IMPROVEMENT OF HYDRATION PROPERTIES OF PECTIN/ ALGINATE FILMS WITH ZnO NANOPARTICLES

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Abstract - This study aims to develop hydration properties of P/AG films by using ZnO nanoparticles. Pectin/ alginate/ ZnO nanoparticles (P/AG/ZnO-NPs) films are fabricated at various ZnO-NPs contents (0, 0.01, 0.05, 0.1 and 0.5 g/100g solution). The addition of ZnO-NPs at content 0.1 g/100g solution in the film decreases swelling degree (SD) from 327.98% to 110.12% and water vapor permeability (WVP) from 0.873 g.mm/m2.day.kPa to 0.358 g.mm/m2.day.kPa. Moisture sorption isotherm shows that P/AG/ZnO-NPs films should be used at lower than 86% RH. The Peleg model is the best model for predicting the equilibrium moisture content (EMC) of P/AG/ZnO-NPs films. Scanning electron microscope (SEM) micrographs of surface and cross section morphology of P/AG and P/AG with 0.1% ZnO-NPs films have indicated that there are interactions between ZnO-NPs and pectin-alginate matrix. Results have suggested that it would be favorable to prepare P/AG/ZnO-NPs film by using ZnO-NPs at the amount of 0.1 g/100g solution for food preservation.

Key words - alginate; moisture sorption isotherm; pectin; ZnO-NPs; water vapor permeability

1. Introduction

Nowadays, polysaccharides may be promising materials for preparing films and coatings because of their biocompatibility and biodegradability. Pectin and alginate are widely used because they are due to their good film forming characteristics, moderate mechanical properties and good gas barrier properties[1].

However, polysaccharides based packaging materials, especially pectin and alginate have been rarely applied to the packaging technology, mainly because of high water vapor permeability, high swelling degree, high equilibrium moisture contents and processing properties as well as higher production cost compared with commodity plastic films [2]. The addition of ZnO-NPs could improve some properties of films based on biopolymers [3], including hydration properties. Moreover, ZnO-NPs could be used as an antimicrobial agent and they are not harmful for humans [4]. For above reasons, P/AG edible films incorporated with ZnO-NPs have been applied to food packaging.

The main objective of this study is to develop P/AG films by mixing of various ZnO-NPs in order to improve the hydration properties of pectin/alginate films.

2. Materials and methods

2.1. Materials

Sodium alginate (AG) was purchased from Lianyungang Zhongda Seaweed Industrial Co. Ltd. (China). Pectin (P) was extracted from Yanang leaves by Phuong and Xo [5]. ZnO nanoparticles (ZnO-NPs) were obtained at the LAB of the University of Technology and Education, which belongs to the University of Danang, Vietnam and was according to Nam and Hoi method [6]. Glycerol and $CaCl_2$ were purchased from Xilong, China.

2.2. Methods

2.2.1. Film preparation

Pectin and alginate solutions were prepared by dissolving P/AG polymers in water at a concentration of 2% w/v with the ratio of alginate to pectin 1:1 (w/w). $CaCl_2$ was dispersed at a concentration of 0.01 g/g polymer and glycerol at 50%w/w of polymer. In this research, the concentration of ZnO-NPs was investigated at 4 levels: 0.01, 0.05, 0.1 and 0.5 g/100g solution [7].

The film forming dispersion was homogenized by a homogenizer for 15 minutes at speed of 400 rpm. Afterwards, it was cooled at 4°C for 24 hours for degassing. Each film was always prepared by 60 g film-forming solution and this solution was poured onto a mold with dimension (15cm x 15cm). Films were formed by drying at 25°C and 53% relative humidity (RH) during 24 h (using a fan). These films were taken out and dipped in 5% $CaCl_2$ solution in 20 minutes [8]. Films were dried at 40°C in a fan oven for two hours (Memmert, Germany). The dried films were conditioned at 53% RH, 25°C for 5 days in a chamber before testing [7].

2.2.2. Moisture content (MC)

The prepared film samples (2 cm x 2 cm) were dried at 105°C in an oven and their moisture contents were analyzed gravimetrically after 24h of drying using the following equation 1:

$$MC = \frac{m_i}{m_f} x100 \quad (1)$$

Where, m_i and m_f are the initial and final weights of film samples, respectively.

2.2.3. Swelling degree (SD)

Preweighed film samples (25 mm in diameter), were immersed in distilled water at 25°C for 60 min. During this period, at each 10 min, the wet films were wiped between two dry filter papers to remove excess liquid from the surface of film and weighed. The measurements were repeated three times for each type of film. The degree of swelling was calculated in percentages using Equation 2 [9]:

$$SD = \frac{m_1 - m_2}{m_{2i}} x100 \quad (2)$$

Where, m_1 and m_2 are the mass of the wetted and initial samples, respectively.

