ผลกระทบของความชื้นสัมพัทธ์ต่อค่าการซึมผ่านแก๊สของฟิล์มพลาสติกชีวภาพ: การบ่งชี้ถึงอายุการเก็บรักษาเห็ดฟางในบรรจุภัณฑ์ดัดแปลงบรรยากาศ

นางสาวนภพรรณ คุณานุสนธิ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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EFFECT OF RELATIVE HUMIDITY ON GAS PERMEATION OF BIOPLASTIC FILMS: INDICATION ON SHELF LIFE OF STRAW MUSHROOMS STORED IN MODIFIED ATMOSPHERE PACKAGING

Miss Nappaphan Kunanusont

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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Thesis Title	EFFECT OF RELATIVE HUMIDITY ON GAS PERMEATION OF BIOPLASTIC FILMS: INDICATION ON SHELF LIFE OF STRAW MUSHROOMS STORED IN MODIFIED ATMOSPHERE PACKAGING
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นภพรรณ คุณานุสนธิ์ : ผลกระทบของความชื้นสัมพัทธ์ต่อค่าการซึมผ่านแก๊สของฟิล์มพลาสติกชีวภาพ: การบ่งชี้ถึงอายุการเก็บรักษาเห็ดฟางในบรรจุภัณฑ์ดัดแปลงบรรยากาศ. (EFFECT OF RELATIVE HUMIDITY ON GAS PERMEATION OF BIOPLASTIC FILMS: INDICATION ON SHELF LIFE OF STRAW MUSHROOMS STORED IN MODIFIED ATMOSPHERE PACKAGING) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. อนงค์นาฏ สมหวังธนโรจน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: อ. ดร. อภิตา บุญศิริ, 78 หน้า.

งานวิจัยนี้สนใจศึกษาผลกระทบของความชื้นต่อการซึมผ่านแก๊สของฟิล์มพลาสติก 3 ชนิด คือ ฟิล์มยืดอายุทางการค้าพอลิเอทิลีนความหนาแน่นต่ำ (bLDPE) พอลิแลคติคแอซิด (PLA) และ พอลิแลคติคแอซิดดัดแปร (mPLA) ซึ่งเป็นฟิล์มพลาสติกที่ใช้ในการเก็บรักษาเห็ดฟางในงานวิจัยของดร.อภิตา บุญศิริ และคณะ (2012) โดยการเก็บรักษาเห็ดฟางในถุง bLDPE, PLA และ mPLA สามารถยืดอายุเห็ดฟางจาก 1 วันเป็น 4, 6 และ 6 วันตามลำดับ เนื่องจากค่าการซึมผ่านก๊าซออกซิเจน (OTR) ของ bLDPE มีค่ามากกว่า PLA และ mPLA จึงเกิดข้อสงสัยว่าเหตุใด bLDPE ที่มี OTR สูงกว่าสามารถยืดอายุเห็ดฟางได้ระยะเวลาสั้นกว่า เนื่องจากเห็ดฟางถูกเก็บรักษาที่อุณหภูมิ 15°C และความชื้นสัมพัทธ์ร้อยละ 90 จึงเกิดสมมติฐานว่าความชื้นอาจทำให้ฟิล์ม PLA และ mPLA มี OTR สูงขึ้นจนมากกว่า bLDPE จึงทำให้เก็บเห็ดฟางได้นานกว่า ผลการทดลองวัดการซึมผ่านก๊าซออกซิเจน (OTR) ด้วยวิธีสภาวะคงตัว (Steady state) ที่อุณหภูมิ 23°C และความชื้นสัมพัทธ์ร้อยละ 0, 40, 60, 80 และ 90 ตามลำดับ พบว่า OTR ของ bLDPE และ PLA มีค่าไม่เปลี่ยนแปลงตามความชื้นสัมพัทธ์ ขณะที่ OTR ของ mPLA มีค่าเพิ่มขึ้นกว่าสองเท่าจาก 1,069.3 cc/m^2 day ที่ 0%RH เป็น 2,561.1 cc/m^2 day ที่ 40%RH และมีค่าค่อนข้างคงที่เมื่อระดับความชื้นสัมพัทธ์สูงขึ้น ทั้งนี้เนื่องจาก mPLA มีความมีขั้วสูงเมื่อเทียบกับ PLA และ bLDPE ซึ่งสามารถดึงไอน้ำเข้าไปทำหน้าที่เป็นสารเสริมสภาพพลาสติก (plasticizer) ทำให้มีช่องว่างในเนื้อฟิล์มเพิ่มขึ้นทำให้ก๊าซซึมผ่านได้สะดวกขึ้น การวัดการซึมผ่านก๊าซของฟิล์มทั้งสามชนิดที่อุณหภูมิ 15°C และความชื้นสัมพัทธ์ร้อยละ 90 โดยใช้วิธีสภาวะไม่คงตัว (Unsteady state) พบว่า OTR และการซึมผ่านของคาร์บอนไดออกไซด์ (CO_2TR) ของ bLDPE ยังคงมากกว่า PLA และ mPLA จากการคำนวณอัตราการหายใจของเห็ดฟางพบว่าอัตราการหายใจของเห็ดฟางที่เก็บในถุง bLDPE มีค่าสูงกว่าเห็ดฟางที่เก็บในถุง PLA และ mPLA ซึ่งอัตราการหายใจสูงกว่านี้ส่งผลเห็ดฟางคายน้ำมาก เนื่องจาก bLDPE มีค่าการซึมผ่านไอน้ำ (WVTR) เพียง 19.5 กรัมต่อตารางเมตรต่อวัน (gm/m^2 day) ซึ่งต่ำกว่า PLA และ mPLA ประมาณ 6 เท่า (120.9 and 132.9 gm/m^2 day, ตามลำดับ) ทำให้มีไอน้ำสะสมในถุงมาก เห็ดฟางจึงดูดซับน้ำกลับไปและกระตุ้นการย่อยสลายตัวเอง (Autolysis) ทำให้เน่าเสียเร็ว จึงเป็นสาเหตุที่ทำให้เห็ดฟางที่เก็บในถุง bLDPE มีอายุสั้นกว่าเมื่อเทียบกับเห็ดฟางที่เก็บในถุง PLA และ mPLA

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก	....
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KEYWORDS: STRAW MUSHROOM / MODIFIED ATMOSPHERE PACKAGING / RELATIVE HUMIDITY / GAS TRANSMISSION RATE

NAPPAPHAN KUNANUSONT: EFFECT OF RELATIVE HUMIDITY ON GAS PERMEATION OF BIOPLASTIC FILMS: INDICATION ON SHELF LIFE OF STRAW MUSHROOMS STORED IN MODIFIED ATMOSPHERE PACKAGING. ADVISOR: ASSOC. PROF. ANONGNAT SOMWANGTHANAROJ, Ph.D., CO-ADVISOR: APITA BUNSIRI, Ph.D., 78 pp.

This study was designed to study effects of humidity on gas transmission rate of the three films; commercial breathable low density polyethylene (bLDPE), poly(lactic acid) (PLA) and modified poly(lactic acid). These films were used in the study of Bunsiri and coworkers (2012) that extended shelf life of straw mushroom from one day to four, six and six days when bLDPE, PLA and mPLA were used respectively. With the findings that oxygen transmission rates (OTR) of bLDPE was twice higher than OTR of PLA and mPLA, a question arose why bLDPE with higher OTR had shorter shelf life. As the storage condition was at 15°C and 90%RH, an assumption was made that humidity might have increased OTR of PLA and mPLA to be higher than that of bLDPE. Our study measured OTR using steady state method at 23°C and 0, 40, 60, 80 and 90%RH and found that. OTR of bLDPE and PLA did not change when %RH increased while OTR of mPLA changed more than two folds from 1,069.3 cc/m^2 day at 0%RH to 2,561.1 cc/m^2 day at 40%RH. At %RH higher than 40% OTR of mPLA was quite stable. With higher polarity of mPLA than PLA and bLDPE, water was absorbed to plasticize mPLA and that had increased free volume so gas could permeate easier. Another set of equipment using unsteady state method was used to measure OTR and CO_2TR at 15°C and 90%RH and found OTR and CO_2TR of bLDPE also more than OTR of PLA and mPLA. Respiration rate of straw mushroom were calculated. It was also found that respiration rate of straw mushroom stored in bLDPE was higher than PLA and mPLA. Higher respiration rate resulted in higher transpiration of water. As water transmission rate (WVTR) of bLDPE was only 19.5 gm/m^2 day, around six times lower than PLA and mPLA (120.9 and 133 gm/m^2 day, respectively), water was accumulated in bLDPE packages and resulted in reabsorption and triggering of autolysis, which eventually caused quicker deterioration. These explained why bLDPE had shorter shelf life of straw mushrooms compared with PLA and mPLA.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2013	Co-Advisor's Signature	....

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Modified atmosphere packaging is a method to create an environment with lower oxygen and higher carbon dioxide concentration. Lower oxygen level reduces respiration and metabolism of fresh produces while higher carbon dioxide level prevents microbial growth and also helps reducing respiration of fresh produces. The lower respiration rate can result in longer shelf life of fresh produces[1, 2].

An experiment conducted by Bunsiri and coworkers in 2012 could extend shelf life of straw mushrooms from one to more than four days by keeping the mushrooms in plastic bags at 15°C and 90 percent relative humidity (%RH). Composition of gases in the plastic bags was determined by gas transmission through the plastic bag and respiration rate of fresh produce. The plastic bags that were used in the experiment were commercial breathable low density poly(ethylene) (bLDPE), poly(lactic acid) (PLA) and modified poly(lactic acid) (mPLA). The mPLA was a compound of PLA, natural rubber graft maleic anhydride (NR-g-MA) and hydrophilic particles to improve mechanical properties and for increased gas transmission rate[3]. Gas transmission rates of oxygen, carbon dioxide and water vapor through these films are illustrated in Table 1.1.

Shelf life of straw mushrooms was determined from number of days in which there is no any rot of mushrooms in the packages. From Figure 1.1, more than 80 percent of mushrooms stored in bLDPE were rotted after storage for four days while those stored in PLA and mPLA were rotten after storage for six days. This means shelf life of straw mushrooms in bLDPE, PLA and mPLA were four, six and six days, respectively. Although, PLA and mPLA could equally extend shelf life of straw mushrooms, the visual quality scores of mushrooms for mPLA were higher than those for PLA at day 6 as shown in Figure 1.2. In addition, the mPLA is preferred to PLA because it is convenient to use. With the anti-blocking additives, mPLA was easy-to-open. It also has better mechanical properties than PLA in the aspects of elongation at break, tensile toughness, and impact strength due to the presence of natural rubber.

Table 1.1 Gas transmission rates of bLDPE, PLA and mPLA films

Films	OTR* (cc/[m^2-day])	CO_2TR* (cc/[m^2-day])	WVTR** (gm/[m^2-day])	References
bLDPE	12,500	42,250	19.5	[4]
PLA	638	987	120.9	[3]
mPLA	5,569	1,300	132.9	[3]

*condition: 23°C, 0%Relative humidity

**condition: 37.8°C, 90%Relative humidity

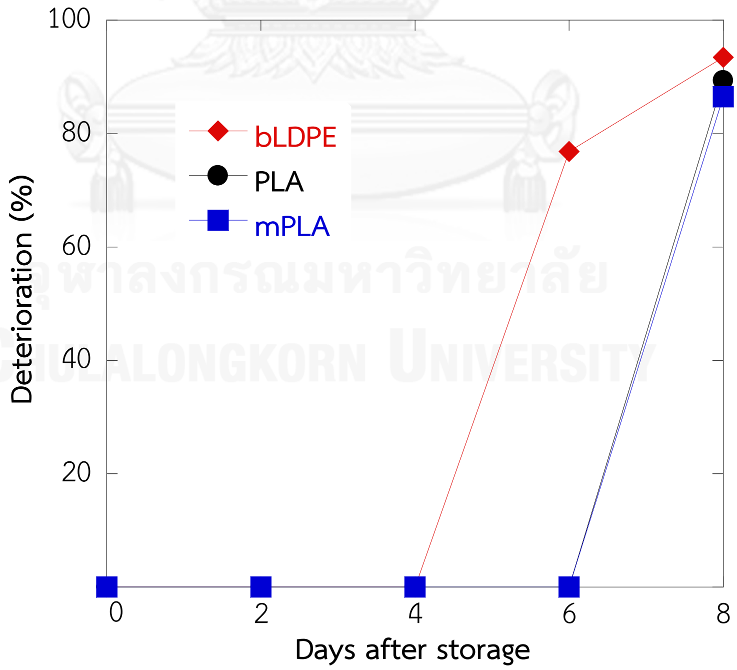


Figure 1.1 Percent of deterioration of straw mushrooms in package [3]

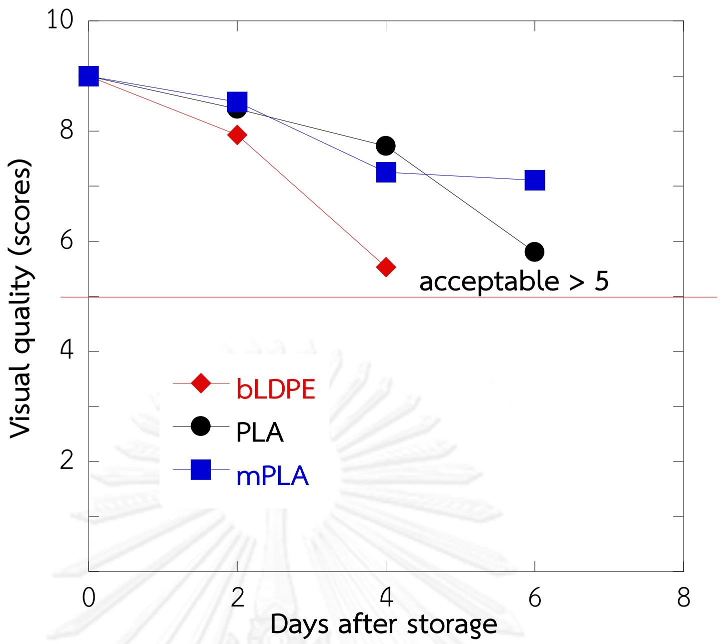


Figure 1.2 Visual quality scores of straw mushrooms in package [3]

This has raised a question why both PLA and mPLA could prolong shelf life of straw mushrooms longer than bLDPE. There are two assumptions for this work, i.e., gas transmission rate of PLA and mPLA might be higher than bLDPE at storage condition and different respiration rate of straw mushroom at different level of oxygen and carbon dioxide in each package.

Standard measurement of gas transmission rate was performed at temperature of 23°C and 0 percent relative humidity (%RH) as described in Table 1.1 while storage condition for prolong shelf life of straw mushroom was 15°C and 90%RH[3]. Temperature is positively correlated with gas transmission rate [5-7]. Humidity might be another determinant of gas transmission rate of these films. To assess effects of relative humidity on gas transmission rate of films, the OTRs of bLDPE, PLA and mPLA films were measured at various levels of relative humidity using oxygen transmission rate analyzer (OX-TRAN 2/21, MOCON) at Chulalongkorn University. Because this equipment has a preset fixed temperature of 23°C and does not provide measurement of carbon dioxide transmission rate, the facility at Kamphaengsaen Campus of Kasetsart University was used. Equipment at Kamphaengsaen Campus operates at different temperature and humidity and measurement of carbon dioxide transmission rate is also possible. A specially designed set of equipment was used to measure transmission rates of oxygen and carbon dioxide through mPLA, PLA and bLDPE films at different temperatures with 90%RH.

Oxygen and carbon dioxide levels in package are one of factor that affects respiration rates of fresh produces. Levels of gas composition are determined by gas transmission rate of package. Respiration rate of fresh produces can directly measure by various methods namely closed system and opened system[1, 2]. For straw mushrooms, there is only respiration rate of carbon dioxide reported in literature[8]. Another way to find respiration rate of straw mushrooms in package is calculated from mass balance of oxygen and carbon dioxide in package via modified atmosphere packaging modeling. The respiration rates of straw mushrooms at each storage day and each package were compared and discussed with the results from previous experiment.

For this research, effect of humidity on gas transmission rate of three films at various level of relative humidity and gas transmission rate at storage condition of prolonging shelf life of straw mushrooms were measured. Respiration rates of straw mushrooms in each package were also calculated using mass balance of modified atmosphere packaging modeling to answer the question why PLA and mPLA can prolong shelf life of straw mushroom longer than bLDPE.

1.2 Objectives

To study the effects of humidity on gas transmission rate of bioplastic films that subsequently affects shelf life of straw mushrooms stored in modified atmosphere packaging

1.3 Research Scopes

1.3.1 Explore the intrinsic properties of bLDPE, PLA and mPLA films

1.3.2 Measure oxygen transmission rate of films at 23°C and 0, 40, 60, 80 and 90%RH using oxygen transmission rate analyzer with coulometric sensor

1.3.3 Measure oxygen and carbon dioxide concentrations in the system at 15°C and 90%RH (Storage condition for prolonging shelf life of straw mushrooms) using gas chromatograph

CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter describes theory of mass transfer through polymeric films, method of measuring gas transmission rate of films, factors that affect the gas permeability of plastic films, respiration of fresh produces and modified atmosphere packaging (MAP).

2.1 Mass transfer through polymeric films

There are three steps for gases or small molecules to permeate through polymeric materials.

a. Absorption – gases or small molecules are captured by a polymeric material.

