over a wide range (10^1–10^3 ml O_2/m^2/day). Film materials, specific film constructions and/or film vendors were not recorded or reported because this comparative study can be repeated with any particular film samples.

Determining OTR from the DA model

OTR is estimated from data collected during DA experiments using the following model that was developed starting from the well-known relationship used to describe gas permeation through packaging films (Equation (1)):

$$\frac{dn_{O_2}}{dt} = \frac{\bar{P}_{O_2}A}{l}\left(p_{O_2}^{ambient} - p_{O_2}^{t}\right) \tag{1}$$

where n is the moles of oxygen, $\bar{P}_{O_2}$ is the permeation coefficient of the permeant gas through the film, A is the sample's permeation area, l is the sample film thickness, $p_{O_2}^{ambient}$ is the partial pressure of oxygen on the oxygen-rich side of the sample and $p_{O_2}^{t}$ is the partial pressure of oxygen in the DA chamber at time, t. Equation (1) describes the rate at which oxygen permeates through a sample of known area and thickness under a driving force defined by the partial pressure difference on either side of the sample.

When using oxygen (or air) and nitrogen, it has been shown that it may be safely assumed that the volume of the sensor side of the permeation chamber remains constant throughout the measurement (e.g. rates of transfer of oxygen and nitrogen into and from the chamber are similar).[10] If permeation rates of the opposing gases are not similar, as might be the case for carbon dioxide and oxygen, then bulging of the sample could occur, which would change chamber volume and/or pressure, and if extreme, could damage the sample. In our experience using oxygen and nitrogen, bulging has never been observed, and any slight differences in permeation rates between the two gases have been deemed to be insignificant. With volume and pressure constant, oxygen partial pressure is directly related to moles of oxygen via Equation (2):

$$p_{O_2} = \frac{n_{O_2}RT}{V_{total}} \tag{2}$$

where V_{total} is the total chamber volume (sensor side), R is the ideal gas law constant and T is the absolute temperature. The substitution of Equation (2) into Equation (1) yields

$$\frac{dp_{O_2}}{dt} = \frac{RT}{V_{total}} \cdot \frac{\bar{P}_{O_2}A}{l} \left(p_{O_2}^{ambient} - p_{O_2}^t \right) \tag{3}$$

Integrating Equation (3) from the beginning of the experiment ($t = 0$) to time, t, yields

$$\ln \left[\frac{\left(p_{O_2}^{ambient} - p_{O_2}^t \right)}{\left(p_{O_2}^{ambient} - p_{O_2}^0 \right)} \right] = \frac{RT}{V_{total}} \cdot \frac{\bar{P}_{O_2}A}{l} \cdot t \tag{4}$$

We refer to the bracketed ratio on the left-hand side of Equation (4) as the accomplished oxygen ratio (AOR). Initially, AOR is unity. As oxygen accumulates over time, AOR tends to zero. Equation (4) suggests that plotting the natural logarithm of AOR versus time should yield a straight line with a slope proportional to OTR. Converting from moles to conventional OTR units of cubic centimetres of O_2 at standard temperature and pressure (STP) yields Equation (5):

$$OTR = \frac{|Slope| V_{total}}{A} \tag{5}$$

When performed at 23 °C, the absolute value of the slope from a plot of the natural logarithm of AOR versus time and Equation (5) provides the standard OTR value used to specify oxygen transmission performance of packaging materials.

MATERIALS AND METHODS

Three commercially produced film samples were selected from laboratory film stock to provide a broad range of OTR for measurement comparisons. Because this comparative measurement study can be repeated with any available film sample, film suppliers and film constructions were not recorded here. For our purposes, films were labelled in a relative sense as 'high barrier,' 'medium barrier' and 'low barrier' according to the expected approximate OTR levels shown in Table 1.

ASTM D3985 (steady-state method)

Steady-state measurements were performed in accordance with ASTM D3985 using a Mocon Oxtran 2/20 (Mocon, Inc.). Temperature was set to 23 °C, and the instrument was set to convergence mode, which instructs the instrument to take readings until two consecutive readings differ by less than 5%. Six repetitions were made for the high-barrier film on our Oxtran 2/20 'MH' module (Mocon, Inc.), which is pretuned for higher barrier (low OTR) samples. Twelve measurements were made on the moderate and high transmitter films on our Oxtran 2/20 'ST' module (Mocon, Inc.), which is tuned for low-barrier (high OTR) samples.