2.2.4. Water vapor permeability (WVP)

WVP of films was measured gravimetrically at 25°C (±1°C) according to method from ASTM E96-00. The aluminum cups with 8 cm diameter containing 10 g of silicagel were covered by the film specimens and fixed using paraffin on the wide rim [10]. The cups were placed in desiccators which provided 53±1% RH at 25±1°C using a saturated solution of $Mg(NO_3)_2$. The weight gain of the cups was recorded every 12 hours for 6 days [11]. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. All tests were conducted in duplicate. The WVP was calculated using the following equation 3:

$$WVP = \frac{w.x}{t.A.P_0(RH_1 - RH_2)} \quad (3)$$

Where, w/t is the permeation rate (g/day) calculated by linear regression of the mass gain versus time (R^2>0.99); x is the film average thickness (mm), A is the permeation area (23.76 cm^2); P_o is the partial water vapor pressure at test temperature (3159 kPa at 25°C) [6]; (RH_1- RH_2) is the relative humidity difference between the two sides of the film.

2.2.5. Sorption isotherm

The films were prepared with the size of 30 mm x 30 mm square and dried at 105°C for three hours before being kept in chambers containing silicagel for two days. After that, the samples were kept in chambers containing saturated salt solutions to control the relative humidity at 11, 33, 53, 64, 75, 86 and 93%. The film samples were weighed everyday until in equilibrium the change in weight did not exceed 0.1% was achieved. The equilibrium moisture content (EMC) of the films at each relative humidity was calculated using following equation 4:

$$EMC = \frac{W_e}{W_i}(M_i + 1) - 1 \quad (4)$$

Where, EMC is the equilibrium moisture content (g water/100 g dry solid); W_e is the equilibrium weight of the film sample (g); W_i is the initial weight of the film sample (g) and M_i is the initial moisture content of the film sample (g/g) [12]. All measurements were in triplicate. The BET, GAB, Oswin and Peleg models were the most widely used theoretical models to describe sorption isotherms of food. The constants of the equations were determined by using *Origin 6.0 Professional (*Microcal Software, Inc, USA). The best model to estimate the EMC of all films was selected depending on the fitting ability of a model in association with the number of data points throughout the determination coefficient (R^2) and the relative deviation (P). The *P* was calculated using the following equation 5. For a good fit, P value should be less than 10% and R^2 close to 1.

$$P = \frac{100}{n}\sum_{i=1}^{n}\left\{\frac{Y-\dot{Y}}{Y}\right\} \quad (5)$$

Where, P is the relative deviation (%); n is number of experimental observations; Y is equal to experimental value; $\dot{Y}$ is the estimated value by the model.

The Peleg's model was used for fitting sorption isotherms of films according to equation 6:

$$u = a.a_w^b + c.a_w^d \quad (6)$$

where, a, b, c, d are constants of equation; a_w is the water activity; u is the water content (g water/ g solids) [11].

The GAB, BET and Oswin models were used to fit sorption isotherms of films using equations 7 [13]:

The GAB model:

$$M = \frac{M_O.C.k.a_w}{(1-k.a_w).(1+(C-1).k.a_w} \quad (7)$$

Where, M is the equilibrium moisture content on dry basis at a water activity (a_w); M_o is the monolayer moisture value (g water/g solids); a_w is the water activity

C and k are the equation parameters

The BET model:

$$M = \frac{M_O.C.a_w}{(1-a_w).(1+(C-1).a_w} \quad (8)$$

Where, M is the equilibrium moisture content of the film at a water activity (a_w); M_o is the monolayer moisture value (g water/g solids); C and k are the constants of equation.

The Oswin model:

$$M = k.[\frac{a_w}{1-a_w}]^c \quad (9)$$

Where, M is the equilibrium moisture content of the film at a water activity (a_w); C and k are the constants of equation

2.2.6. Scanning electron microscopy (SEM)

The surface and cross section of the films were analyzed using scanning electron microscopy (JSM-5910LV, JEOL Ltd., Japan) conducted at 15kV. Cross section samples were cryofractured and fractured in liquid nitrogen. Then, the samples were coated with gold under vacuum. The surface and cross section of films were observed with 50000 and 2000 magnification.

3. Results and discussion

3.1. Moisture content and swelling degree of P/AG/ZnO-NPs films

Table 1 shows the moisture content and swelling degree of film specimens.

Table 1. *Moisture content and swelling degree of P/AG/ZnO-NPs films*

ZnO-NPs content (g/100g solution)	Moisture content, %	Swelling degree %
0	16.67 ± 1.3[a]	328.97 ± 10.1[a]
0.01	15.76 ± 0.9[a]	210.31 ± 7.9[b]
0.05	15.53 ± 0.5[a]	190.12 ± 8.1[b]
0.1	13.79 ± 0.3[b]	187.76 ± 8.5[b]
0.5	12.35 ± 0.9[c]	110.12 ± 6.8[c]

The calculation of the moisture content showed that the addition of ZnO-NPs to pectin – alginate matrix resulted in changes in the moisture content. Like moisture content, swelling degree of the specimens decreased with increasing ZnO-NPs content. This reduction may be explained by the interaction of the pectin and alginate's hydroxyl groups and oxygen atoms of the ZnO-NPs, which improved the cohesiveness of the film matrix and could decrease the absorbance of water molecules in the P/AG/ZnO-NPs films.