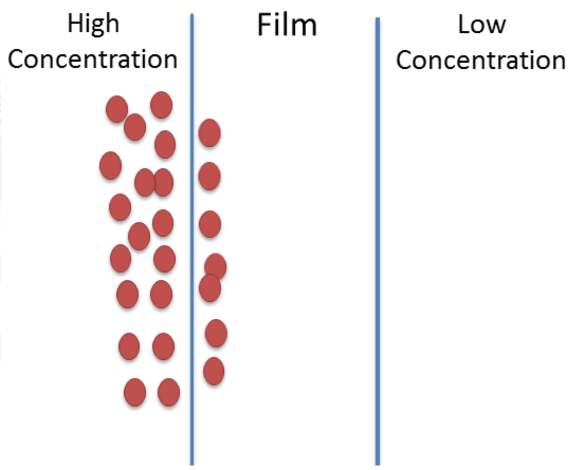


Figure 2.1 Absorption step

b. Diffusion – gases or small molecules move within the polymer material

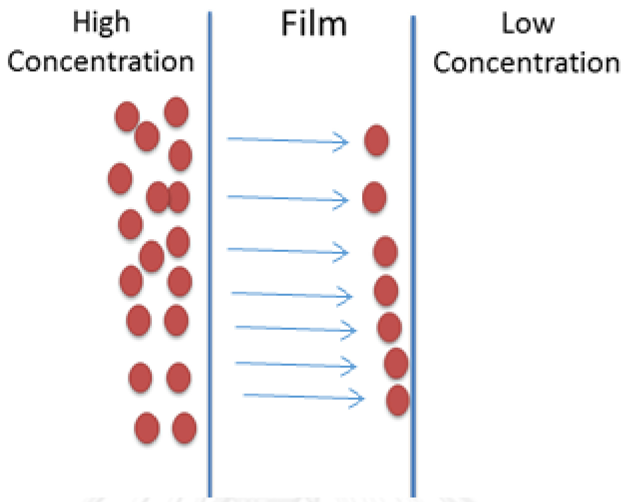


Figure 2.2 Diffusion step

c. Desorption – gases or small molecules are released from polymer material

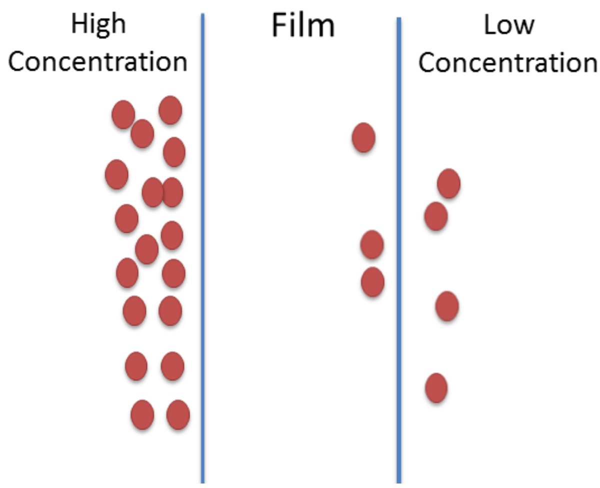


Figure 2.3 Desorption step

The whole process of mass transfer through polymeric films and gas concentration is illustrated in Figure 2.4.

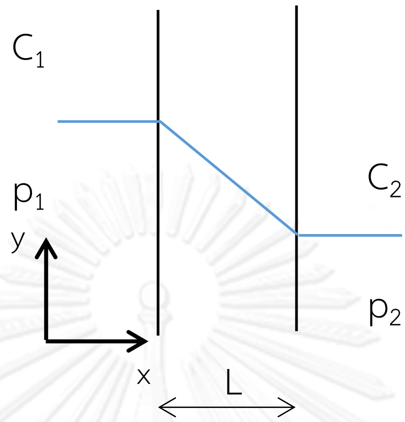


Figure 2.4 Schematic drawing of mass transfer through polymeric films

C_1 and C_2 represent concentration of gases in each side.

p_1 and p_2 represent partial pressure of gases in each side.

The Fick's first law (Equation (1)) describes diffusion step.

$$J = -D\frac{\partial C}{\partial x} \qquad (1)$$

Where J = mole flux or volume flux = Transmission rate (TR)

D = Diffusion coefficient

Equation (1) is integrated from C_1 to C_2 and 0 to x. The result is in Equation (2)

$$TR = D\frac{(C_1 - C_2)}{L} \qquad (2)$$

Where L = film thickness

Henry's law describes absorption and desorption steps. Concentration of gas can be converted to partial pressure by using Equation (3)

$$\mathrm{C} = \mathrm{Sp} \tag{3}$$

Where C = concentration

S = solubility of gas (Henry's constant)

p = partial pressure

Using Fick's and Henry's laws to explain permeability of gases, the Equation (2) and (3) are combined with defined permeability (P) from P = DS then Equation (4) is created [9].

$$\mathrm{TR} = \frac{\mathrm{P}\,(\mathrm{p}_1 - \mathrm{p}_2)}{\mathrm{L}} \tag{4}$$

2.2 The method of measuring gas transmission rate of films

Various ways to measure gas transmission rate are generally categorized into steady state and unsteady state methods. The steady state method is widely used as it can provide results quicker (in hours), which follows ASTM D3985. However, there are certain conditions such as fixed temperature and continuous gas flow. Another way is using unsteady state method, which follows ASTM D1434. Gas transmission rate is calculated from difference in total pressure of gases on two sides of films. This method requires more time (many days) to yield results.

Ghosh [10] invented an equipment for static method of gas transmission rate measurement using containers filled with gases in which tested films were sealed at the opening. Concentration of gases inside and outside of the container were measured then $\ln\frac{(\mathrm{c_{air}}-\mathrm{c})}{(\mathrm{c_{air}}-\mathrm{c_0})}$ will be plotted against time (t) as shown in Figure 2.5. The slope of this graph denoted as TR equals to $\frac{-\mathrm{TR}\times\mathrm{A}}{\mathrm{V}}$ represents transmission rate, A is an area of film and V is a container's volume. Transmission rate (TR) will then be calculated from these known values.

Here is how the equation was derived.

$$\frac{dc}{dt} = \frac{TR \times A\,(c_{air} - c)}{V} \tag{5}$$

$$\int_{c_0}^{c} \frac{dc}{(c_{air} - c)} = \frac{TR \times A}{V} \int_{0}^{t} dt \tag{6}$$

$$-ln(c_{air} - c)\Big|_{c_0}^{c} = \frac{TR \times A}{V}\, t\Big|_{0}^{t} \tag{7}$$

$$ln\frac{(c_{air} - c)}{(c_{air} - c_0)} = \frac{-TR \times A}{V}\, t \tag{8}$$

$$TR\left[\frac{cc}{m^2\ day\ atm}\right] = -slope \times \frac{V}{A} \tag{9}$$

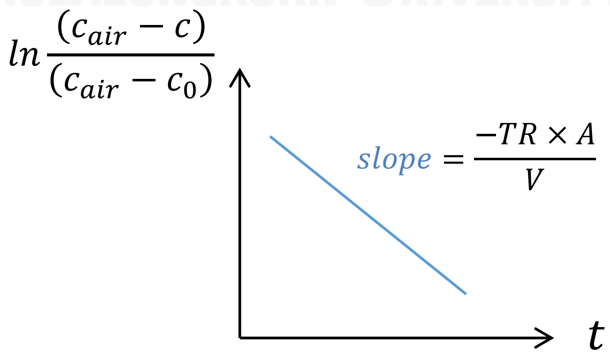


Figure 2.5 ln(C_{air} – C)/(C_{air} – C_0) versus time

2.3 Factors affecting gas permeability of polymer films

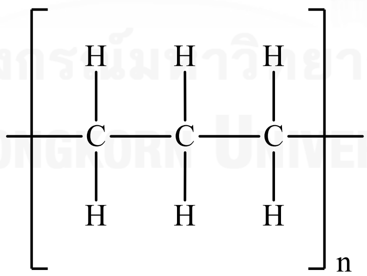
The factors affect gas permeability of polymer films are properties of polymer such as polarity and free volume; nature of permeant gas such as molecular size and polarity of molecules; and environment factors such as temperature and humidity.

2.3.1 Properties of a polymer

2.3.1.1 Polarity

Polarity of a polymer can be observed from its molecular structure. Electronegativity is the ability of atom that attracts electron cloud to it. Due to the difference of electronegativity of an atom which bonds another atom together, electron cloud is attracted by an atom that has more electronegativity. This results in polarity. Elements with higher electronegativity are at upper right hand side of a periodic table, with the order of electronegativity as follows: F (Fluorine) > O (Oxygen) > Cl (Chlorine), N (Nitrogen) > Br (Bromine) > C (Carbon), H (Hydrogen) [11].

From Figure 2.6, poly(ethylene) consists of C and H atoms. C and H do not differ in electronegativity. So C-H bond does not have polarity. This is why poly(ethylene) is a nonpolar polymer. Poly(lactic acid), as shown in Figure 2.7 has C=O bonds with a little difference in electronegativity, thus PLA is a weak polar polymer.



Low density poly(ethylene) (LDPE)

Figure 2.6 Molecular structure of Low density poly(ethylene)

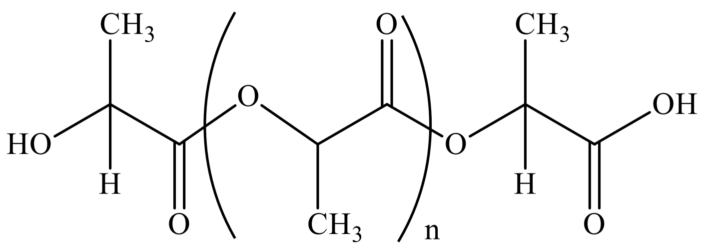


Figure 2.7 Molecular structure of Poly(lactic acid)

Polarity of polymer is related to hydrophobicity. Simple hydrophobicity measurement is contact angle of water drop on surface of films [12]. If the angle is more than 90°, this is more hydrophobic or less hydrophilic as shown in Figure 2.8.

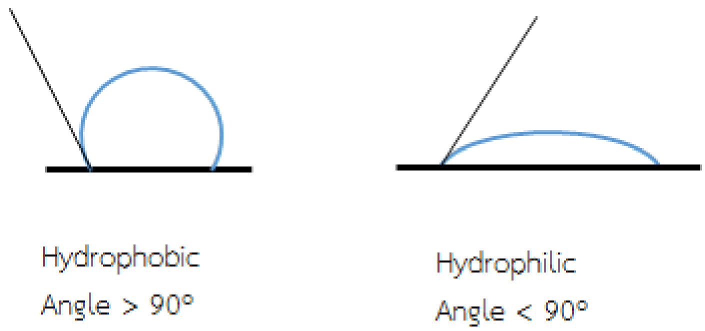


Figure 2.8 Contact angle of water drop on hydrophobic surface and hydrophilic surface [12]

2.3.1.2 Free volume

Free volume is the space between polymeric chains as shown in Figure *2.9*. Gas or small molecules can then diffuse through this space. Free volume of polymer can be calculated from equation (10). Gases and small molecules can then diffuse more freely through polymers with greater free volume [13, 14].

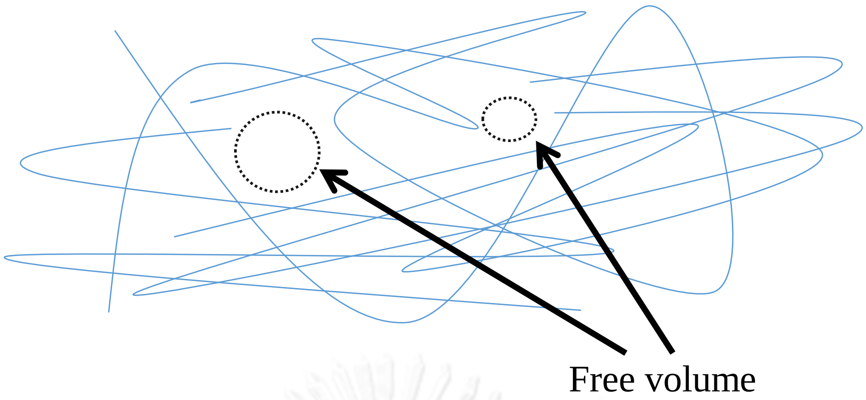


Figure 2.9 Free volume of a polymer

$$V_f = V - V_o \qquad (10)$$

Where V_f is free volume of polymer

V is total volume of polymer

V_o is occupied volume (volume of polymer chain).

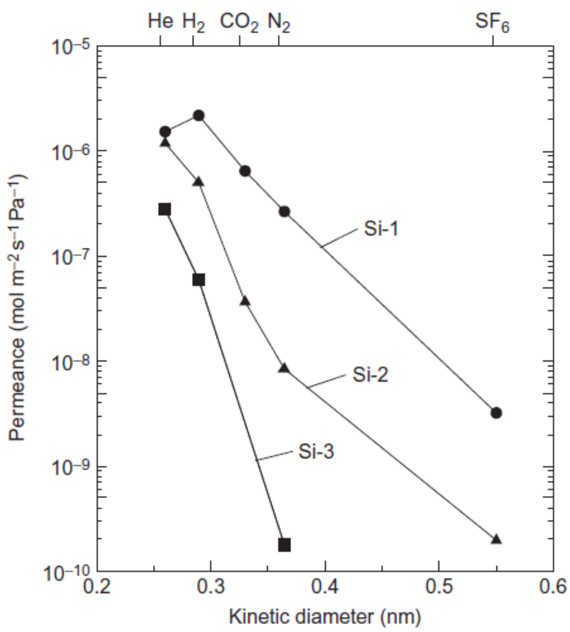
2.3.2 Nature of permeant gas

2.3.2.1 Molecular size

Molecular size of molecules is described by kinetic diameter of molecule which is presented in Table 2.1. Kinetic diameter is calculated from kinetic theory of gas. This is the size of gas when gas molecule is moving. In general, substance or elements of smaller molecular size diffuse easier than those with larger molecular size. Figure 2.10 shows that the smaller kinetic diameters such as helium and hydrogen have higher permeability than the larger molecules such sulfur hexafluoride (SF_6)

Table 2.1 Kinetic diameter for various molecules [15]

Molecules	Kinetic Diameter (nm)	Molecules	Kinetic Diameter (nm)
He	0.26	CO_2	0.33
H_2O	0.27	CO	0.38
H_2	0.29	C_2H_4	0.39
N_2	0.36	Cl_2	0.32
O_2	0.35	HCl	0.32



(Noted that Si-1, Si-2 and Si-3 are silica membrane with average pore size of 0.5-0.6, 0.4-0.5 and 0.3 nm, respectively)

Figure 2.10 Permeance as a function of kinetic diameter of gas molecules **[16]**

2.3.2.2 Polarity of molecules

Polarity of molecules is determined by the dipole moment which shows different electronegativity of each atom. Hydrogen, nitrogen and oxygen atoms are symmetric so their dipole moment equals zero. Substances with asymmetric molecules such as water (H_2O) and hydrofluoric acid (HF) are much different in electronegativity of each molecule, so their dipole moment does not equal zero as illustrated in Table 2.2.

Table 2.2 Dipole moment for various molecules [11]

Molecules	Dipole Moment	Molecules	Dipole Moment	Molecules	Dipole Moment
H_2	0	HF	1.75	CH_4	0
O_2	0	H_2O	1.84	CH_3Cl	1.86
N_2	0	NH_3	1.46	CCl_4	0
Cl_2	0	NF_3	0.24	CO_2	0
Br_2	0	BF_3	0		

2.3.3 Environmental factors

2.3.3.1 Temperature

Effects of temperature on gas permeability can be described using Arrhenius equation, which is shown as equation (11)[7]. Pre exponential term (P_0) and activation energy for permeation (E_p) are calculated from experimental data of P (Permeability) at each T (Temperature) of each plastic type using linear regression method. Because P (permeability) is directly correlated with T (temperature), gas permeability and temperature is then positively correlated. In another words, higher temperature results in higher gas permeability because gas molecules have more kinetic energy and move faster. P_0 and Ep of LDPE and PLA are reported in previous experiment and shown in Table 2.3

$$P = P_0 \exp(-\frac{E_p}{RT}) \tag{11}$$

Where P is permeability (ml (STP) cm/m^2 day atm)

P_0 is pre exponential term (ml (STP) cm/m^2 day atm)

E_p is activation energy for permeation (kJ/mol)

R is gas constant (kJ/mol K)

T is temperature (K)

Table 2.3 E_p and P_0 of oxygen permeability of LDPE and PLA

Materials	**E_p (kJ/mol)**	**P_0 (ml (STP) cm/m^2 day atm)**	**References**
LDPE	44.1	1.21	[17]
PLA 4031*	23.62	55,137 (9.00 kg m / m^2 s Pa)	[6]
PLA 4041*	21.12	18,440 (3.01 kg m / m^2 s Pa)	[6]

*at humidity equals zero and convert unit

2.3.3.2 Humidity

Humidity affects gas permeability in particular of those hydrophilic polymers. A hydrophilic polymer is the polymer with an affinity to water. Water molecules are absorbed in matrix of a polymer and bond with polymer chain called hydrogen bond. Polymer matrix is swelled and has more free volume thus enable gases to permeate easily. For this situation, water molecules act as plasticizer due to similar mechanism. This phenomenon is called “plasticization effect”. Plasticization effect of water molecules has higher effects on polymers with high polarity functional group such as amide group of polyamide (PA) or Nylon and hydroxyl group of ethylene vinyl alcohol (EVOH) copolymer [5] resulting in the increase of oxygen transmission rate (OTR) increase with relative humidity increase as shown in Figure 2.11 [18].