DA method

Dynamic accumulation experiments were performed using permeation cells and fluorescence oxygen detection equipment from Oxysense, Inc. (Model 301). The oxygen accumulation chamber had a sample area of 16.62 cm^2 and a volume of 8.3 cm^3 as measured using water displacement weight. Initially, the cell was purged with industrial-grade compressed nitrogen. For the low-barrier film, the oxygen-enriched side was fed compressed air from our laboratory's air compressor. For the

Table 1. Target OTR ranges for test samples.

Description	Approximate OTR range (ml/m^2/day)
High barrier	10
Medium barrier	1 000
Low barrier	10 000

high-barrier and medium-barrier samples, industrial-grade oxygen was used. The oxygen concentration in the DA chamber was measured and recorded periodically during the test using a commercially available oxygen fluorescence sensor (Model 301; Oxysense, Inc.). OTR was subsequently calculated as described previously.

Temperature control was achieved using a shelf-top mini-refrigerator (NuCool Model C-RNU281VS; Haier America Trading, LLC, NY, USA) equipped with a 100 W light bulb controlled by a PID temperature controller (Omega Model CSC32; Omega Engineering, Inc., Stamford, CT, USA). The PID controller was set to 23 °C and was capable of controlling temperature to ± 0.2C°.

RESULTS AND DISCUSSION

Figure 4 shows a typical experimental response using the DA method. It confirms the expectation provided by Equation (4), which suggested a straight line from a plot of natural log of accomplished oxygen concentration ratio versus time.

Results from OTR measurements using both methods are summarized in Table 2. Mean results were tested for differences at the 95% CI. Results of the means tests are shown in Table 3.

Tables 2 and 3 show that there are no differences at a 95% CI in the average OTR of the films measured by both the DA method using a fluorescence oxygen sensor and the steady-state method using a coulometric sensor.

Because the DA method measures an increase in oxygen concentration in a sealed chamber, the method requires considerably less gas to perform a test than the steady-state method. Fluorescence oxygen sensors are relatively inexpensive compared with coulometric sensors, and although fluorescence sensors offer less sensitivity and resolution than coulometric sensors, the DA method calculates a response based on the trend (slope of a the curve) of accumulation rather than on any one instantaneous measurement as with the steady-state method. Therefore, the DA method is capable of delivering results of similar accuracy as the steady-state method.
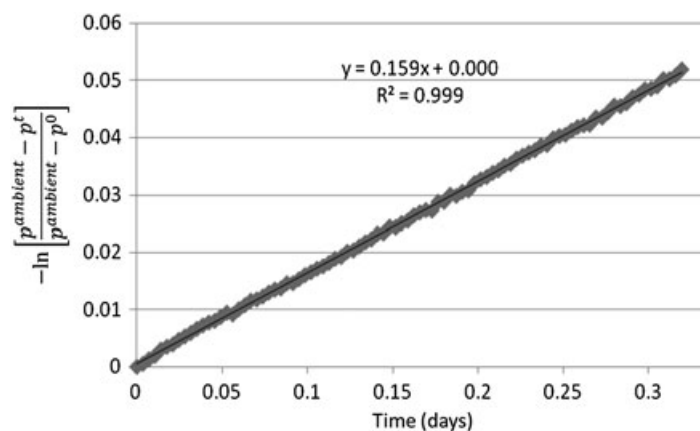

Figure 4. Typical data trace for DA test (OTR = 794 ml/m^2/day).

Table 2. Measured OTR values using DA and steady-state methods.

Description	Samples (n)	DA (ml/m^2/day)		Steady state (ml/m^2/day)	
		OTR	$\pm$95 CI	OTR	$\pm$95 CI
High barrier	6	6.8	0.5	7.4	0.3
Medium barrier	12	840	30	780	70
Low barrier	12	9700	200	9600	700

Table 3. 95% CI on differences of means between the DA and the steady-state Methods.

| | Samples (n) | $\mu_{DA} - \mu_{steady\ state}$ (ml/m^2/day) | | |
		Lower bound (95% CI)	Mean differences	Upper bound (95% CI)
High barrier	6	−1.3	−0.6	0
Medium barrier	12	−31	60	140
Low barrier	12	−660	100	950

Results show no difference in using both methods at the 95% CI level.

