EFFECT OF THICKNESS OF POLY(L-LACTIC ACID) FIBER MEMBRANE ON GAS PERMEABILITY PROPERTY FOR MODIFIED ATMOSPHERE PACKAGING IN FRESH PRODUCES

Damrongpol Kamhangwong[1], Orawan Suwantong[2], Sornram Sukpisit[1,*]

[1]School of Agro-Industry, Mae Fah Luang University, Thasud, Chiang Rai 57100, Thailand
[2]School of Science, Mae Fah Luang University, Thasud, Chiang Rai 57100, Thailand
*e-mail: circleshop@hotmail.com

Abstract

Permeability of packaging material is an important factor for designing modified atmosphere packaging system (MAP) to prolong shelf life of produces. At present, the properties of this material have the limited range of gas permeability and the ratio of CO_2-to-O_2 permeability coefficient which do not satisfy and match the wide ranges of produce respiration. Using fiber membrane as a selective membrane is a way to solve these problems because fiber membrane has a high surface area to mass or volume ratio, small pore size with high porosity, etc. These properties are the key advantages for application of fiber membrane in many MAP systems. In this research, the effect of thickness (i.e., 100, 200, and 300 µm) of poly (L-lactic acid) (PLLA) fiber membrane on gas permeability property for modified atmosphere packaging in fresh produces was studied. The results showed that the tensile strength of the PLLA fiber membrane decreased with increasing the thickness of the PLLA fiber membrane while the increase of the thickness of the PLLA fiber membrane caused the carbon dioxide permeability coefficient and oxygen permeability coefficient to increase. The PLLA fiber membrane at thickness of 300 µm had the highest carbon dioxide permeability coefficient, oxygen permeability coefficient and ratio of CO_2-to-O_2 permeability coefficient at 79,413 $cm^3·µm/m^2·d.atm$, 31,513 $cm^3·µm/m^2·d·atm$, and 2.52, respectively. The PLLA fiber membrane at thickness of 100 µm had more water vapor transmission rate (WVTR) than the PLLA fiber membrane at thickness of 200 and 300 µm. From these results, the PLLA fiber membrane with the thickness of 100 – 300 µm had the potential for using in the modified atmosphere packaging for fresh produces having ratio of CO_2-to-O_2 permeability coefficient in range of 2-3. The optimized variables could be used to scale up the PLLA fiber membrane based passive MAP of fresh produce in bulk storage and transportation.

Keywords: poly(L-lactic acid), modified atmosphere packaging, permeability, fiber membrane and fresh produces.

Introduction

Fiber membranes generally have high gas and water vapor permeability as compared to synthetic film. These advantages render polymer fiber a good candidate for various applications such as modified atmosphere packaging (MAP). Modified atmosphere can be defined as an atmosphere that is created by altering normal a composition, in order to provide an appropriate atmosphere surrounding the product for decreasing its deterioration rate and increasing its shelf life (Phillips 1996; Farber et al. 2003).

Permeability to CO_2 and O_2 and water vapor transmission rate (WVTR) are the most important factor to be considered when selecting a film for MAP. These permeabilities are key factors in determining package atmosphere composition and humidity inside packages, and therefore they might influence product's deterioration rate (Gaston et al. 2007). However, the permeability property of fiber material have had the limited range of gas permeability and the ratio of CO_2-to-O_2 permeability coefficient which do not satisfy and match the wider ranges of produce respiration.
The permeability properties of fiber membrane are mainly influenced by small pore size. Thickness is a factor affecting the small pore size of fiber membrane. Thus the objective of present study were to study the effect of thickness of poly(L-lactic acid) (PLLA) fiber membrane on gas permeability property for modified atmosphere packaging application in fresh produces.

Methodology

Fiber membrane preparation
The thickness of PLLA fiber membrane was 100, 200 and 300 μm.The base PLLA solution in 7:3 v/v dichloromethane (DCM)/dimethylformamide (DMF) was first prepared at a fixed concentration of 10 % w/v. The solution was then electrospun under a fixed electric field of 20 kV/18 cm. The varying collection time was 12 – 36 hours, resulting in the different thickness (100 – 300±25 μm) of the PLLA fiber membrane.

Fiber membrane thickness
The thickness of the PLLA fiber membrane was measured using a digital micrometer. Ten random locations of each membrane were used for the thickness determination of fiber membrane.

Characterization of fiber membrane
The morphological appearances of the PLLA fiber membrane were observed using a LEO (Cambridge, UK) 1450 VP scanning electron microscope (SEM). Prior to being observed under the SEM, each sample was coated with a thin layer of gold using a Polaron SC-7620 sputtering device (Quorum Technologies, Newhaven,UK). Fiber diameters were measured directly from SEM images using the SemAphore 4.0 software package.