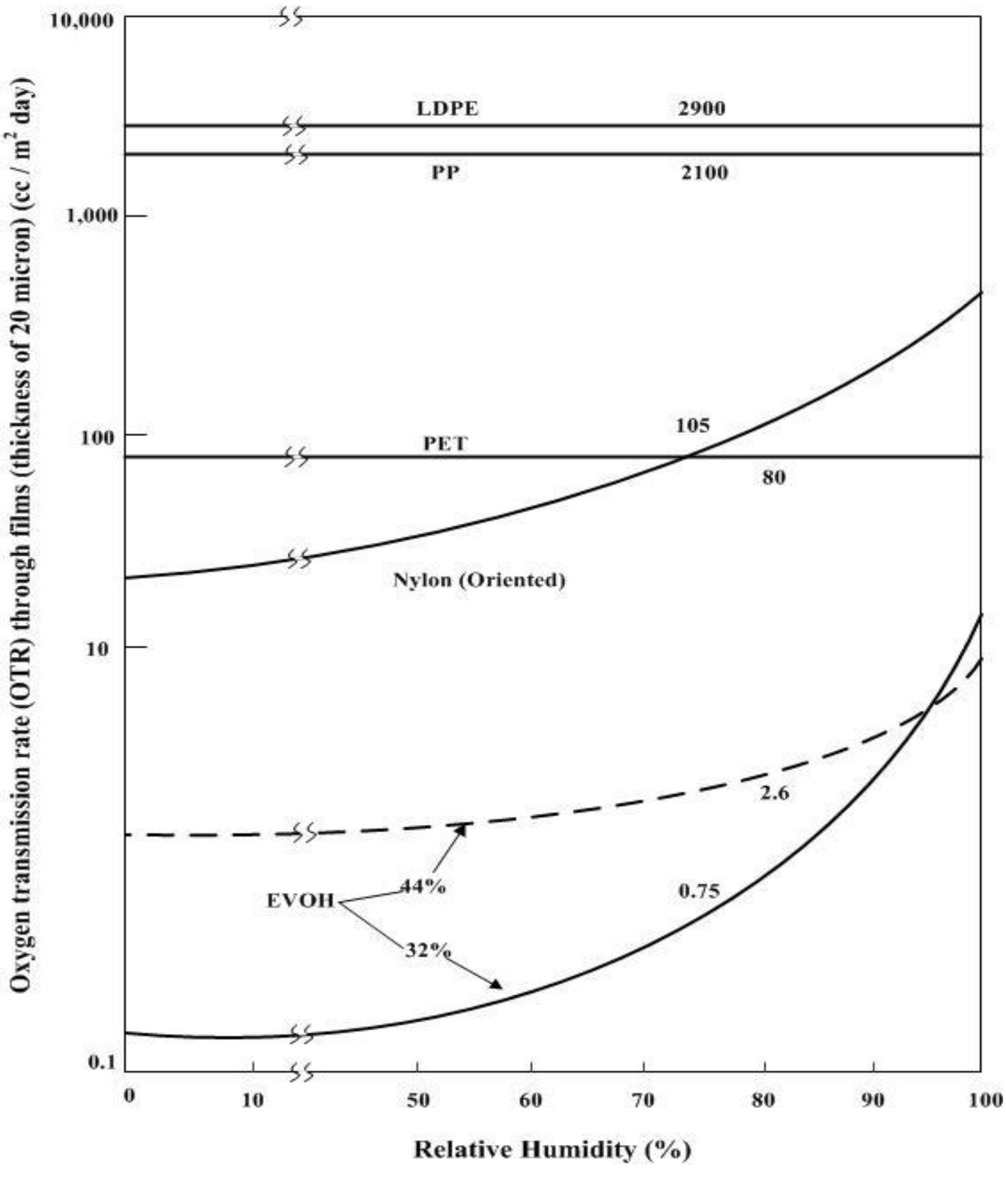


Figure 2.11 Oxygen transmission rate of various plastic (Low density polyethylene (LDPE), Polypropylene (PP), Poly(ethylene terephthalate) (PET), Polyamide (PA) or Nylon and Ethylene vinyl alcohol copolymer (EVOH)) versus relative humidity (adapted from [18])

2.4 Respiration of fresh produces

Fresh produces use oxygen for their aerobic respiration. Aerobic respiration is a mechanism that fresh produces uptake oxygen to burn carbohydrates and generate carbon dioxide, water vapor and energy that let fresh produces live. Aerobic respiration mechanism can be explained in a simple way in equation (12). Aerobic respiration occurs only in the atmosphere with sufficient oxygen concentration i.e. more than 3% [19].

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Energy} \quad (12)$$

Respiration rate of fresh produces is usually measured as the amount of carbon dioxide that fresh produces release in milligram of carbon dioxide per kilogram of fresh produces per hour (mg CO_2 /kg hr). Respiration rates of various fresh produces from literature are shown in Table 2.4 [1, 2].

Table 2.4 Respiration rates of some fresh produces at 5°C [2] and 25°C [1]

Class	Range of respiration rates (mg CO_2 / kg hr) at 5 °C	Fresh produces	Range of respiration rates (mg CO_2 / kg hr) at 25 °C	Fresh produces
Very low	<5	Cassava, Garlic, Pumpkin, Potato	<5	Cashew nut
Low	5-10	Beet, Tomato, Celery	5-20	Orange, Cabbage, Onion
Medium	11-20	Carrot, Eggplant	20-100	Rambutan, Papaya, Tomato
High	21-30	Artichoke, Spinach	100-200	Mango, Asparagus
Very high	>30	Asparagus, Broccoli, Mushroom	>200	Durian, Babycorn, Mushroom

Srisawat in 2008 measured the respiration rate of straw mushrooms at different temperature using closed system. At room temperature (29°C) the respiration rate is 1,308 mg CO_2 /kg hr at initial state then decreases to 981 mg CO_2 /kg hr after 24 hours. At 10, 12, 14, 16 and 18 °C, the respiration rates are 960 – 1,180 mg CO_2 /kg hr at initial state then drop to 100 – 300 mg CO_2 /kg hr after 6 hours as shown in Figure 2.12[8].

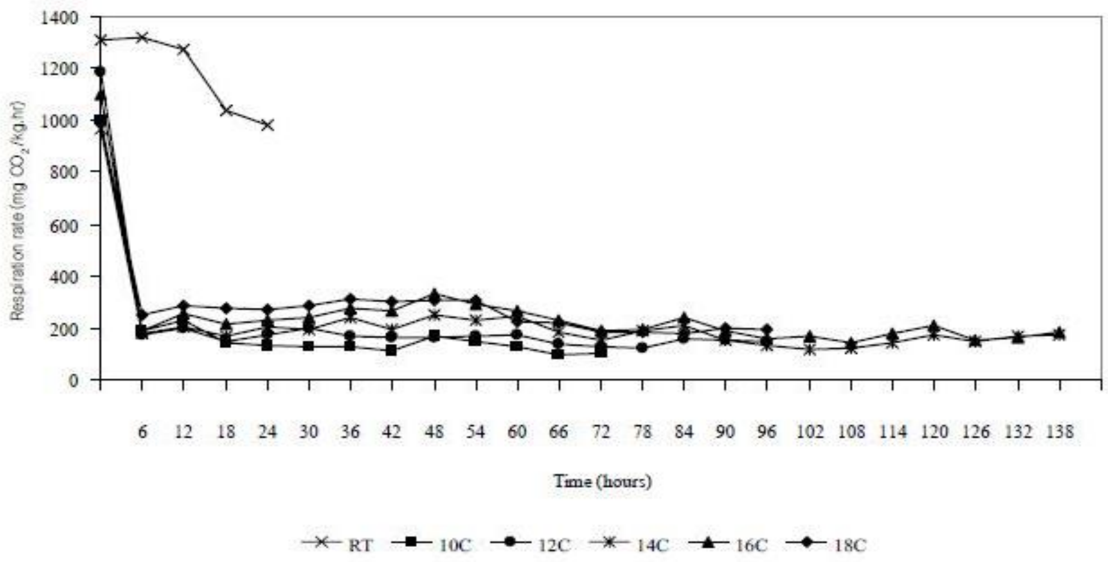


Figure 2.12 Respiration rate of straw mushrooms stored in foam tray wrapped with PVC film with 16 holes perforated at temperature of 10, 12, 14, 16, 18 and room temperature (RT) of 29°C [8]

2.5 Modified atmosphere packaging (MAP)

Modified atmosphere packaging is a method to create an environment in a package with lower oxygen and higher carbon dioxide concentration. The lower oxygen concentration is the lower respiration and metabolism of fresh produces could be observed. However, oxygen concentration should be kept at least 3% to maintain aerobic respiration[19]. Higher carbon dioxide concentration level prevents microbial growth and also results in the lower respiration rate. However, too much of carbon dioxide concentration can cause “CO_2 injury” which makes the surface of fruit becomes brown.

Modified atmosphere package relies on two major factors, i.e., (i) balance of gases that permeate into and out of the package and (ii) respiration of fresh produces. These two factors determine gas composition inside the package.

CHAPTER III

EXPERIMENTS

This chapter contains materials, film characterization and gas transmission rate measurement. Appearance, morphology and hydrophobicity of films were studied. Two methods of gas transmission rate measurement were used, steady state method at 23°C for oxygen transmission rate at various level of relative humidity and unsteady state method for oxygen and carbon dioxide transmission rates at 15°C and 90%RH (storage condition for prolonging shelf life of straw mushrooms). The schematic diagram of experimental procedure of this work is illustrated in Figure 3.3.

3.1 Materials

Poly(lactic acid) (PLA) grade 2003D, modified poly(lactic acid) (mPLA) which is PLA blended with natural rubber graft maleic anhydride (NR-g-MA) and hydrophilic particles were blown by single screw extruder (L/D = 25, D = 20) attached to blown film line (Collins, Germany) using screw speed of 85 rpm and temperature was set at 180-200°C.

Commercial breathable low density poly(ethylene) (bLDPE) was obtained from Tantawan Industry PLC, Thailand.

Oxygen gas (O_2) at 99.7% purity and carbon dioxide gas (CO_2) at 99.9% purity were purchased from Praxair, Thailand.

3.2 Film characterization

3.2.1 Morphology

Cross-section of bLDPE, PLA and mPLA films were observed with scanning electron microscope (SEM, JEOL JSM 5800LV, Japan) at acceleration voltage of 15 kV. The film was cut under liquid nitrogen, fixed on stub and then coated with gold before SEM observation.

3.2.2 Hydrophobicity

Hydrophobicity of films was determined by a contact angle of a water droplet on film surface. Higher angles represent lower polarity of films. The contact angle of water droplet was observed using contact angle meter; Tantec Inc. Water was dropped on film surface. A water droplet was captured by camera and contact angle was then measured using Tantec CAM v3.0.8 software.

3.3 Measurement of gas transmission rate through films

Two sets of equipment to measure gas transmission rate of film were used in this experiment. The first set, which is located in Chulalongkorn University, is a steady method using two chambers of gases separated by tested films. Oxygen flows into one chamber while mixed gas flows into another chamber. A coulometric sensor, which is in the mixed gas chamber, measures the amount of oxygen that has permeated from oxygen chamber through the film. The whole process follows ASTM D3985 (American Society for Testing and Materials). This equipment has a pre-set fixed temperature of 23°C. Humidity of gas was adjusted by filling water in another chamber where gases flew through a pressure adjustment inlet. These follow the ASTM F1927. This set of equipment was used to study effects of humidity on oxygen transmission rate through the films.

The second set, which is in Kamphaengsaen Campus of Kasetsart University, is an unsteady state method. It is an unsteady state method because concentration of gas inside the system changes over time. A gas container was filled up with pure oxygen and another one with pure carbon dioxide. Each container was sealed with a tested film (bLDPE, PLA or mPLA) and was kept at 15°C, 90%RH (storage condition for extended shelf life of straw mushrooms in the previous experiment) for ten days. A small volume (10 cubic centimetres) of gas in each container was collected at 0, 2, 4, 6, 8 and 10 days to measure oxygen or carbon dioxide concentrations using gas chromatograph (Shimadzu GC-8A). This method was used to measure both oxygen and carbon dioxide transmission rate through films similar to the storage condition.

3.3.1 Assessing the effect of humidity on oxygen transmission rate of films at 23°C using steady state method with coulometric sensor

Oxygen transmission rate analyzer, OX-TRAN model 2/21, module ST (Mocon, USA) was used in this experiment. This module follows ASTM D3985 (at 23°C, 0%RH) and ASTM F1927 (at 23°C, controlled %RH). Oxygen at 99.7% purity and mixed gas (98%nitrogen and 2%hydrogen) were used as tested gas and carrier gases, respectively. For controlled relative humidity, HPLC (High Performance Liquid Chromatography) graded water was added in the module and inlet pressure of gas was adjusted and waited for 3 hours for constant relative humidity. The inlet pressure that was used to adjust gases humidity is shown in Table 3.1. Oxygen and mixed gas flow rate was set at 40 cubic centimeters per minute (cm^3/min) and 20 cm^3/min, respectively for every test. Oxygen transmission rate was measured at 0, 40, 60, 80 and 90%RH.

Table 3.1 Inlet pressure to humidify gas

Target %RH	Pressure (psig)
40	22.1
60	9.8
80	3.7
90	1.6

Source: OX-TRAN® Model 2/21 Operator's Manual

Each film sample was cut according to the template supplied by the OX-TRAN 2/21, which made an area of 100 cm^2. High vacuum grease was applied on the O-ring to prevent leakage of air into the mixed gas chamber. The equipment was set to measure oxygen transmission rate (OTR) until the OTR reaches a steady state. There were 3 replicates for each film (bLDPE, PLA and mPLA) at each level of relative humidity (0%, 40%, 60%, 80% and 90%).

3.3.2 Oxygen and carbon dioxide transmission rates using unsteady state method at 15°C

The equipment consists of a container made of glass with a specific shape. Dimension of container is shown in Figure 3.1 and real container used in this experiment is shown in Figure 3.2. The volumes of container are 2,600 ml and 2,800 ml. Volumes of container were indirectly measured by measuring the volume of water that has filled up the container. Films were cut into circular shape using a circular template of 150 millimeters in diameter. Each film was attached to a container with two rubber pads that allowed a square shape of 80 x 80 millimeters (mm) of film, as shown in Figure 3.1.

The experiment was conducted in a storage room at 15°C and 90%RH, which is the storage condition for prolonging shelf life of straw mushrooms. Test gas was filled at 15 liter/minute (l/min) into the container at sampling port for 20 minutes to ensure completely filling up of gas in the container. A syringe was used to collect gas from the container on the first day then at 2, 4, 6, 8 and 10 days. These gas samples were analyzed using a gas chromatograph (Shimadzu GC-8A). Peak area of each gas was obtained at each time point. Calibration curves (The method to prepare calibration curve of each gas is described in appendix B) were used for converting the peak area to mole of gas. Then the gas concentration in the system was calculated. The unit of gas concentration is percent volume (%vol) that is the same ratio of percent mole when using ideal gas law to convert volume of gas to mole of gas. Gas transmission rate of films was calculated using equation (9) as described in Chapter 2.

Temperature and relative humidity was measured using "Data logger" which is an instrument used to record the temperature and relative humidity. Data logger was placed in each container and inside cold room. The data was recorded at initial and every 6 hours until ten days.

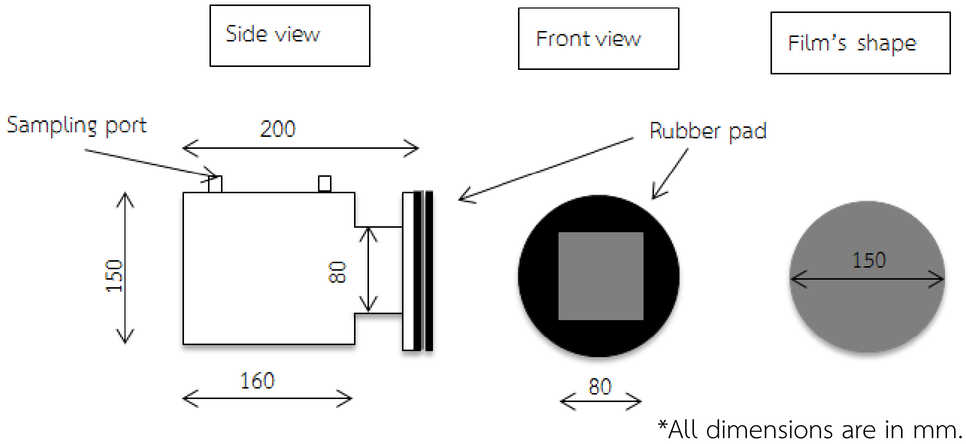


Figure 3.1 Schematic diagram of container and film's shape

Figure 3.2 Equipment for gas transmission rate measurement

The gas chromatograph (GC) uses thermal conductivity detector and a column of stainless steel tube of 0.48 cm in diameter and 200 cm in length. The column used for oxygen and nitrogen analysis is packed with molecular sieve 5A while the column used for carbon dioxide analysis is packed with porapack Q80/100. Ultra high purity helium (with purity of 99.999%) was used as the carrier gas. GC parameters in this experiment were used as follows: injector temperature of 150°C, column temperature of 70°C, electric current of 90 mA and carrier gas inlet pressure of 200 kPa.

