EFFECT OF Ca-5A ZEOLITE-LOADED POLY(L-LACTIC ACID) FIBER MEMBRANE ON GAS PERMEABILITY PROPERTY FOR MODIFIED ATMOSPHERE PACKAGING IN FRESH PRODUCES

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Abstract

Polymer fiber has several interesting characteristics, for example, a high surface area to mass or volume ratio, small pore size with high porosity, etc. These advantages render polymer nano-fiber a good candidate for various applications such as modified atmosphere packaging (MAP) for fresh produces. In this research, the effect of Ca-5A zeolite-loaded poly(L-lactic acid) (PLLA) fiber membrane on gas permeability property for modified atmosphere packaging in fresh produces was studied. The addition of a Ca-5A zeolite at concentration of 5%, 10% and 15% w/w in the PLLA fiber membrane caused the tensile strength of the PLLA fiber membrane to decrease. Moreover, the addition of a Ca-5A zeolite at concentration below 5% w/w caused the carbon dioxide permeability coefficient and oxygen permeability coefficient to decrease. While, the addition of a Ca-5A zeolite at concentration of 10% and 15% w/w caused the carbon dioxide permeability coefficient and oxygen permeability coefficient to increase. However, the addition of a Ca-5A zeolite did not affect the change of the ratio of CO_2-to-O_2 permeability coefficient of PLLA fiber membrane. From these results, The Ca-5A zeolite-loaded PLLA fiber membrane might be have potential for using in the modified atmosphere packaging for fresh produces having ratio of CO_2-to-O_2 permeability coefficient about 2. Moreover, the area of the PLLA fiber membrane can be adjusted for suitable atmospheric modification with respiration rate of such fresh produces.

Keywords: Ca-5A zeolite, poly(L-lactic acid), modified atmosphere packaging, permeability coefficient, fiber membrane

Introduction

The electrospinning has been well received as a simple and efficient method for the production of ultrafine fibers with sizes ranging from few micrometers down to tens of nanometers (Reneker and Yarin 2008). The outstanding characteristics of these fibers are, for example, their high gas permeation, surface area to mass or volume ratios, the small pore sizes of the resulting fibrous matrices, and the myriad possibilities for surface functionalization that they permit. These characteristics make these fibers ideal for various applications. In the field of postharvest technology, they can be used as a modified atmosphere packaging (MAP) to prolong the shelf-life of agriculture product. 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). The use of modified atmosphere includes two kinds of storage: controlled atmosphere storage and modified atmosphere packaging. When controlled atmosphere storage (CAS) is used, the product is stored in cold storage rooms under an atmospheric composition that is maintained constant throughout storage. On the other hand, during modified atmosphere packaging (MAP), fresh produce is generally packaged in polymeric films bags; being the atmosphere inside the package modified due to two processes: respiration of the product and diffusion of gases through the packaging film (Fonseca et al. 2002; Farber et al. 2003). Fresh produces often have significantly different packaging requirements than the whole product. For whole produce, packaging is primarily designed to avoid bruising during post storage handling. The MA packaging technique consists of the enclosure of respiring produced in polymeric films or selective membrane window in which the gaseous environment is actively or passively altered to slow respiration, reduce moisture loss and decay and/or extend the shelf life of the products. Many films used in MAP do not offer all the properties required for a modified atmosphere pack. To provide packaging films with a wide range of physical properties, the addition of Ca-5A that has a pore opening of the calcium form of zeolite type A (5 Ångstrom) will improve both permeation and selectivity of CO_2 and O_2 for packaging films.

Methodology

Polymer fiber membrane preparation

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 Ca-5A zeolite containing PLLA solutions were prepared by dissolving the same amount of PLLA powder and the Ca-5A zeolite in the DCM/DMF mixture at concentration of 0, 5, 10, and 15% w/w. (based on the weight of PLLA powder). Prior to electrospinning, the solutions were characterized for their viscosities and conductivities at room temperature (25±1°C) using a Brookfield RVDV-II + P viscometer and a Cyber Scan (Nijkerk, Netherlands) Con100 conductivity meter, respectively. The solutions were then electrospun under a fixed electric field of 20 kV/18 cm. The collection time was 12 h, resulting in the PLLA fiber membrane of thickness 100±10 μm

Fiber membrane thickness

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

Characterization of fiber membrane

The morphological appearances of both the neat and the Ca-5A zeolite-loaded 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 by ASTM D6380-00 method using the Universal Testing Machine. Prior to each test, the samples were conditioned at 25±0.5°C, 50±2 %RH in incubator for 48 h. 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 ^oC. The ratio of CO_2-to-O_2 permeability coefficient of PLLA fiber membrane (β) was calculated by following equation:

$$\beta = PCO_2 / PO_2 \qquad (3)$$

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 the Ca-5A zeolite addition with different concentration on the thickness and the mechanical properties of the PLLA fiber membrane is shown in Table 1. The addition of the Ca-5A zeolite at concentration of 5%, 10%, and 15% w/w caused the thickness of the PLLA fiber membrane to increase in the range of 107–108 μm. The addition of the Ca-5A zeolite did not affected the tensile strength and the percentage of elongation at break in comparison with the neat PLLA fiber membrane.