CONCLUSION

Experiments show that results using the new DA method for measuring OTR compare well with the results using the widely accepted isostatic, steady-state method described by ASTM D3985. Because fluorescence oxygen sensors are less expensive than coulometric sensors and the DA method uses less gas and does not require specialty gases such as hydrogen containing forming gas, it is likely that the DA method offers an opportunity to perform OTR measurements at lower cost than the widely accepted steady-state method described by ASTM D3985. The rugged and robust nature of fluorescence-based OTR instruments suggests the possibility for broader and deeper penetration of OTR measuring capability in various packaging industries.

ACKNOWLEDGEMENTS

REFERENCES

1. ASTM D-1434 Standard Test Method for Determining Gas Permeability Characteristic of Plastic Film and Sheeting. 2009.
2. George J, Kumara R, Sajeevkumara VA et al. Effect of gamma-irradiation on commercial polypropylene based mono and multi-layered retortable food packaging materials. *Radiation Physics and Chemistry* 2007; **76**(7): 1205–1212.
3. Laohakunjit N, Noomhorm A. Effect of plasticizers on mechanical and barrier properties of rice starch film. *Starch-Starke* 2004; **56**(8): 348–356.
4. Raj B, Jagadish RS, Srinivas P, Siddaramaiah. Crosslinking of low-density polyethylene by diisocyanates for superior barrier properties. *Journal of Applied Polymer Science* 2005; **96**(4): 1193–1199.
5. ASTM D-3985 Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor. 2010.
6. Brennan DJ, Haag AP, White JE, Brown CN. High-barrier poly(hydroxy amide ethers): Effect of polymer structure on oxygen transmission rates. *Macromolecules* 1998; **31**(8): 2622–2630.
7. Dufresne I, Smith JP, Liu JN et al. Effect of films of different oxygen transmission rate on toxin production by Clostridium botulinum type E in vacuum packaged cold and hot smoked trout fillets. *Journal of Food Safety* 2000; **20**(4): 251–268.
8. Kim JG, Luo Y, Tao Y, Saftner RA, Gross KC. Effect of initial oxygen concentration and film oxygen transmission rate on the quality of fresh-cut romaine lettuce. *Journal of the Science of Food and Agriculture* 2005; **85**(10): 1622–1630.
9. Mexis SF, Kontominas MG. Effect of oxygen absorber, nitrogen flushing, packaging material oxygen transmission rate and storage conditions on quality retention of raw whole unpeeled almond kernels (*Prunus dulcis*). *LWT- Food Science and Technology* 2010; **43**(1): 1–11.
10. Abdellatief A, Welt BA. Method for Measuring the Oxygen Transmission Rate of Perforated Packaging Films. *Journal of Applied Packaging Research* 2009; **3**(3): 161–171.
11. Kim JG, Luo YG, Gross KC. Effect of package film on the quality of fresh-cut salad savoy. *Postharvest Biology and Technology* 2004; **32**(1): 99–107.
12. Abdellatief A, Welt BA. Modified atmosphere packaging for fresh-cut produce with microperforated films. *Journal of Applied Packaging Research* 2007; **2**(1): 1–14.
13. Ghosh V, Anantheswaran RC. Oxygen Transmission Rate through Micro-Perforated Films: Measurement and Model Comparison. *Journal of Food Process Engineering.* 2001; **24**(2): 113–133.
14. Moyls L, Hocking R, Beveridge T, Timbers G. Exponential decay method for determining gas transmission rate for films. *Transactions of ASAE* 1992; **35**(4): 1259–1265.
15. Moyls AL. Whole bag method for determining oxygen transmission rate. *Transactions of ASAE* 2004; **47**(1): 159–164.
16. Siro I, Plackett D, Sommer-Larsen P. A Comparative Study of Oxygen Transmission Rates through Polymer Films Based on Fluorescence Quenching. *Packaging Technology and Science* 2010; **23**(6): 302–315.