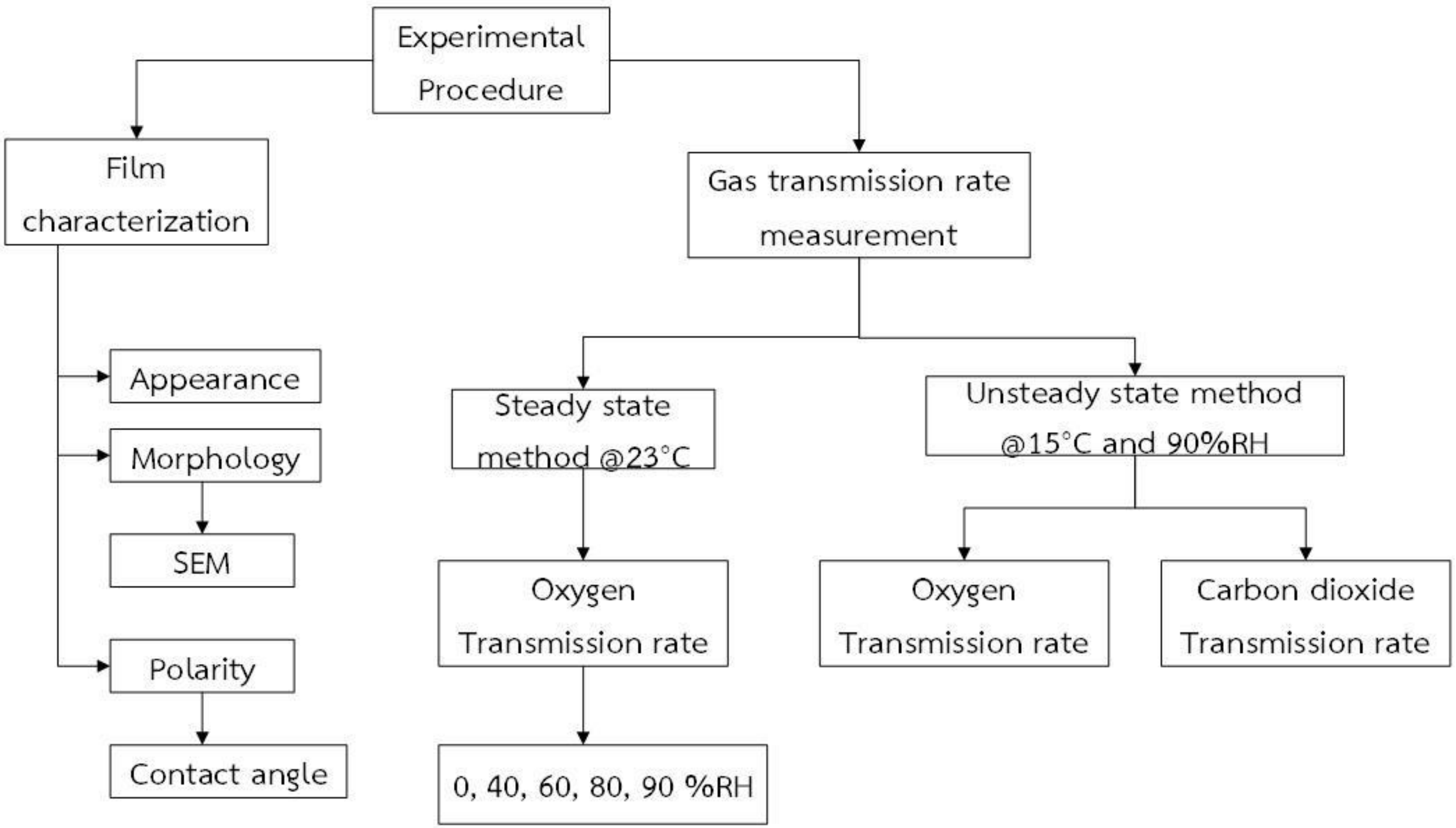


Figure 3.3 Experimental procedure

CHAPTER IV

RESULTS AND DISCUSSION

This chapter contains three parts. The first part describes intrinsic properties of films such as appearance, morphology and polarity. The second part describes gas transmission rate measurement. This part contains four subparts. Subpart 1 describes effects of relative humidity (%RH) on oxygen transmission rate (OTR) of films using steady state method at 23°C at various level of %RH. Subpart 2 describes OTR and carbon dioxide transmission rate (CO_2TR) of films using unsteady state method at 15°C at 90%RH, which is the storage condition of straw mushrooms used in the previous experiment. Subpart 3 is comparing gas transmission rate measured by steady state and unsteady state methods and subpart 4 is difference of water vapor transmission through film in the unsteady state method. Finally, the third part describes factors affecting shelf life of straw mushrooms. The OTR and CO_2TR that were obtained from the unsteady state method and the gas concentration inside straw mushroom package that was reported in the previous experiment were used to calculate respiration rate of straw mushrooms using mass balance equation. Other factors affecting shelf life were also discussed in this part.

4.1 Intrinsic properties of films

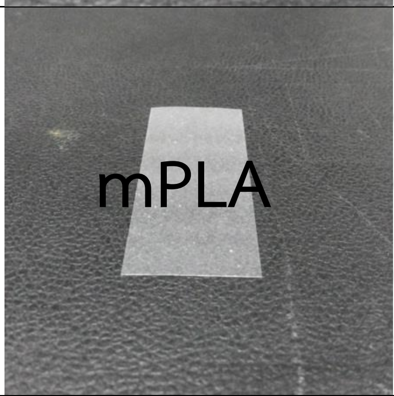
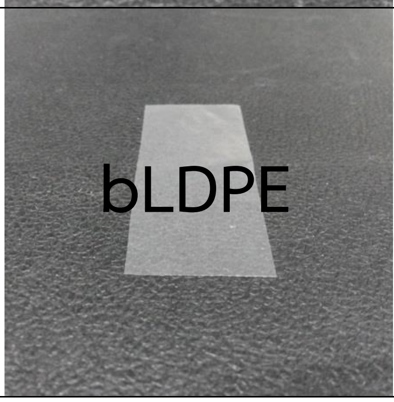
4.1.1 Appearance

Appearance of films is shown in Table 4.1. Neat poly(lactic acid) (PLA) film has naturally transparent and smooth surface. Modified polylactic acid (mPLA) has translucent and rough surface because it is blended with natural rubber graft maleic anhydride (NR-g-MA) and hydrophilic particles. The rough surface of mPLA shows the immiscible blend. Commercial breathable low density polyethylene (bLDPE) has translucent and smooth surface. LDPE is a semi-crystalline polymer that is translucent as its nature.

4.1.2 Morphology

Cross-sectional fracture surface of films in transverse direction (TD) were observed using Scanning Electron Microscope (SEM) micrographs. From Figure 4.1, PLA shows the smooth fracture surface because PLA is brittle in which the fracture surface is naturally smooth. For mPLA, cavities in PLA matrix and particles were observed. The cavities are probably caused when natural rubber (NR) domains in PLA matrix were pulled out during sample preparation because the interaction between PLA matrix and NR domains are weak [20]. The cavity shape is elongated that occurred when the nip roll pulled the molten plastic from die in machine direction (MD). Rubber domains are then pulled out. As schematic drawing in Figure 4.1 shows that NR domain is quite spherical shape in MD but elongated shape in TD of film but the particles are not elongated as observed in SEM micrograph. For bLDPE film, large domain or particles are observed in Figure 4.1. From the reason described above that the shape of rigid particles is not changed during processing, if the shapes of domain are not elongated that might be particles. It can be assumed that bLDPE is modified the gas transmission rate by adding particles or polymer to create the heterogeneous phase that increases more interphase between phases that allows more gas to diffuse through it.

Table 4.1 Visual appearance of PLA, mPLA and bLDPE films

Films	Visual appearance	
	Surface roughness	Transparency
	Smooth	Transparent
	Rough	Translucent
	Smooth	Translucent

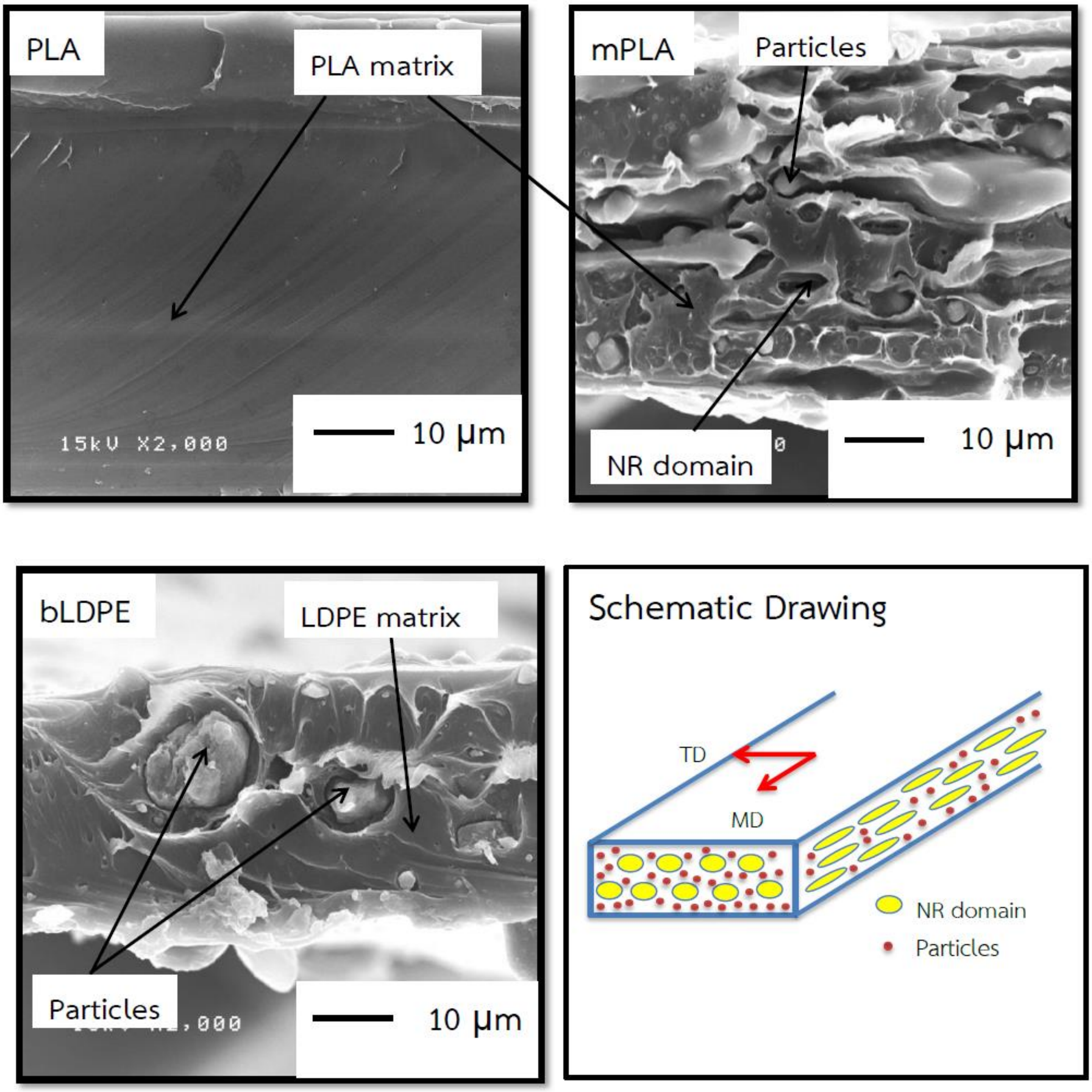


Figure 4.1 Cross-sectional fracture surfaces of PLA, mPLA and bLDPE films in transverse direction (TD) and schematic drawing of films.

4.1.3 Hydrophobicity

The hydrophobicity of films is determined by the contact angle of water drop on film surface. From Figure 4.2, contact angle of bLDPE film is 92.53° while contact angles of PLA and mPLA were 77.10° and 69.47°, respectively (Data are in appendix G). It is clearly seen that PLA and mPLA are more hydrophilic than bLDPE. From section 2.3.1.1, LDPE are nonpolar molecules or hydrophobic in which contact angle also confirm this knowledge. PLA is weak polar due to carbonyl group in repeating units as shown in Figure 2.5 and also has carboxyl group at the end of chains. The mPLA film contains natural rubber grafted with maleic anhydride to increase miscibility between PLA and NR [20] and hydrophilic particles. These result in higher hydrophobicity of mPLA film than PLA.

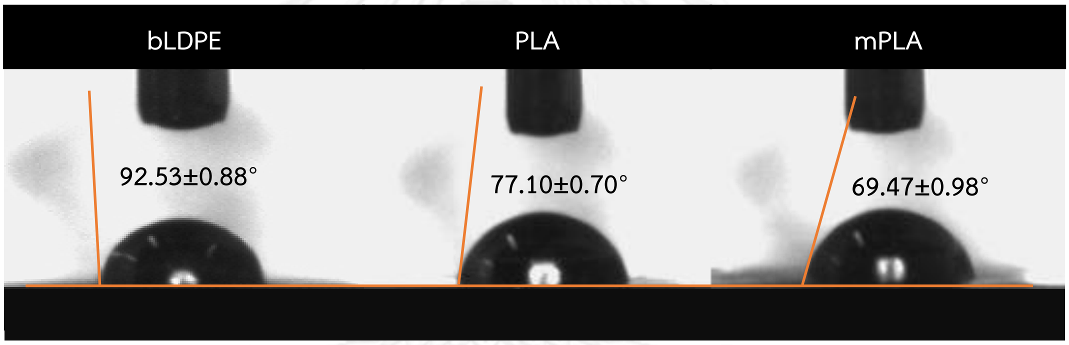


Figure 4.2 Contact angles of water droplets on film surface

4.2 Gas transmission rates

4.2.1 Effects of humidity on oxygen transmission rate (OTR) of films using steady method measured at 23°C and various levels of relative humidity

Oxygen Transmission Rate (OTR) of bLDPE, PLA and mPLA films at various levels of %RH are shown in Figure 4.3. When %RH increases from 0 to 90, OTR of PLA and bLDPE is fairly stable while that of mPLA increases about two times from 0 to 40%RH and is quite stable from 40 to 90%RH.

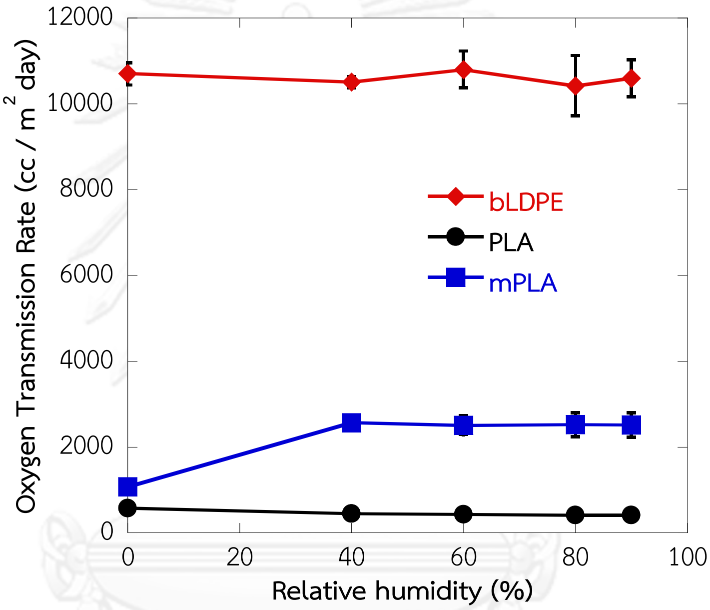


Figure 4.3 Oxygen transmission rate at various levels of relative humidity using steady state method at 23°C

Oxygen transmission rates of bLDPE film do not change at various levels of humidity probably because LDPE is non-polar polymer that does not absorb water, which is polar molecule, so there is little effect of humidity on OTR of bLDPE film.

OTR of PLA film is not affected by humidity. It is likely that PLA, with its weak polarity does not attract water molecules enough to plasticize it. This is consistent with findings of the previous study that OTR of PLA are not increased with %RH increasing[6].

For mPLA film, humidity affects its OTR, with greater effects at 0%RH to 40%RH and less effect at higher RH. OTR of mPLA film is increased probably because of its higher polarity, compared with PLA and bLDPE. As a result of OTR of PLA film which is not changed with increasing %RH. From the reason above that OTR PLA are not affected by humidity. Plasticization effect might occur in NR-g-MA domain. Water molecule are attracted with maleic anhydride functional group and made the NR-g-MA domain have more free volume as described in section 2.3.3.2. From SEM micrograph, mPLA film has more cavities due to its heterogeneous phase and particles that increase free volume so water can easily be absorbed. However, once saturated, probably at 40%RH no more water molecules can be added up in this film, thus OTR is not further increased.

4.2.2 Gas transmission rate of films using unsteady state method measured at 15°C and 90%RH

As explained in Chapter 3, gas transmission rate was calculated using Equation (9) (Detailed calculation is in appendix D). As shown in Figure 4.4, OTR of bLDPE, PLA and mPLA films were found to be 21,668, 8,806.7 and 9,351.3 cc/m^2 day atm, respectively while CO_2TR of bLDPE, PLA and mPLA films were 24,846, 9,119.2 and 16,472 cc/m^2 day atm, respectively.

OTR and CO_2TR values of PLA film are similar while those of mPLA and bLDPE films are different. From Figure 4.1, PLA is homogeneous while mPLA and bLDPE are heterogeneous. Gas molecules might permeate through voids which locate at interphase between matrix and disperse phases (of heterogeneous) more than permeate through polymer matrix. For silicon membrane which is also heterogeneous in Figure 2.10, the different of kinetic diameter is significantly affected transmission rate of each gas through membrane. Small molecules are easy permeated through voids than large molecules. From Table 2.1, kinetic diameter of oxygen and carbon dioxide are 0.35 and 0.33 nm, respectively. Then CO_2TR is more than OTR for mPLA and bLDPE films.