Table 1 The effect of Ca-5A zeolite with different concentration on thickness and mechanical properties of PLLA fiber membrane

Treatment	Thickness (μm)	TS (lb/inch^2)	EAB (%)
0%	105^b±2.2	61.7±2.9	73.12±2.55
5%Ca-5A zeolite	107^a±2.5	60.5±5.0	71.54±4.54
10%Ca-5A zeolite	107^a±2.8	63.5±2.5	73.23±5.43
15%Ca-5A zeolite	108^a±2.0	62.5±2.5	72.22±3.55

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

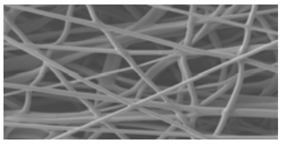
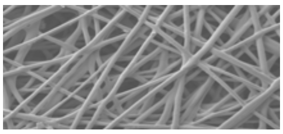
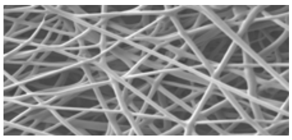
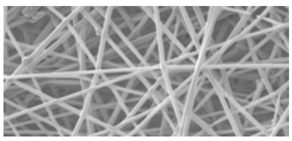
Table 2 The effect of Ca-5A zeolite with different concentration on gas permeability of PLLA fiber membrane

Treatment	P_{CO_2}	P_{O_2}	P_{CO_2}/P_{O_2}
	$(cm^3 \cdot \mu m/ m^{2} \cdot d \cdot atm)$		
0%	28,878[a]	23,264[a]	2.08
5%Ca-5A zeolite	10,567[c]	8,771[c]	2.02
10% Ca-5A zeolite	13,742[b]	11,491[b]	2.00
15% Ca-5A zeolite	15,693[b]	12,475[b]	2.10

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

From Table 2, all treatment have high permeation coefficient (>1000 $cm^3 \cdot \mu m/ m^{2} \cdot d \cdot atm$), thus they have the potential to apply as a membrane for MAP. The addition of the Ca-5A zeolite at concentration of 5% w/w caused the carbon dioxide permeability coefficient and oxygen permeability coefficient to decrease, while, the addition of the Ca-5A zeolite at concentration of 10 and 15% w/w caused the carbon dioxide permeability coefficient and oxygen permeability coefficient to increase. However, the addition of the Ca-5A zeolite did not affect the ratio of CO_2-to-O_2 permeability coefficient of the PLLA fiber membrane.

Table 3 Shear viscosity and electrical conductivity of neat and Ca-5A zeolite-loaded PLLA solutions ($n = 3$) as well as representative SEM images of the corresponding electrospun fiber mats including diameters of the individual fibers ($n \approx 120$)

Type of PLLA solution	Shear viscosity (mPa s)	Electrical conductivity ($\mu S\ cm^{-1}$)	Representative SEM images of electrospun fiber mat	Fiber diameters (µm)
Neat	60.1 ± 0.5	0.62 ± 0.03		0.95 ± 0.18[b]
5% Ca-5A zeolite	72.1 ± 0.1	0.93 ± 0.03		0.98 ± 0.21[a]
10% Ca-5A zeolite	71.1 ± 0.5	1.04 ± 0.04		0.99 ± 0.18[a]
15% Ca-5A zeolite	70.8 ± 0.4	1.06 ± 0.03		0.98 ± 0.11[a]

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

From Table 3, the addition of the Ca-5A zeolite at concentration of 5%, 10%, and 15% w/w caused the shear viscosity to decrease (i.e., 70.8–72.1 mPa s), while, the electrical conductivity to increase (i.e., 0.93–1.06 μS cm^{-1}). In comparison with the neat PLLA fiber membrane, the addition of the Ca-5A zeolite caused the fiber diameter to increase (i.e., 0.99–0.95 μm).

The effect of the Ca-5A zeolite with different concentration on the water vapor transmission rate of the PLLA fiber membrane is shown in Table 4. The results showed that the addition of the Ca-5A zeolite at concentration of 15% wt. in the PLLA fiber membrane had the highest water vapor transmission rate (i.e., 6.23 $g/m^2 \cdot day$). While, the addition of the Ca-5A zeolite at concentration of 5% and 10% w/w in the PLLA fiber membrane had the water vapor transmission rate similar to the neat PLLA fiber membrane.

From these results, it could be concluded that the addition of the Ca-5A zeolite at concentration higher than 15% w/w caused the water vapor transmission rate of the PLLA fiber membrane to increase.

Table 4 The effect of Ca-5A zeolite with different concentration on water vapor transmission rate of PLLA fiber membrane

Treatment	Water vapor transmission rate ($g/m^2 \cdot day$)
Neat	5.79^{b}
Ca-5A 5% Zeolite	5.65^{b}
Ca-5A 10% Zeolite	5.94^{b}
Ca-5A 15% Zeolite	6.23^{a}

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

Discussion and Conclusion

The addition of the Ca-5A zeolite at concentration of 5% w/w caused the carbon dioxide permeability coefficient and oxygen permeability coefficient to decrease, while, the addition of the Ca-5A zeolite at concentration of 10 and 15% w/w caused the carbon dioxide permeability coefficient and oxygen permeability coefficient to increase. However, the addition of the Ca-5A zeolite had no effect to the ratio of CO_2-to-O_2 permeability coefficient of the PLLA fiber membrane. The addition of the Ca-5A zeolite at concentration of 15% w/w in the PLLA fiber membrane had more effect to WVTR than other concentrations. The Ca-5A zeolite-loaded PLLA fiber membrane might be have potential for using in the modified atmosphere packaging in fresh produces with ratio of CO_2-to-O_2 permeability coefficient in range of 2.0–2.5. Moreover, the area of the PLLA fiber membrane can be adjusted to increase or decrease the gas permeability coefficient for suitable atmospheric modification with respiration rate of such fresh produces.

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