Mechanical properties
Tensile strength (TS) and elongation at break (EAB) were determined as previously described by ASTM D6380-00 method using the Universal Testing Machine. Prior to each test, the samples were conditioned at 25±0.5 ^{o}C and 50±2 %RH in incubator for 48h. TS (MPa) was calculated by the following equation:

$$TS\ (MPa) = F\ max/A \qquad (1)$$

where F max is the maximum load (N) needed to pull the sample apart, A is the cross-sectional area (m^2) of the samples. EAB (%) was calculated by following equation:

$$EAB\ (\%) = (E/30)*100 \qquad (2)$$

where E is the film elongation (mm) at the moment of rupture, 30 is the initial grip length (mm) of samples.

Gas permeability
Gas permeability coefficient was tested through ASTM D1434-82, procedure M-Manometric (2009). The instrument is permeation cell used in the continuous flow, isostatic system. Gases used in this study are oxygen and carbon dioxide at 0 %RH and 23±0.1 °C. The ratio of CO_2-to-O_2 permeability coefficient of PLLA fiber membrane (β) was calculated by following equation:

$$\beta = PCO_2 / PO_2$$

Water vapor transmission rate
The water vapor transmission rate (WVTR) was determined gravimetrically using the ASTM Standard Method E 96-00 (2002b).

Statistical analysis
Experiments were run in triplicate. Data were subjected to analysis of variance (ANOVA) and mean comparisons were carried out by Duncan's multiple range test (Steel and Torrie 1980). Analysis was performed using the SPSS package (SPSS 11.0 for windows, SPSS Inc., Chicago, IL, USA).The statistical significance was considered to be $p<0.5$.

Results

The effect of thickness of the PLLA fiber membrane on the mechanical properties of the PLLA fiber membrane is shown in Table 1. The results showed that the increase of the thickness of the PLLA fiber membrane caused the tensile strength to decrease. While, the thickness of the PLLA fiber membrane did not affect to the elongation at break.

Table 1 The effect of thickness on mechanical properties of PLLA fiber membrane

Treatment	Thickness (µm)	TS (lb/inch^2)	EAB (%)
PLLA 100 µm	105^c±2.1	61.67^a±2.88	73.12±2.55
PLLA 200 µm	221^b±6.0	36.67^b±0.72	71.54±4.54
PLLA 300 µm	321^a±5.1	26.12^c±1.73	73.23±5.43

^{a,b} Different letters within a column indicate significantly different ($p<0.05$).

Table 2 The effect of thickness on gas permeability of PLLA fiber membrane

Treatment	P_{CO_2} (cm^3·µm/ m^2·d·atm)	P_{O_2} (cm^3·µm/ m^2·d·atm)	P_{CO_2}/P_{O_2}
PLLA 100 µm	28,878^c	14,018^c	2.06
PLLA 200 µm	61,057^b	29,354^b	2.08
PLLA 300 µm	79,413^a	31,513^a	2.52

^{a,b} Different letters within a column indicate significantly different ($p<0.05$) for carbon dioxide and oxygen permeability coefficient respectively.

From Table 2, the increase of the thickness caused both the gas permeability coefficient of the PLLA fiber membrane and the ratio of CO_2-to-O_2permeability coefficient increased. The PLLA fiber membrane at thickness of 300 µm had the highest carbon dioxide permeability coefficient, oxygen permeability coefficient and ratio of CO_2-to-O_2permeability coefficient at 79,413 $cm^3 \cdot µm/m^2 \cdot d \cdot atm$, 31,513 $cm^3 \cdot µm/m^2 \cdot d \cdot atm$, and 2.52, respectively.

Table 3 The effect of thickness on water vapor transmission rate of PLLA fiber membrane

Treatment	Water vapor transmission rate ($g/m^2 \cdot day$)
PLLA 100 µm	6.63[a]
PLLA 200 µm	5.79[b]
PLLA 300 µm	5.71[b]

[a,b] Different letters within a column indicate significantly different ($p<0.05$).

The results from Table 3 showed that the thickness of the PLLA fiber membrane did not affected the water vapor transmission rate of the PLLA fiber membrane. The PLLA fiber membrane at the thickness of 100 µm had more water vapor transmission rate than the PLLA fiber membrane at the thickness of 200 and 300 µm.

Discussion and Conclusion

The increase of the thickness of the PLLA fiber membrane caused the carbon dioxide permeability coefficient and oxygen permeability coefficient ($cm^3 \cdot µm/m^2 \cdot d \cdot atm$) to increase. Because the increasing of thickness of the PLLA fiber membrane had more effect than the decreasing of permeance ($cm^3/m^2 \cdot d \cdot atm$) The PLLA fiber membrane at the thickness of 300 µm had the ratio of CO_2-to-O_2 permeability coefficient of the PLLA fiber membrane at the value of 2.5. The PLLA fiber membrane at thickness of 100 µm had more water vapor transmission rate (WVTR) than the PLLA fiber membrane at thickness of 200 and 300 µm. These results suggested that increasing the thickness of fiber membrane had tendency to display some interesting properties for applying in modified atmosphere packaging for fresh produce because it can be enhanced in both permeability and perm selectivity of CO_2-to-O_2 properties of the membrane

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