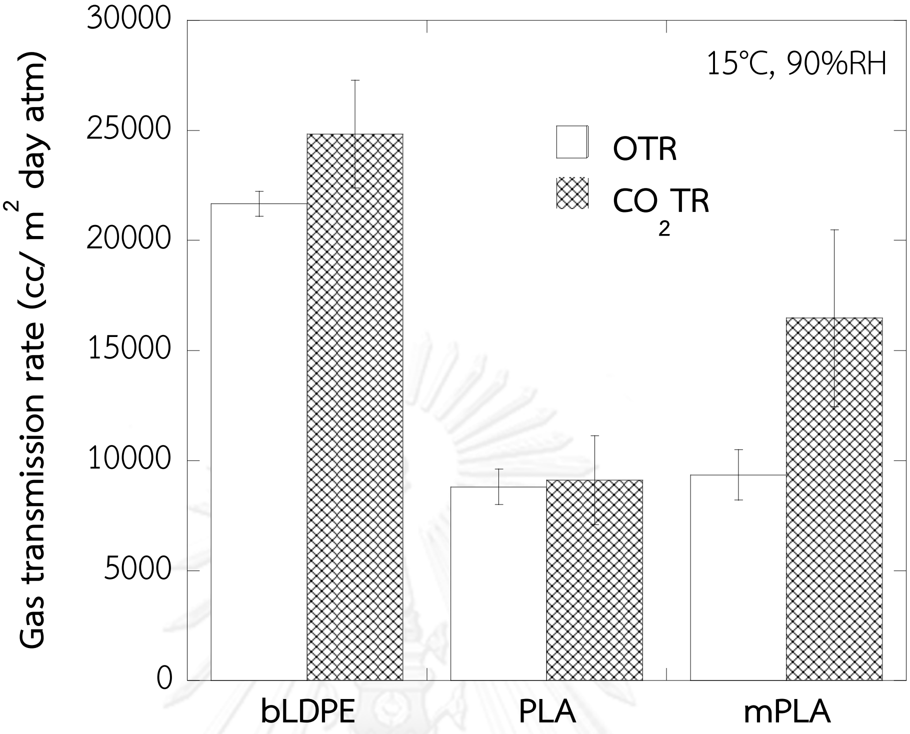


Figure 4.4 Oxygen and carbon dioxide transmission rates using unsteady state method at 15°C, 90%RH

4.2.3 Comparing gas transmission rate measured by the two methods

The two methods (steady state and unsteady state) yielded different values of OTR probably because of different measurement methods and different calculation. The steady state directly measures amount of oxygen that reaches sensors. On the contrary, the unsteady state method indirectly measures OTR and CO_2TR by measuring concentration of oxygen or carbon dioxide in the samples of gases drawn from the container at various time points. Values of oxygen and carbon dioxide concentrations are then used to calculate OTR and CO_2TR. For the steady state method, oxygen molecules that permeate through films are carried by carrier gas to sensor. Sensor measures amount of oxygen and shows as coulox values from coulometric sensor. The coulox value is converted to OTR by the equipment through comparing it with reference values stored in the equipment's software.

Comparing to OTR of the steady state method, OTRs of the unsteady state method are consistently higher probably because there were some unexpected contamination of gases in the unsteady state method. The contaminations could happen at three steps of the experiments, while the containers were stored in the storage room, when sample gases in the containers were collected and after sample gases were collected.

1) While the containers were stored in the storage room, nitrogen from outside could slowly permeate into the containers through films resulting in a little lower concentration of oxygen in the container.
2) When sample gases in the containers were collected with a syringe and a needle, a small amount of outside gases might leak into the syringe through the connecting point between the syringe and the needle, causing concentration of oxygen in the samples to be lower.
3) After sample gases were collected a small negative pressure that was created by the process of sample collection pulled some amount of nitrogen from outside to permeate in, causing concentration of oxygen to be lower.

As explained earlier, concentration of oxygen in the sample gases at various time points were used to calculate OTR, the faster decreasing of oxygen inside the containers reflects higher OTR.

With probable contamination of outside gases into samples and the containers, concentration of carbon dioxide also appeared to decrease rapidly. This resulted in higher CO_2TR values, if it were measured by the steady state method.

OTR and CO_2TR of the unsteady method were used for respiration rate calculation because they were measured at 15°C with 90%RH, which is the storage condition for extending shelf life of straw mushroom.

4.2.4 Different water vapor transmission through films in the unsteady state method

With the data logger placed in the storage room and in the containers (described in Chapter 3), humidity in the storage room was detected to be around 80-90%RH. As dry gases were used, %RH of both oxygen and carbon dioxide in the containers were rather low on the first day (20-30%RH). It was found that %RH increased slowly in the bLDPE container, compared with those in PLA and mPLA containers, as shown in Figure 4.5.

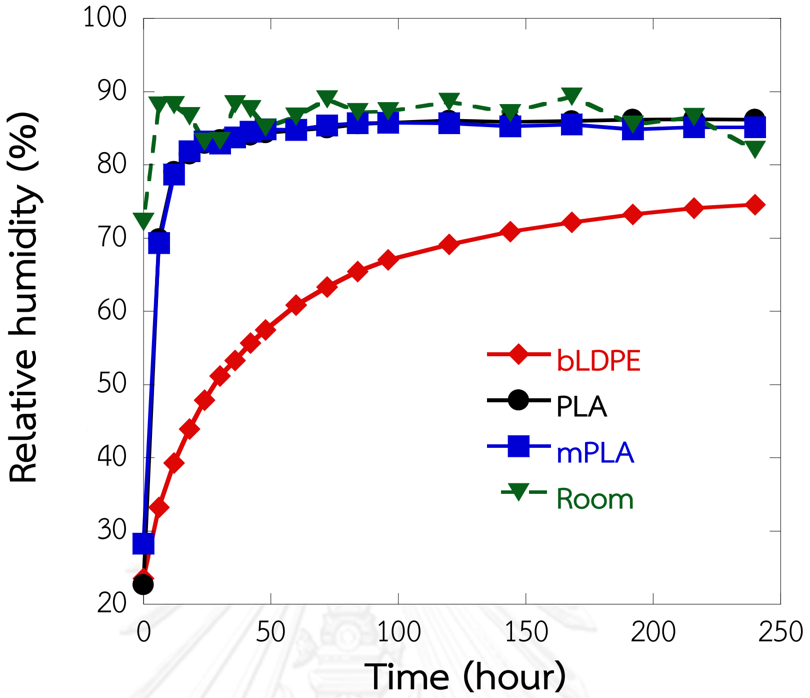


Figure 4.5 Relative humidity inside container and in the storage room during experiment

This result is consistent with water vapor transmission rate (WVTR) which measured at standard condition as shown in Table 1.1, WVTR of bLDPE, PLA and mPLA is 19.5, 120.9 and 132.9 gm/m^2 day. The higher WVTR leads to the faster equilibrium of %RH inside container. Thus equilibrium of %RH of PLA and mPLA film were achieved faster than %RH of bLDPE film.

4.3 Factors affecting shelf life of straw mushroom

As found by Bunsiri and coworkers in 2012, bLDPE package could prolong shelf life of straw mushrooms to four days while PLA and mPLA package could prolong its shelf life up to six days. Therefore, an assumption was made that OTR and CO_2TR of both PLA and mPLA films would be higher than that of bLDPE film at least at storage environment. However, findings in section 4.2.1 and 4.2.2 did not support this assumption. There must be other factors affecting shelf life of straw mushrooms rather than only magnitude of gas transmission rate.

4.3.1. Respiration rates of straw mushrooms in the MAP

In this work, respiration rates of straw mushrooms in the package were calculated from mass balance of oxygen and carbon dioxide in package. The mass balance equation is set up from following equation (*13*).

$$\text{Rate of accumulation} = \text{Rate of input} - \text{Rate of output} + \text{Rate of generation} - \text{Rate of consumption} \quad (13)$$

The system is shown in Figure 4.6 with assumptions as follow;

Assumptions

1. Ideal gas law
2. Constant temperature
3. Constant total pressure = 1 atm
4. Oxygen only permeates from outside to inside package and carbon dioxide only permeates from inside to outside package.
5. Change of gas concentration in package in each storage day is in a linear relationship.

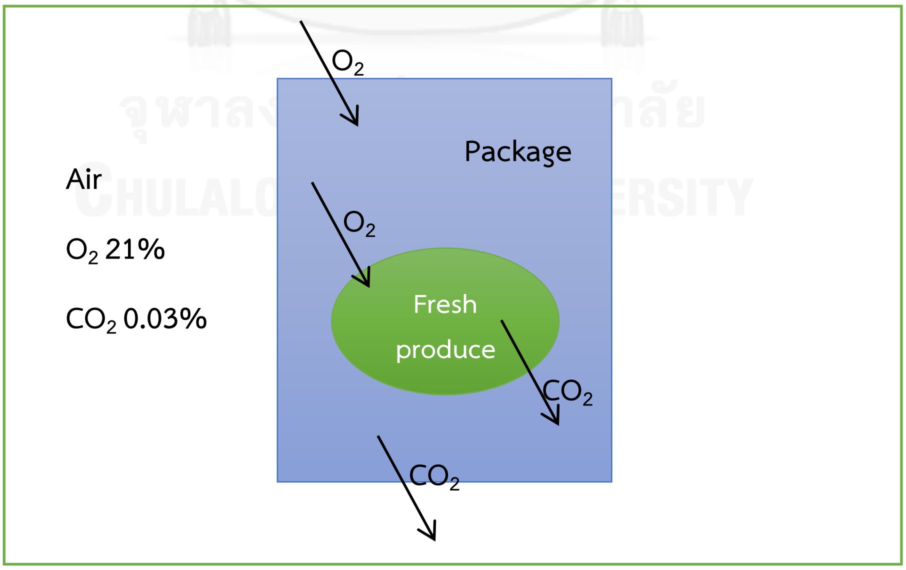


Figure 4.6 Schematic drawing of mass balance of oxygen and carbon dioxide of modified atmosphere package

From equation (13), net rate of input and output and net rate of generation and consumption can be rewrite to equation (14) and (15). Equation (13) becomes equation (16).

$$\text{Net rate of gas transmission} = \text{Rate of input} - \text{Rate of output} \tag{14}$$

$$\text{Net rate of respiration} = \text{Rate of generation} - \text{Rate of consumption} \tag{15}$$

$$\text{Rate of accumulation} = \text{Net rate of gas transmission} + \text{Net rate of respiration} \tag{16}$$

Fresh produces use oxygen and release carbon dioxide. Oxygen level in package decreases while carbon dioxide level increases thus making difference of gas concentration between inside and outside of the package. Oxygen then transmits into the package while carbon dioxide transmits out of the package. Oxygen balance is set from equation (17) and becomes equation (18) while carbon dioxide balance is set from equation (20) and becomes equation (21) Equation for oxygen and carbon dioxide balance are shown in equations (19) and (22), respectively.

$$\begin{aligned}\text{Rate of oxygen accumulation} = {} & \text{Net rate of oxygen transmission} \\ & + \text{Net rate of oxygen respiration}\end{aligned} \tag{17}$$

$$\begin{aligned}\text{Rate of oxygen accumulation} = {} & \text{Rate of oxygen transmission in} \\ & - \text{Rate of oxygen consumption}\end{aligned} \tag{18}$$

$$V_f \frac{dy_{O_2(in)}}{dt} = OTR \times A\left(p_{O_2(out)} - p_{O_2(in)}\right) - W \times RR[O_2] \tag{19}$$

Where $\boldsymbol{V_f}$ = Headspace of package = Package volume- Fresh produce volume (ml)

A = Surface area of package (m^2)

W = Weight of fresh produces (kg)

$\boldsymbol{y_{O_2(in)}}$ = Volume fraction of oxygen inside package

OTR = Oxygen transmission rate of package (cc/m^2 day atm)

$p_{O_2(in)}$ = Oxygen partial pressure inside the package (atm)

$p_{O_2(out)}$ = Oxygen partial pressure outside the package (atm)

$RR[O_2]$ = Rate of oxygen consumption by fresh produce (cc/kg day)

$$\begin{aligned}\text{Rate of carbon dioxide accumulation} = &\ \text{Net rate of carbon dioxide transmission}\\ &+\text{Net rate of oxygen respiration}\end{aligned} \tag{20}$$

$$\begin{aligned}\text{Rate of carbon dioxide accumulation} = &-\text{Rate of carbon dioxide transmission out}\\ &+\text{Rate of carbon dioxide generation}\end{aligned} \tag{21}$$

$$V_f \frac{dy_{CO_2(in)}}{dt} = CO_2TR \times A\left(p_{CO_2(out)} - p_{CO_2(in)}\right) + W \times RR[CO_2] \tag{22}$$

Where $y_{CO_2(in)}$ = Volume fraction of carbon dioxide inside package

$\mathrm{CO_2TR}$ = Carbon dioxide transmission rate of package (cc/m^2 day atm)

$p_{CO_2(in)}$ = Carbon dioxide partial pressure inside the package (atm)

$p_{CO_2(out)}$ = Carbon dioxide partial pressure outside the package (atm)

$RR[CO_2]$ = Rate of carbon dioxide generation from fresh produces (cc/kg day)

From ideal gas law; $p_i = y_i \times P$

Where p_i = partial pressure (atm)

y_i = mole fraction

P = atmospheric pressure = 1 atm

Partial pressure ($\mathrm{p_i}$) in equation (19) and equation (22) were changed to mole fraction or volume fraction as shown in equation (*23*) and equation (*24*) and were used to calculate the respiration rates (RR) of straw mushroom in each film package.

$$V_f \frac{dy_{O_2(in)}}{dt} = OTR \times A\left(y_{O_2(out)} - y_{O_2(in)}\right) + W \times RR[O_2] \tag{23}$$

Where $y_{O_2(out)}$ = Volume fraction of oxygen in air =0.21

$$V_f \frac{dy_{CO_2(in)}}{dt} = CO_2TR \times A\left(y_{CO_2(out)} - y_{CO_2(in)}\right) + W \times RR[CO_2] \tag{24}$$

Where $y_{CO_2(out)}$ = Volume fraction of carbon dioxide in air =0.0003

An example of calculation of rate of oxygen consumption (RR[O_2]) of straw mushroom in bLDPE package at day 0 and day 2 were performed in this part. The results of RR[O_2] and rate of carbon dioxide production (RR[CO_2]) for all films are shown in Figure 4.10 and Figure 4.11 (Data are in Table E.10 to Table E.15). Calculations for other films are in Table E.4 to Table E.9 in appendix E.

Headspace volume of straw mushroom package was indirectly measured by replaced water in package with 0.255 kg of straw mushrooms. The headspace volume is 570 ml. Area of straw mushroom package is calculated from the height and width of package is 0.17 and 0.15 m, respectively. There are two sides of the package. The surface area of package is 0.17 x 0.15 x 2 = 0.0051 m^2. Initial weight of straw mushrooms is 0.255 kg per package. Volume fraction of oxygen and carbon dioxide inside mushroom package from the experiment of Bunsiri and coworkers (2012) are shown in Figure 4.7 and Figure 4.8 (data are in Table E.1 and Table E.2, respectively)[3]. OTR of bLDPE film from section 4.2.2 is 21,262.7 cc/m^2 day atm (data are in Table D.4).

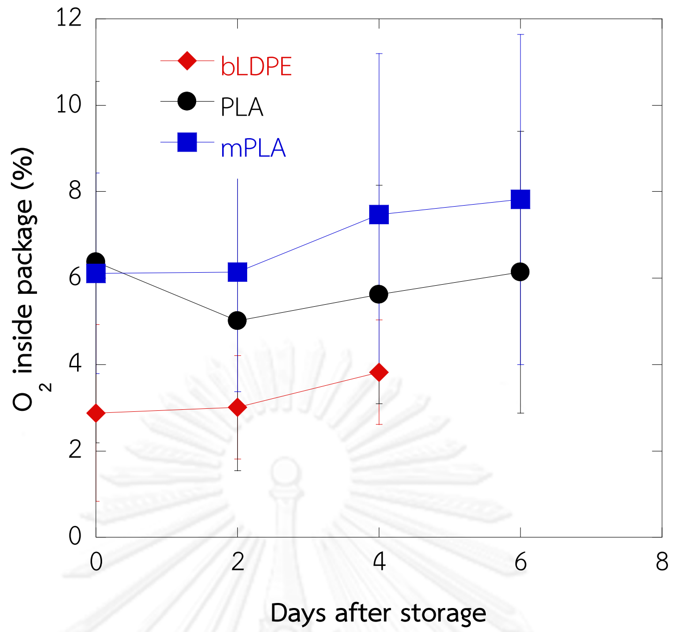


Figure 4.7 Oxygen concentration inside straw mushroom package at 15°C, 90%RH [3]

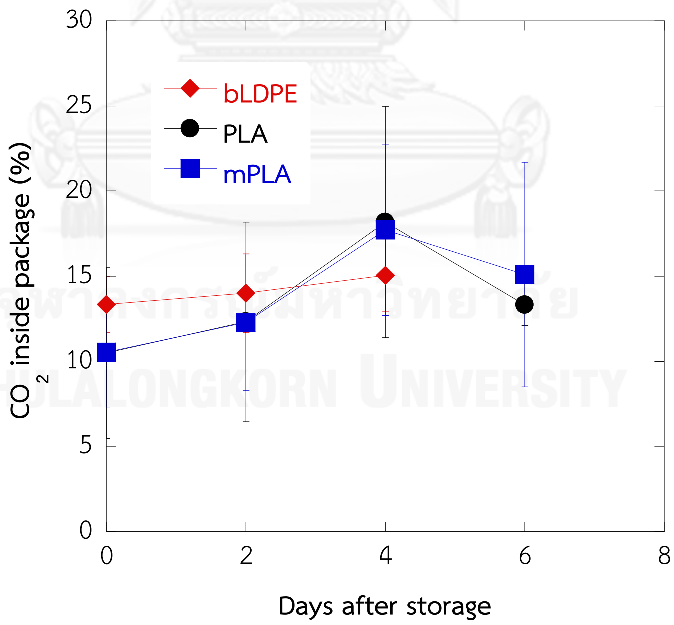


Figure 4.8 Carbon dioxide concentration inside straw mushroom package at 15°C, 90%RH [3]

At day 0

The gas concentration at day 0 in the experiment was collected after stored for 6 hours.

Assume initial gas concentration inside package is air (O_2 = 21%, CO_2 = 0.03%).

Differential term in accumulation term from equation (23) is estimated using this following equation:

$$V_f \frac{dy_{O_2(in)}}{dt} = V_f \frac{y_{O_2(in)}(t_i) - y_{O_2(in)}(t_{i-1})}{t_i - t_{i-1}}$$

Where $y_{O_2(in)}(t_i)$ = Oxygen volume fraction in package at time i

$y_{O_2(in)}(t_{i-1})$ = Oxygen volume fraction in package at time i-1

Calculated accumulation term

$$V_f \frac{dy_{O_2(in)}}{dt} = 570\ cc\ \times \frac{2.88/100-0.21}{0.25-0} = -413.17\ \frac{\mathrm{cc}}{day}$$

(Negative value shows that oxygen disappeared from system)

Calculated transmission term

$$OTR \times A\left(y_{O_2(out)} - y_{O_2(in)}\right) = 21{,}262.7 \times 0.051\ \times \left(0.21 - \frac{2.88}{100}\right)$$

$$= 196.13 \frac{cc}{day}$$

Calculated respiration term

$$W \times RR[O_2]\ = OTR \times A\left(y_{O_2(out)} - y_{O_2(in)}\right) - V_f \frac{dy_{O_2(in)}}{dt}$$

$$W \times RR[O_2]\ = 196.53 - (-413.17) =\ 609.70\ \frac{\mathrm{cc}}{day}$$

$$RR[O_2]\ =\ \frac{609.70}{0.255} = 2{,}390.98 \frac{cc}{kg\ day}$$

For day 2

Calculated accumulation term

$$\mathrm{V_f}\frac{\mathrm{dy_{O_2(in)}}}{\mathrm{dt}} = 570\ \mathrm{cc}\ \times\ \frac{3.01/100-2.88/100}{2-0.25}\ =\ 0.42\ \frac{cc}{day}$$

(Positive value shows that oxygen accumulated in system)

Calculated transmission term

$$\mathrm{OTR} \times \mathrm{A}\left(\mathrm{y_{O_2(out)}} - \mathrm{y_{O_2(in)}}\right) = 21262.7 \times 0.051\ \times\ \left(0.21 - \frac{3.01}{100}\right)$$

$$= 195.13\,\frac{\mathrm{cc}}{\mathrm{day}}$$

Calculated respiration term

$$W \times RR[O_2]\ = OTR \times A\left(y_{O_2(out)} - y_{O_2(in)}\right) - V_f\,\frac{dy_{O_2(in)}}{dt}$$

$$\mathrm{W}(RR[O_2])\ \ = 195.13 - 0.42 =\ 194.71\ \frac{cc}{day}$$

There were weight loss data of straw mushrooms that illustrated in Figure 4.9 (Data are in Table E.3), %weight loss at day 2 of mushrooms in bLDPE is 0.26wt%

Weight of mushrooms at day 2 = $0.255 \times (1 - \frac{0.26}{100}) =\ 0.254\ \mathrm{kg}$

$$RR[O_2]\ =\ \frac{194.71}{0.254} = 765.54\,\frac{cc}{kg\ day}$$

Rate of oxygen consumption and carbon dioxide generation for all film at each storage day are illustrated in Figure 4.10 and Figure 4.11, respectively (Data are in Table E.4 to Table E.9).

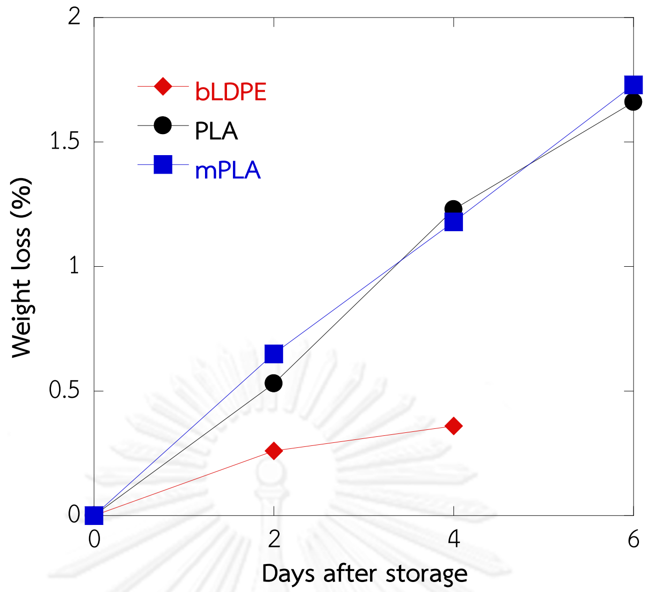


Figure 4.9 Percent weight loss of straw mushrooms in package at 15°C, 90%RH [3]

Straw mushrooms have non-climacteric respiratory pattern, i.e. respiration decreases with age [21]. In the modified atmospheric package (MAP) with high oxygen and carbon dioxide transmission rate such as bLDPE film, straw mushrooms kept their high respiration rate throughout storage period. Figure 4.10 shows high oxygen consumption of mushrooms in bLDPE MAP while Figure 4.11 shows corresponding high carbon dioxide production in bLDPE MAP when compared with both PLA and mPLA MAP. This contributed to faster deterioration of straw mushrooms in bLDPE MAP. This indicated that higher oxygen and carbon dioxide transmission rate of bLDPE resulted in shorter shelf life of straw mushrooms in bLDPE MAP.

In 2010 Bunsiri and coworkers demonstrated another important finding that shelf life of straw mushrooms kept in neat LDPE (lower OTR and CO_2TR than bLDPE) was only two days [4, 8]. This indicated that even at lower oxygen and carbon dioxide transmission rates similar to both PLA and mPLA MAP, there was another important factor determining shelf life of straw mushrooms stored in bLDPE MAP that is water vapor transmission rate of film.

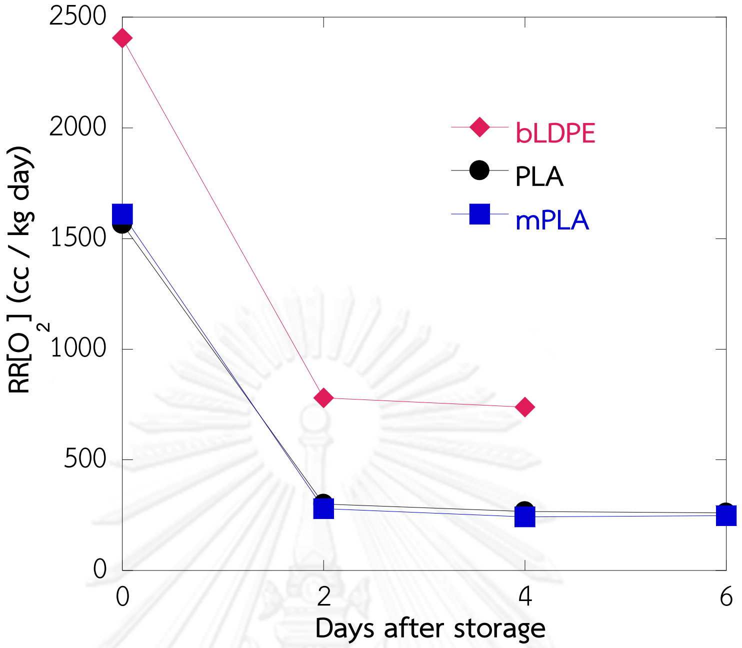


Figure 4.10 Rate of oxygen consumption of straw mushrooms

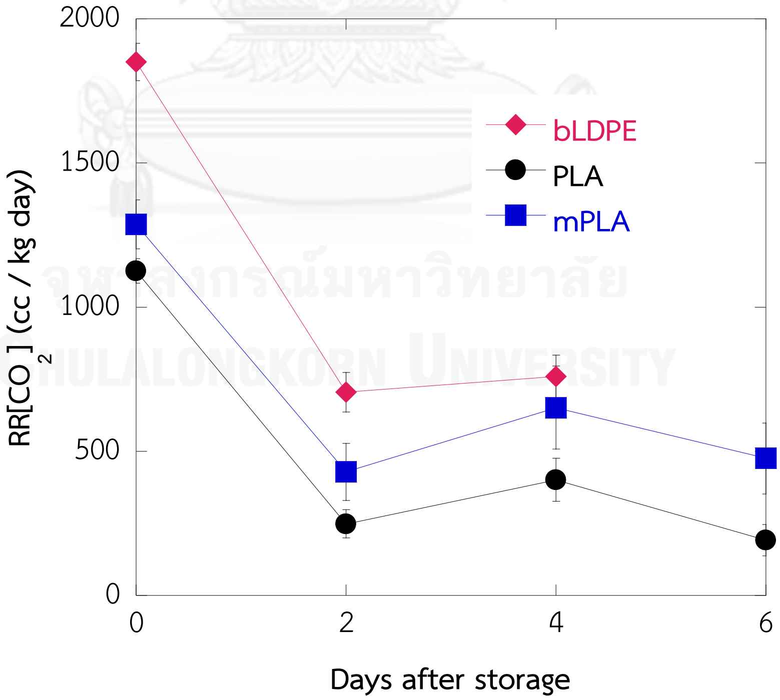


Figure 4.11 Rate of carbon dioxide generation of straw mushrooms

4.3.2. Effects of water vapor transmission of bLDPE film on shelf life of straw mushrooms in bLDPE MAP

With higher respiration rate, straw mushrooms in bLDPE MAP produced greater amount of water as shown in aerobic respiration mechanism (equation (*12*)). From Table 1.1, bLDPE has six times lower transmission rate of water vapor (19.5 gm/m^2 day) when compared with PLA (120.9 gm/m^2 day) and mPLA (132.9 gm/m^2 day). Results from data logger (section 4.2.2 and Figure 4.5) confirmed this. Straw mushrooms in bLDPE MAP were soaked with their own water and excess water was then reabsorbed. The reabsorption triggered production of beta-glucanase enzyme that digested beta-glucan in which cell wall of straw mushrooms comprised[22]. Straw mushrooms then underwent autolysis. As a result, high respiration with high humidity in bLDPE MAP jointly contributed to shorter shelf life of straw mushrooms.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

This experiment aimed to determine the factors for prolonging storage of straw mushrooms in modified atmosphere packaging, with specific focuses on effects of humidity on gas transmission rates through bLDPE, PLA and mPLA and respiration rates of straw mushroom in these packages.

Humidity affects oxygen transmission rate of mPLA but not PLA nor bLDPE. With steady state method, oxygen transmission rate of mPLA at 23°C increased from 1,069.3 cc/m^2/day at 0%RH to 2,561.1 cc/m^2/day at 40%RH. Oxygen transmission rate of mPLA did not increase significantly at higher levels of humidity.

An explanation why humidity affects gas transmission rates of mPLA more than the other films is that water vapor can be absorbed by mPLA better than bLDPE and PLA. This is because mPLA was modified with maleic anhydride grafted natural rubber (NR) and hydrophilic particles. The modification results in higher polarity of mPLA, which subsequently attracts water to plasticize mPLA. The process increases free volume of mPLA so oxygen can transmit through the film easily. PLA has lower polarity and bLDPE is nonpolar so their oxygen transmission rate was lower than that of mPLA.

OTR and CO_2TR of bLDPE, mPLA and PLA which were measured with unsteady state method at 15°C and 90%RH showed the same trend as those measured with steady state method at 23°C and 90%RH. However, OTR values measured with the unsteady state method were around twice higher. This could be due to different measurement methods and different calculation. The steady state directly measures amount of oxygen that reaches sensors while the unsteady state method indirectly measures OTR and CO_2TR by collecting concentration of oxygen or carbon dioxide in the samples of gases drawn from the container at various time points. Assuming that the steady state is a method of choice, errors of the unsteady state method could happen at three steps of the experiments, while the containers were stored in the storage room, when sample gases in the containers were collected and after sample gases were collected.

It is likely that high oxygen and carbon dioxide transmission rates of bLDPE resulted in high respiration rate of straw mushrooms thus speeding up the deterioration rate. With high respiration, greater amount of water was transpired. Because bLDPE has lower water transmission rate, excess water in bLDPE modified atmosphere package (MAP) was reabsorbed and autolysis was induced. These contributed to shorter shelf life of straw mushrooms in bLDPE MAP.

According to our research, WVTR of films affects shelf life of straw mushrooms more than OTR and CO_2TR. WVTR of package should be high to prevent humidity accumulation. OTR and CO_2TR should be moderate to prevent either anaerobic respiration or more respiration that causes faster deterioration.

5.2. Recommendations

5.2.1. Because information on respiration rates of straw mushrooms as a function of different concentration of oxygen and carbon dioxide will provide better prediction for dynamic of oxygen and carbon dioxide in MAP, it is recommended to conduct more studies on this factor of straw mushrooms and perhaps other produces.

5.2.2. Interactions among gases in the atmosphere on transmission rates of oxygen and carbon dioxide through various types of films categorized by level of polarity should be assessed.

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APPENDIX

Appendix A
Experimental data of oxygen transmission rate measurement using steady state method at 23°C and various relative humidity

Oxygen transmission rate (OTR) was measured using a steady state method at 23°C which follows ASTM D3985 (at 0%RH) and ASTM F1927 (at controlled %RH).

Table A.1 Oxygen transmission rate at 0 – 90 %RH of bLDPE film

No.	Relative humidity (%)				
	0	40	60	80	90
1	10,726.29	10,626.23	11,242.15	10,001.92	10,141.15
2	10,436.36	10,371.74	10,390.38	11,229.25	10,654.15
3	10,948.09	10,517.17	10,765.17	10,028.21	10,991.99
Avg	10,703.58	10,505.05	10,799.23	10,419.79	10,595.76
S.D.	256.62	127.68	426.91	701.13	428.41

Table A.2 Oxygen transmission rate at 0 – 90 %RH of PLA film

No.	Relative humidity (%)				
	0	40	60	80	90
1	587.55	437.26	405.73	431.58	395.30
2	590.61	449.24	427.77	394.44	405.49
3	526.48	466.48	438.63	412.79	422.29
Avg	568.21	450.99	424.04	412.94	407.69
S.D.	36.18	14.69	16.76	18.57	13.63

Table A.3 Oxygen transmission rate at 0 – 90 %RH of mPLA film

No.	Relative humidity (%)				
	0	40	60	80	90
1	1,028.25	2,586.32	2,633.15	2,679.87	2,705.18
2	918.17	2,542.89	2,248.11	2,692.91	2,178.67
3	1,261.47	2,554.07	2,633.54	2,200.92	2,651.11
Avg	1,069.30	2,561.09	2,504.93	2,524.57	2,511.65
S.D.	175.29	22.55	222.42	280.36	289.64

Appendix B
Calibration curve for gas chromatography

Calibration curve for carbon dioxide

1. Carbon dioxide with 99.9% purity with volume of 0.25, 0.5, 1, 1.5 and 2 cc were injected to gas chromatography and areas of each volume were obtained as shown in Table B.1.
2. Use ideal gas law to calculate mole of carbon dioxide from each volume
3. Plot mole vs. area and use linear regression to find the linear equation for carbon dioxide by using curve fit of Kaleida 3.6 program

Calibration curve for oxygen and nitrogen

1. Air with volume of 0.25, 0.5, 1, 1.5 and 2 ml were injected to gas chromatography and areas of each volume were obtained as shown in Table B.2 and Table B.3 for oxygen and nitrogen, respectively.
2. Use ideal gas law to calculate mole of oxygen and nitrogen contain in air from each volume
3. Plot mole vs. area and use linear regression to find the linear equation for oxygen and nitrogen by using curve fit of Kaleida 3.6 program

<u>Example for calculated from volume to mole of gas</u>

Ideal gas law: $PV = nRT$

V = Volume of gas = 1 cc

P = Atmospheric pressure = 1 atm

R = Gas constant = 82.06 cc atm / (gmol K)

T = Room temperature = 25°C = 298 K

$$n = \frac{PV}{RT} = \frac{1\ atm \times 1\ cc}{82.06\,\frac{cc\,atm}{gmol\,K} \times 298\ K} = 4.09 \times 10^{-5} gmol$$

Table B.1 Peak area and mole of CO_2

CO_2 volume (cc)	Peak area				CO_2 mole (gmol)
	1	2	3	Avg	
1	773815	798337	793725	788625.7	4.090E-05
0.75	532992	534218	536417	534542.3	3.067E-05
0.5	324590	343117	375012	347573.0	2.045E-05
0.25	183399	171895	188506	181266.7	1.022E-05
0.1	71397	79661	89822	80293.3	4.090E-06

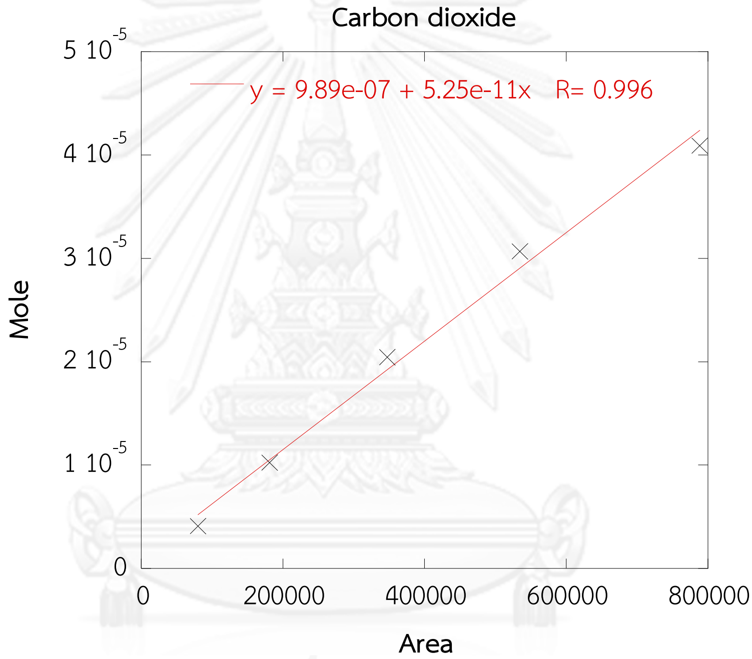

Figure B.1 Calibration curve for CO_2

Table B.2 Peak area and mole of O_2

Air volume (cc)	O_2 volume (cc)	Peak area				O_2 mole (gmol)
		1	2	3	Avg	
0.25	0.0525	32785	30961	30890	31545.3	2.15E-06
0.5	0.105	64893	70301	79898	71697.3	4.29E-06
1	0.21	152576	162759	171970	162435.0	8.59E-06
1.5	0.315	258471	254621	258325	257139.0	1.29E-05
2	0.42	361253	364482	374483	366739.3	1.72E-05

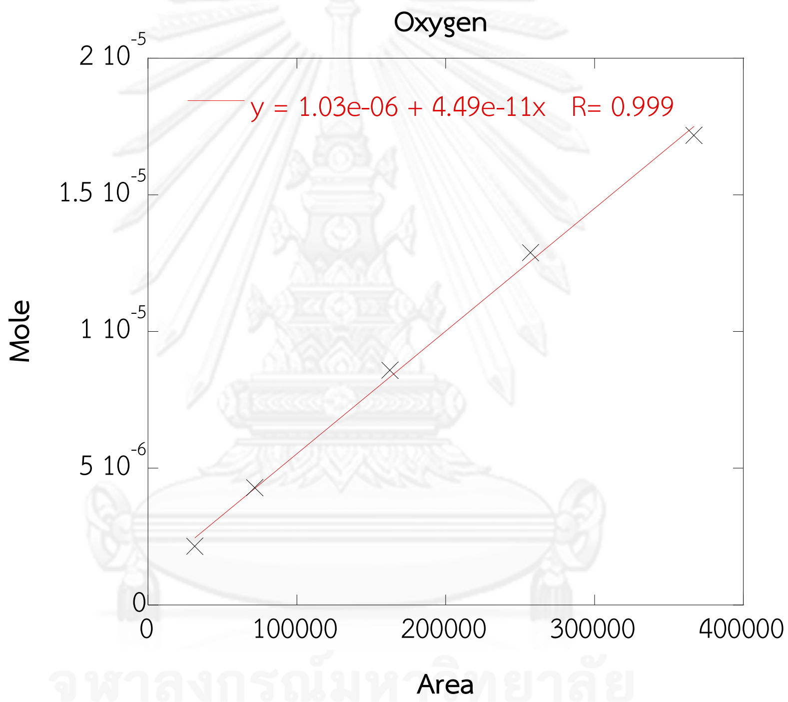

Figure B.2 Calibration curve for O_2

Table B.3 Peak area and mole of N_2

Air volume (cc)	N_2 volume (cc)	Peak area				Mole (gmol)
		1	2	3	Avg	
0.25	0.1952	129407	122539	122112	124686.0	7.98E-06
0.5	0.3904	255676	276792	314406	282291.3	1.60E-05
1	0.7808	598889	637118	673921	636642.7	3.19E-05
1.5	1.1712	935368	957298	1009141	967269.0	4.79E-05
2	1.5616	1409338	1421790	1461790	1430972.7	6.39E-05

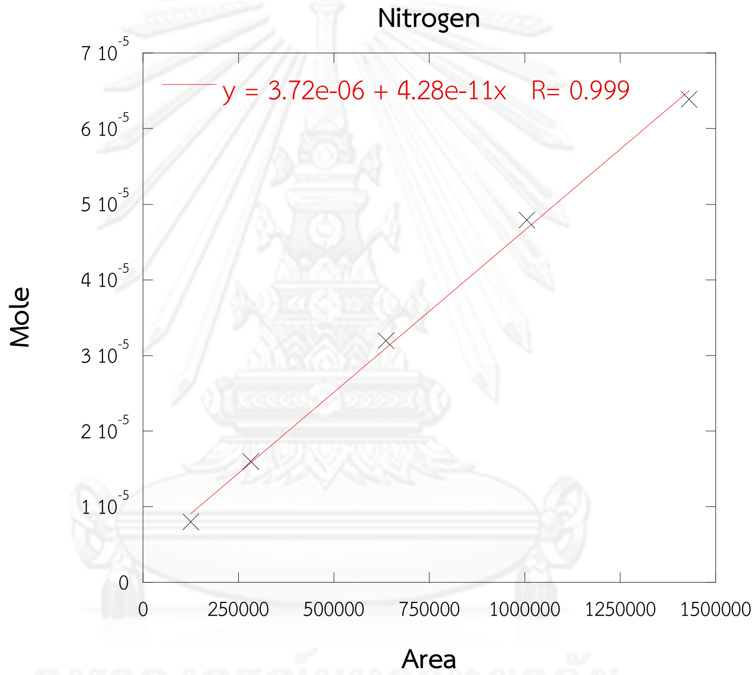

Figure B.3 Calibration curve for N_2

Appendix C

Experimental data of gas concentration in container at 15°C and 90%RH

Peak area that obtained from GC is converted to mole by using calibration curve from appendix B as follows

Carbon dioxide; $mole\ CO_2 = (5.25 \times 10^{-11}) \times area\ CO_2 + 9.89 \times 10^{-7}$

Oxygen; $mole\ O_2 = (4.49 \times 10^{-11}) \times area\ O_2 + 1.03 \times 10^{-6}$

Nitrogen; $mole\ N_2 = (4.28 \times 10^{-11}) \times area\ N_2 + 3.72 \times 10^{-6}$

Mole fraction (%mol) then calculate using the following equation

$$\%mol = \frac{mol\ of\ gas\ i}{total\ mol\ of\ gas} \times 100$$

From ideal gas law; volume fraction = mole fraction

Table C.1 Peak area of bLDPE for container volume of 2,600 cc for OTR measurement

Time (day)	Peak area		Mole			%mol	
	Oxygen	Nitrogen	Oxygen	Nitrogen	Total	Oxygen	Nitrogen
0	726863.5	12460.5	3.366E-05	4.254E-06	3.791E-05	88.78	11.22
2	680014.5	131822.0	3.156E-05	9.367E-06	4.092E-05	77.11	22.89
4	649231.5	157918.0	3.017E-05	1.048E-05	4.066E-05	74.21	25.79
6	620581.5	211043.0	2.889E-05	1.276E-05	4.165E-05	69.36	30.64
8	543401.0	239343.5	2.542E-05	1.397E-05	3.940E-05	64.53	35.47
10	536443.0	309462.0	2.511E-05	1.698E-05	4.209E-05	59.66	40.34

Table C.2 Peak area of bLDPE for container volume of 2,800 cc for OTR measurement

Time (day)	Peak area		Mole			%mol	
	Oxygen	Nitrogen	Oxygen	Nitrogen	Total	Oxygen	Nitrogen
0	702399.0	112476.0	3.256E-05	8.538E-06	4.110E-05	79.23	20.77
2	650829.5	185756.5	3.025E-05	1.168E-05	4.192E-05	72.15	27.85
4	639759.0	212109.5	2.975E-05	1.281E-05	4.255E-05	69.91	30.09
6	584431.0	259566.5	2.727E-05	1.484E-05	4.210E-05	64.76	35.24
8	534802.0	302821.5	2.504E-05	1.669E-05	4.173E-05	60.00	40.00
10	468669.5	325134.5	2.207E-05	1.765E-05	3.972E-05	55.57	44.43

Table C.3 Peak area of PLA for container volume of 2,600 cc for OTR measurement

Time (day)	Peak area		Mole			%mol	
	Oxygen	Nitrogen	Oxygen	Nitrogen	Total	Oxygen	Nitrogen
0	759997.5	14920.5	3.515E-05	4.359E-06	3.950E-05	88.97	11.03
2	707700.0	32839.5	3.280E-05	5.127E-06	3.792E-05	86.48	13.52
4	677626.5	64412.0	3.145E-05	6.479E-06	3.793E-05	82.92	17.08
6	659787.5	80345.5	3.065E-05	7.162E-06	3.781E-05	81.06	18.94
8	618841.5	98660.5	2.881E-05	7.946E-06	3.676E-05	78.38	21.62
10	587638.5	107165.0	2.741E-05	8.311E-06	3.572E-05	76.73	23.27

Table C.4 Peak area of PLA for container volume of 2,800 cc for OTR measurement

Time (day)	Peak area		Mole			%mol	
	Oxygen	Nitrogen	Oxygen	Nitrogen	Total	Oxygen	Nitrogen
0	803340.0	7185.0	3.709E-05	4.028E-06	4.112E-05	90.20	9.80
2	742217.5	27414.5	3.435E-05	4.894E-06	3.924E-05	87.53	12.47
4	707793.5	75958.0	3.280E-05	6.974E-06	3.978E-05	82.47	17.53
6	702467.5	93727.5	3.256E-05	7.735E-06	4.030E-05	80.81	19.19
8	705994.5	115087.0	3.272E-05	8.650E-06	4.137E-05	79.09	20.91
10	687035.0	136526.0	3.187E-05	9.568E-06	4.144E-05	76.91	23.09

Table C.5 Peak area of mPLA for container volume of 2,600 cc for OTR measurement

Time (day)	Peak area		Mole			%mol	
	Oxygen	Nitrogen	Oxygen	Nitrogen	Total	Oxygen	Nitrogen
0	832576.0	29570.5	3.840E-05	4.987E-06	4.339E-05	88.51	11.49
2	875242.0	133577.5	4.032E-05	9.442E-06	4.976E-05	81.03	18.97
4	782649.0	123548.5	3.616E-05	9.012E-06	4.517E-05	80.05	19.95
6	680272.0	144403.5	3.157E-05	9.906E-06	4.147E-05	76.12	23.88
8	668836.5	154711.5	3.105E-05	1.035E-05	4.140E-05	75.01	24.99
10	606660.0	164995.5	2.826E-05	1.079E-05	3.905E-05	72.37	27.63

Table C.6 Peak area of mPLA for container volume of 2,800 cc for OTR measurement

Time (day)	Peak area		Mole			%mol	
	Oxygen	Nitrogen	Oxygen	Nitrogen	Total	Oxygen	Nitrogen
0	881467.5	17615.5	4.060E-05	4.475E-06	4.507E-05	90.07	9.93
2	843687.0	74279.0	3.890E-05	6.902E-06	4.580E-05	84.93	15.07
4	767154.0	85986.0	3.547E-05	7.403E-06	4.287E-05	82.73	17.27
6	729505.0	105584.0	3.378E-05	8.243E-06	4.202E-05	80.38	19.62
8	790430.0	130559.0	3.651E-05	9.313E-06	4.582E-05	79.68	20.32
10	698360.0	132823.0	3.238E-05	9.410E-06	4.179E-05	77.48	22.52

Table C.7 Peak area of bLDPE for container volume of 2,600 cc for CO_2TR measurement

Time (day)	Peak area			Mole				%mol		
	Oxygen	Nitrogen	Carbon dioxide	Oxygen	Nitrogen	Carbon dioxide	Total	Oxygen	Nitrogen	Carbon dioxide
0	23704.0	80229.0	693587.5	2.096E-06	7.157E-06	3.738E-05	4.664E-05	4.50	15.35	80.16
2	51280.5	183315.0	678142.0	3.334E-06	1.157E-05	3.657E-05	5.148E-05	6.48	22.48	71.04
4	82349.0	301354.0	569423.0	4.729E-06	1.663E-05	3.087E-05	5.222E-05	9.05	31.84	59.10
6	83990.5	305746.0	549194.0	4.802E-06	1.682E-05	2.981E-05	5.143E-05	9.34	32.70	57.96
8	93431.0	339774.5	455027.5	5.226E-06	1.827E-05	2.486E-05	4.837E-05	10.81	37.78	51.41
10	101936.0	367360.5	357546.5	5.608E-06	1.946E-05	1.975E-05	4.481E-05	12.51	43.42	44.07

Table C.8 Peak area of bLDPE for container volume of 2,800 cc for CO_2TR measurement

Time (day)	Peak area			Mole				%mol		
	Oxygen	Nitrogen	Carbon dioxide	Oxygen	Nitrogen	Carbon dioxide	Total	Oxygen	Nitrogen	Carbon dioxide
0	21087.5	70825.0	839641.5	1.979E-06	6.754E-06	4.505E-05	5.378E-05	3.68	12.56	83.76
2	52317.0	190119.5	691596.0	3.381E-06	1.186E-05	3.728E-05	5.252E-05	6.44	22.59	70.98
4	81996.0	298973.0	542641.0	4.713E-06	1.653E-05	2.946E-05	5.070E-05	9.30	32.60	58.11
6	108513.0	387740.0	586929.0	5.903E-06	2.033E-05	3.179E-05	5.802E-05	10.17	35.04	54.79
8	93148.5	332523.5	416832.5	5.213E-06	1.796E-05	2.286E-05	4.604E-05	11.32	39.02	49.66
10	107323.5	392498.5	390575.5	5.850E-06	2.053E-05	2.148E-05	4.787E-05	12.22	42.90	44.88

Table C.9 Peak area of PLA for container volume of 2,600 cc for CO_2TR measurement

Time (day)	Peak area			Mole				%mol		
	Oxygen	Nitrogen	Carbon dioxide	Oxygen	Nitrogen	Carbon dioxide	Total	Oxygen	Nitrogen	Carbon dioxide
0	32333.5	111892.5	677216.0	2.484E-06	8.513E-06	3.652E-05	4.752E-05	5.23	17.91	76.86
2	44130.5	158690.5	739700.5	3.013E-06	1.052E-05	3.980E-05	5.333E-05	5.65	19.72	74.63
4	43471.0	163335.5	556109.0	2.984E-06	1.072E-05	3.017E-05	4.387E-05	6.80	24.43	68.77
6	52760.5	200803.0	494010.5	3.401E-06	1.232E-05	2.691E-05	4.263E-05	7.98	28.90	63.12
8	65209.0	246506.0	502146.5	3.959E-06	1.428E-05	2.734E-05	4.558E-05	8.69	31.33	59.98
10	79358.0	300785.0	490140.5	4.594E-06	1.660E-05	2.671E-05	4.791E-05	9.59	34.66	55.75

Table C.10 Peak area of PLA for container volume of 2,800 cc for CO_2TR measurement

Time (day)	Peak area			Mole				%mol		
	Oxygen	Nitrogen	Carbon dioxide	Oxygen	Nitrogen	Carbon dioxide	Total	Oxygen	Nitrogen	Carbon dioxide
0	41873.0	153382.5	831938.5	2.912E-06	1.029E-05	4.464E-05	5.784E-05	5.03	17.79	77.18
2	40021.0	145374.0	735274.0	2.829E-06	9.947E-06	3.957E-05	5.235E-05	5.40	19.00	75.59
4	41963.5	152621.0	694897.5	2.916E-06	1.026E-05	3.745E-05	5.062E-05	5.76	20.26	73.98
6	51805.0	193028.0	679501.5	3.358E-06	1.199E-05	3.664E-05	5.199E-05	6.46	23.06	70.48
8	58907.5	221323.5	662685.5	3.676E-06	1.320E-05	3.576E-05	5.264E-05	6.98	25.08	67.94
10	62096.5	233363.0	600797.0	3.820E-06	1.372E-05	3.251E-05	5.005E-05	7.63	27.41	64.96

Table C.11 Peak area of mPLA for container volume of 2,600 cc for CO_2TR

Time (day)	Peak area			Mole				%mol		
	Oxygen	Nitrogen	Carbon dioxide	Oxygen	Nitrogen	Carbon dioxide	Total	Oxygen	Nitrogen	Carbon dioxide
0	32333.5	111892.5	677216.0	2.484E-06	8.513E-06	3.652E-05	4.752E-05	5.23	17.91	76.86
2	44130.5	158690.5	739700.5	3.013E-06	1.052E-05	3.980E-05	5.333E-05	5.65	19.72	74.63
4	43471.0	163335.5	556109.0	2.984E-06	1.072E-05	3.017E-05	4.387E-05	6.80	24.43	68.77
6	52760.5	200803.0	494010.5	3.401E-06	1.232E-05	2.691E-05	4.263E-05	7.98	28.90	63.12
8	65209.0	246506.0	502146.5	3.959E-06	1.428E-05	2.734E-05	4.558E-05	8.69	31.33	59.98
10	79358.0	300785.0	490140.5	4.594E-06	1.660E-05	2.671E-05	4.791E-05	9.59	34.66	55.75

Table C.12 Peak area of mPLA for container volume of 2,800 cc for CO_2TR

Time (day)	Peak area			Mole				%mol		
	Oxygen	Nitrogen	Carbon dioxide	Oxygen	Nitrogen	Carbon dioxide	Total	Oxygen	Nitrogen	Carbon dioxide
0	32893.0	114343.5	692547.5	2.509E-06	8.618E-06	3.733E-05	4.845E-05	5.18	17.79	77.04
2	61137.0	231715.0	611581.0	3.776E-06	1.365E-05	3.308E-05	5.050E-05	7.48	27.02	65.50
4	58843.0	221690.0	550435.5	3.674E-06	1.322E-05	2.987E-05	4.676E-05	7.86	28.26	63.88
6	60750.5	231285.0	477620.5	3.759E-06	1.363E-05	2.605E-05	4.344E-05	8.65	31.37	59.97
8	77669.0	298296.5	404237.5	4.519E-06	1.650E-05	2.220E-05	4.322E-05	10.46	38.18	51.37
10	85183.0	325019.5	387560.0	4.856E-06	1.764E-05	2.132E-05	4.382E-05	11.08	40.26	48.66

Appendix D
Calculation of oxygen and carbon dioxide transmission rate at 15°C and 90%RH

Gas transmission rates were calculated using the method described in section 2.2 using the following equation (25)

$$ln\frac{(y_{air}-y)}{(y_{air}-y_0)} = \frac{-TR \times A}{V}t \tag{25}$$

Where y = %gas / 100

y_0 = %gas (at day 0) / 100

y_{air} = %gas in air (For oxygen is 21% and carbon dioxide is 0.03%) / 100

A = area of films (m^2)

V = volume of container (ml)

TR = transmission rate (cc / m^2 day atm)

t = time (day)

$ln\frac{(y_{air}-y)}{(y_{air}-y_0)}$ were plotted against time and slope of this graph was obtained. TR then calculated from the equation (26).

$$TR = -slope \times \frac{V}{A} \tag{26}$$

Example for oxygen transmission rate of PLA films and container volume of 2,600 cc

The data that used for transmission rate calculation

1. Oxygen concentration inside container from Table C.3

2. Volume of container is 2600 ml
3. Area of film in this experiment is 0.0064 m^2

Table D.1 Calculated $\%O_2$ to $\ln([y_{air} - y]/[y_{air}-y_0])$ of PLA films attached to container 2,600 cc

Time (days)	$\%O_2$	$ln\dfrac{y_{air}-y}{y_{air}-y_0}$
0	88.97	0
2	86.48	-0.03723
4	82.92	-0.09321
6	81.06	-0.12368
8	78.38	-0.16929
10	76.73	-0.19841

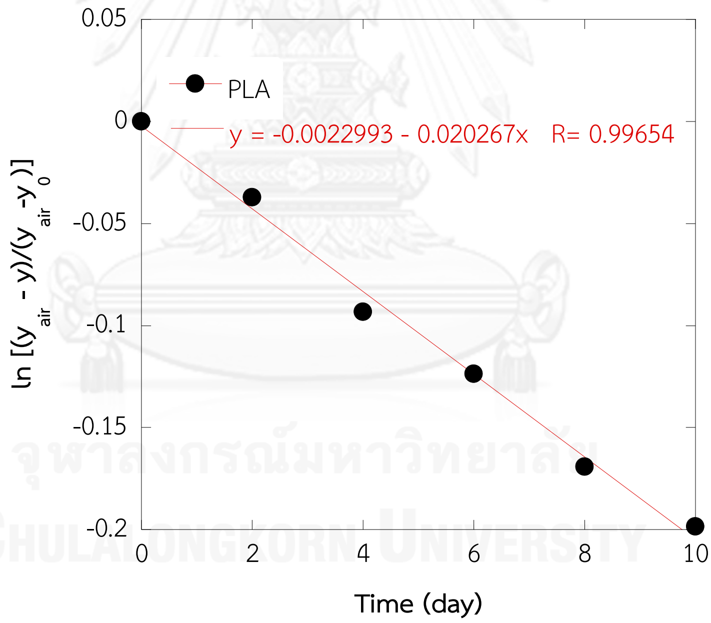

Figure D.1 Linear regression $\ln([y_{air} - y]/[y_{air}-y_0])$ vs. time

Slope = -0.020267

From equation (20);

$$OTR = -(-0.020267) \times \frac{2600}{0.0064} = 8233.5\ \frac{cc}{m^2 day}$$

Table D.2 OTR of bLDPE, PLA and mPLA calculation

Film	Volume	Linear regression	slope	TR
bLDPE	2,600	y = -0.02502x – 0.00819	-0.05234	21,262.7
bLDPE	2,800	y = -0.02502x – 0.00819	-0.05046	22,074.1
PLA	2,600	y = -0.02027x – 0.00230	-0.02027	8,233.5
PLA	2,800	y = -0.02144x – 0.00819	-0.02144	9,380.0
mPLA	2,600	y = -0.02502x – 0.00819	-0.02502	10,164.0
mPLA	2,800	y = -0.02502x – 0.00819	-0.01952	8,538.7

Table D.3 CO_2TR of bLDPE, PLA and mPLA calculation

Film	Volume	Linear regression	slope	TR
bLDPE	2,600	y = -0.05690x – 0.01432	-0.05690	23,115.6
bLDPE	2,800	y = -0.06075x – 0.04686	-0.06075	26,577.2
PLA	2,600	y = -0.02596x + 0.02936	-0.02596	10,546.7
PLA	2,800	y = -0.01758x + 0.01228	-0.01758	7,691.7
mPLA	2,600	y = -0.03354x + 0.01654	-0.03354	13,625.6
mPLA	2,800	y = -0.04416x - 0.02342	-0.04416	19,317.8

Table D.4 OTR of bLDPE, PLA and mPLA

Films	OTR (cc/ m^2 day)			
	1	2	avg	sd
bLDPE	21,262.7	22,074.1	21,668.40	573.75
PLA	8,233.5	9,380	8,806.75	810.70
mPLA	8,538.7	10,164	9,351.35	1,149.26

Table D.5 CO_2TR of bLDPE, PLA and mPLA

Films	CO_2TR (cc/ m^2 day)			
	1	2	Avg	sd
bLDPE	23,115.6	26,577.2	24,846.40	2,447.72
PLA	7,691.7	10,546.7	9,119.20	2,018.79
mPLA	13,625.6	19,317.8	16,471.70	4,024.99

Appendix E

Rate of oxygen consumed and carbon dioxide generated from straw mushrooms inside modified atmosphere package using mass balance

The data of Figure 4.7, Figure 4.8 and Figure 4.9 are illustrated in Table E.1, Table E.2 and Table E.3, respectively. Values of accumulation, transmission and respiration terms of oxygen consumption rate (RR[O_2]) and carbon dioxide generation rate (RR[CO_2])calculation of bLDPE, PLA and mPLA are shown in Table E.4 to Table E.9.

Table E.1 Oxygen concentration (%vol) of straw mushrooms inside package

Film	Days after storage			
	0	2	4	6
bLDPE	2.88	3.01	3.82	-
PLA	6.37	5.01	5.62	6.14
mPLA	6.11	6.14	7.47	7.82

Table E.2 Carbon dioxide concentration (%vol) of straw mushrooms inside package

Films	Days after storage			
	0	2	4	6
LDPE+NP	13.34	14.00	15.04	-
PLA+NP	10.49	12.32	18.18	13.33
MPLA+NP	10.55	12.28	17.73	15.10

Table E.3 Percent weight loss of straw mushrooms inside package

Films	Days after storage			
	0	2	4	6
LDPE+NP	0.00	0.26	0.36	-
PLA+NP	0.00	0.53	1.23	1.66
MPLA+NP	0.00	0.65	1.18	1.73

Table E.5 Rate of oxygen consumption (RR[O_2]) of straw mushrooms in bLDPE film

Time (days)	Weight of mushroom (kg)	$V_f \frac{dy_{O_2(in)}}{dt}$ (cc/day)	$OTR \times A\left(y_{O_2(out)} - y_{O_2(in)}\right)$ (cc/day)		$W \times RR[O_2]$ (cc/day)		$RR[O_2]$ (cc/kg day)	
			OTR = 21,262.7	OTR = 22,074.0				
0	0.2550	-413.17	196.51	204.01	609.68	617.18	2,390.91	2,420.32
2	0.2543	0.42	195.11	202.56	194.69	202.14	765.47	794.74
4	0.2541	2.32	186.27	193.38	183.95	191.06	724.01	751.98

Table E.4 Rate of oxygen consumption (RR[O_2]) of straw mushrooms in PLA film

Time (days)	Weight of mushroom (kg)	$V_f \frac{dy_{O_2(in)}}{dt}$ (cc/day)	$OTR \times A\left(y_{O_2(out)} - y_{O_2(in)}\right)$ (cc/day)		$W \times RR[O_2]$ (cc/day)		$RR[O_2]$ (cc/ kg day)	
			OTR = 8,233	OTR = 9,380				
0	0.2550	-333.60	61.44	70.00	395.04	403.60	1,549.19	1,582.74
2	0.2536	-4.43	67.15	76.50	71.58	80.93	282.19	319.06
4	0.2519	1.75	64.57	73.56	62.82	71.81	249.41	285.11
6	0.2508	1.47	62.40	71.09	60.93	69.62	242.95	277.60

Table E.7 Rate of oxygen consumption ($RR[O_2]$) of straw mushrooms in mPLA film

Time (days)	Weight of mushroom (kg)	$V_f \frac{dy_{O_2(in)}}{dt}$ (cc/day)	$OTR \times A(y_{O_2(out)} - y_{O_2(in)})$ (cc/day)		$W \times RR[O_2]$ (cc/day)		$RR[O_2]$ (cc/ kg day)	
			OTR = 8,539	OTR = 10,164				
0	0.2550	-339.6	64.86	77.21	404.47	416.81	1,586.14	1,634.56
2	0.2533	0.113	64.71	77.03	64.60	76.918	254.99	303.61
4	0.2520	3.78	58.94	70.16	55.16	66.38	218.91	263.43
6	0.2506	1.01	57.40	68.32	56.39	67.32	225.05	268.65

Table E.6 Rate of carbon dioxide generation ($RR[CO_2]$) of straw mushrooms in bLDPE

Time (days)	Weight of mushroom (kg)	$V_f \frac{dy_{CO_2(in)}}{dt}$ (cc/day)	$CO_2TR \times A(y_{CO_2(out)} - y_{CO_2(in)})$ (cc/day)		$W \times RR[CO_2]$ (cc/day)		$RR[CO_2]$ (cc/ kg day)	
			CO_2TR = 23,116	CO_2TR = 26,577				
0	0.2550	303.37	156.86	180.35	460.24	483.73	1,804.85	1,896.97
2	0.2543	2.18	164.75	189.42	166.93	191.60	656.31	753.31
4	0.2541	2.95	176.95	203.45	179.90	206.40	708.07	812.36

Table E.8 Rate of carbon dioxide generation (RR[CO_2]) of straw mushrooms in PLA film

Time (days)	Weight of mushroom (kg)	$V_f \frac{dy_{CO_2(in)}}{dt}$ (cc/day)	$CO_2TR \times A\left(y_{CO_2(out)} - y_{CO_2(in)}\right)$ (cc/day)		$W \times RR[CO_2]$ (cc/day)		$RR[CO_2]$ (cc/ kg day)	
			CO_2TR = 7,692	CO_2TR = 10,547				
0	0.2550	238.58	41.05	56.28	279.63	294.86	1,096.57	1,156.32
2	0.2536	5.95	48.21	66.10	54.15	72.05	213.50	284.04
4	0.2519	16.70	71.20	97.63	87.90	114.33	349.02	453.94
6	0.2508	-13.82	52.17	71.54	38.35	57.72	152.93	230.15

Table E.9 Rate of carbon dioxide generation (RR[CO_2]) of straw mushrooms in mPLA film

Time (days)	Weight of mushroom (kg)	$V_f \frac{dy_{CO_2(in)}}{dt}$ (cc/day)	$CO_2TR \times A\left(y_{CO_2(out)} - y_{CO_2(in)}\right)$ (cc/day)		$W \times RR[CO_2]$ (cc/day)		$RR[CO_2]$ (cc/ kg day)	
			CO_2TR = 13,626	CO_2TR = 19,318				
0	0.2550	239.77	73.08	103.61	312.85	343.38	1,226.86	1,346.58
2	0.2533	5.65	85.14	120.71	90.79	126.36	358.38	498.78
4	0.2520	15.53	123.00	174.38	138.53	189.91	549.73	753.64
6	0.2506	-7.50	104.72	148.47	97.23	140.98	388.01	562.60

Table E.10 Rate of oxygen consumption (RR[O_2]) of straw mushrooms in bLDPE film

Time (days)	RR[O_2] (cc/ kg day)			
	1	2	Avg	sd
0	2,390.91	2,420.32	2,405.62	20.79
2	765.47	794.74	780.10	20.70
4	724.01	751.98	737.99	19.78

Table E.11 Rate of oxygen consumption (RR[O_2]) of straw mushrooms in PLA film

Time (days)	RR[O_2] (cc/ kg day)			
	1	2	avg	sd
0	1,549.19	1,582.74	1,565.96	23.72
2	282.19	319.06	300.63	26.07
4	249.41	285.11	267.26	25.24
6	242.95	277.60	260.27	24.50

Table E.12 Rate of oxygen consumption (RR[O_2]) of straw mushrooms in mPLA film

Time (days)	RR[O_2] (cc/ kg day)			
	1	2	avg	sd
0	1,586.14	1,634.56	1,610.35	34.24
2	254.99	303.61	279.30	34.38
4	218.91	263.43	241.17	31.48
6	225.05	268.65	246.85	30.83

Table E.13 Rate of carbon dioxide generation (RR[CO_2]) of straw mushrooms in bLDPE film

Time (days)	RR[CO_2] (cc/ kg day)			
	1	2	avg	sd
0	1,804.85	1,896.97	1,850.91	65.14
2	656.31	753.31	704.81	68.59
4	708.07	812.36	760.22	73.75

Table E.14 Rate of carbon dioxide generation (RR[CO_2]) of straw mushrooms in PLA film

Time (days)	RR[CO_2] (cc/ kg day)			
	1	2	avg	sd
0	1,096.57	1,156.32	1,126.45	42.25
2	213.50	284.04	248.77	49.88
4	349.02	453.94	401.48	74.20
6	152.93	230.15	191.54	54.60

Table E.15 Rate of carbon dioxide generation (RR[CO_2]) of straw mushrooms in mPLA film

Time (days)	RR[CO_2] (cc/ kg day)			
	1	2	avg	sd
0	1,226.86	1,346.58	1,286.72	84.66
2	358.38	498.78	428.58	99.27
4	549.73	753.64	651.68	144.19
6	388.01	562.60	475.30	123.45

Appendix F
Temperature and relative humidity inside container measured by data logger

Table F.1 Relative humidity in container and storage room during OTR measurement

Time (hours)	bLDPE	PLA	mPLA	Room
0	23.51	22.65	28.29	72.19
6	33.23	69.86	69.31	88.07
12	39.27	79.07	78.65	88.20
18	43.91	81.44	81.87	86.64
24	47.90	82.93	83.23	83.16
30	51.20	83.37	82.94	83.27
36	53.31	83.75	83.78	88.31
42	55.67	84.03	84.53	87.64
48	57.45	84.36	84.83	85.09
60	60.87	84.69	84.77	86.61
72	63.31	85.00	85.40	88.93
84	65.46	85.60	85.69	87.19
96	67.02	85.78	85.72	87.31
120	69.13	86.03	85.66	88.57
144	70.89	85.87	85.24	87.07
168	72.12	86.02	85.52	89.30
192	73.28	86.15	84.82	85.48
216	74.11	86.25	85.15	86.57
240	74.56	86.19	85.13	82.09

Table F.2 Relative humidity in container and storage room during CO_2TR measurement

Time (hours)	bLDPE	PLA	mPLA	Room
0	18.17	26.47	25.67	73.59
6	26.58	58.43	57.51	86.37
12	31.63	65.37	65.76	87.38
18	35.44	68.05	68.89	88.39
24	38.58	69.51	70.27	85.20
30	41.41	70.40	70.29	87.96
36	44.04	70.60	71.12	87.76
42	45.91	70.79	72.08	86.51
48	47.88	70.84	72.21	84.71
60	51.11	71.49	72.65	87.29
72	53.41	71.76	73.49	88.97
84	55.40	72.34	73.89	81.87
96	57.36	72.26	74.37	86.55
120	59.78	73.00	74.25	88.89
144	62.11	73.16	74.15	86.02
168	63.82	73.78	74.46	89.14
192	65.47	74.60	74.21	86.44
216	66.80	75.02	74.75	87.17
240	68.23	74.91	75.33	81.46

Table F.3 Temperature in container and storage room during OTR measurement

Time (hours)	bLDPE	PLA	mPLA	Room
0	15.04	14.48	15.53	15.13
6	14.64	14.00	14.40	14.72
12	14.80	14.24	14.40	14.88
18	14.88	14.32	14.48	14.72
24	14.64	14.16	14.00	14.64
30	14.56	14.16	14.40	14.64
36	14.80	14.16	14.48	14.80
42	14.72	14.32	14.56	14.88
48	14.64	14.08	14.40	14.64
60	14.64	14.24	14.56	14.88
72	14.72	14.32	14.40	14.64
84	14.64	14.24	14.40	14.88
96	14.64	14.24	14.56	14.72
120	14.64	14.24	14.48	14.88
144	14.72	14.40	14.72	14.96
168	14.64	14.24	14.32	14.64
192	14.56	14.16	14.40	14.56
216	14.48	14.16	14.56	14.64
240	14.64	14.32	14.48	14.64

Table F.4 Temperature in container and storage room during CO_2TR measurement

Time (hours)	bLDPE	PLA	mPLA	Room
0	15.69	15.53	16.09	15.21
6	14.24	14.40	14.56	14.48
12	14.16	14.48	14.80	14.56
18	14.32	14.48	14.80	14.72
24	14.40	14.32	14.00	14.48
30	14.40	14.40	14.72	14.88
36	14.24	14.32	14.80	14.80
42	14.32	14.48	14.72	14.64
48	14.40	14.48	14.32	14.72
60	14.32	14.48	14.64	14.80
72	14.48	14.48	14.56	14.80
84	14.48	14.40	14.72	14.64
96	14.32	14.56	14.72	14.64
120	14.40	14.48	14.64	15.04
144	14.40	14.48	14.96	14.64
168	14.32	14.40	14.64	14.56
192	14.40	14.56	14.72	14.56
216	14.32	14.32	14.80	14.72
240	14.24	14.56	14.56	14.56

Appendix G
Raw data of contact angle measurement

Contact angle of a water droplet on film surface were observed using contact angle meter; Tantec Inc. Water was dropped on film surface. A water droplet was captured by camera and contact angle was then measured using Tantec CAM v3.0.8 software. There were three replicates for each film.

Table G.1 Contact angles of water droplets on bLDPE, PLA and mPLA

Films	Contact angle (degree)				
	1st	2nd	3rd	Average	S.D.
bLDPE	91.71	93.46	92.41	92.53	0.88
PLA	77.32	76.31	77.66	77.10	0.70
mPLA	69.39	68.53	70.48	69.47	0.98

VITA

Miss Nappaphan Kunanusont was born on February 13th, 1990 in Bangkok, Thailand. She studied high school at Wattana Wittaya Academy. In 2012, she received her Bachalor degree in Chemical Engineering from Chulalongkorn University. After graduation, she pursued her graduate study for Master's Degree in Chemical Engineering at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in 2012. During January 8-10, 2014 she was invited for poster presentation on "Effect of relative humidity on modified poly(lactic acid) blown films" at Pure and Applied Chemistry International Conference 2014, 8 – 10 January 2014, Khon Kaen, Thailand.