3.2. Water vapor permeability of P/AG/ZnO-NPs films

Water vapor permeability (WVP) changes of film specimens were shown in Figure 1.

WVP is another property related to the hydrophilic of the film. The more hydrophilic films, the lower vapor barrier of films is. The WVP changes were mainly due to the interactions of water molecules with hydroxyl and carboxyl groups in the P/AG matrices and the pathway for water molecules absorbance. WVP values of the specimens decreased from 0.873 to 0.329 (g.m/m^2.day.kPa), respectively with increasing ZnO-NPs content from 0 to 0.5 g/100g solution. A significant change of WVP value was observed with increasing ZnO-NPs content from 0.01 to 0.5 g/100g solution. This means in the range of studying ZnO-NPs concentration, vapor barrier property of P/AG films is better as ZnO-NPs content increased. These results were consistent with moisture content and swelling degree of films.

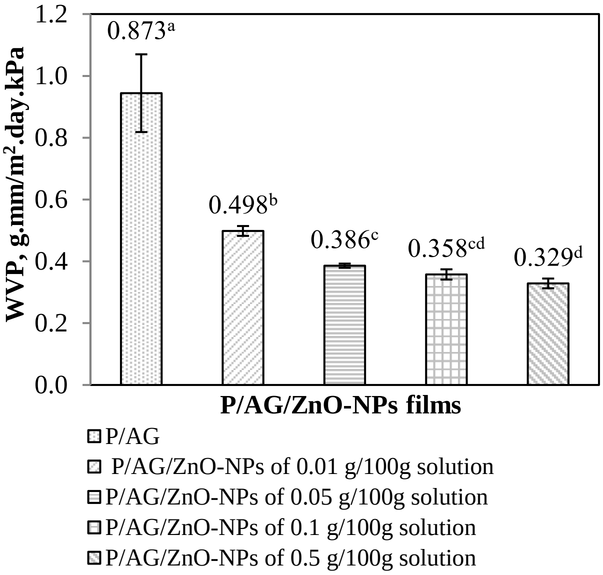


Figure 1. *WVP of P/AG/ZnO-NPs films*

3.3. Moisture sorption isotherms

Figure 2 shows the moisture sorption isotherms of the P/AG/ZnO-NPs films.

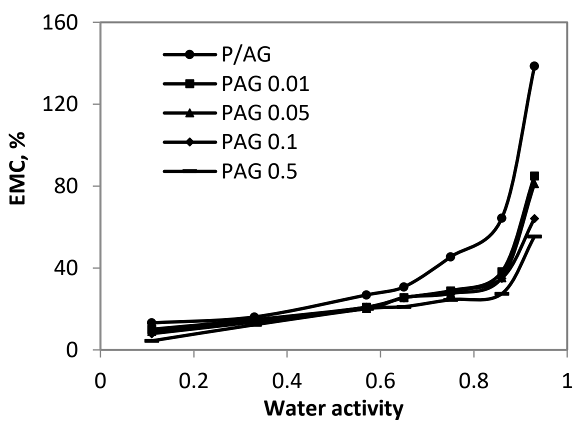


Figure 2. *Moisture sorption isotherms of P/AG/ZnO-NPs films at 25± 0.5°C*

The sorption isotherms curves of all films had a similar sigmoidal shape (Figure 2). A significantly lower change in moisture content was observed for the P/AG film incorporated with various contents of ZnO-NPs with water activity from 0.75 to 0.93. As can be seen, the moisture sorption of P/AG film was higher than that of P/AG with ZnO-NPs films and water content increased sharply with water activity from 0.86 to 0.93. Normally, the OH-groups of pectin and alginate units form hydrogen bonds with water molecules. Reduction in moisture absorbency was achieved by increasing the amount of ZnO-NPs in the film. These results indicated that the addition of ZnO could improve the water resistance of the P/AG matrix. The reason could be that the pectin and alginate chains were able to form hydrogen bonds with the oxygen atoms of the ZnO-NPs and this strong structure led to a decrease in diffusion of water molecules in films.

To model the relationship between the moisture content of the analyzed films and the water activity, an equation was chosen as EMC = f(aw). The Peleg, GAB, BET and Oswin models were used to fit the moisture sorption values of the films. Constants, regression coefficient (R^2) and the relative deviation (%P) in each model for each film are shown in Table 2.

Table 2. *Constants, regression coefficient (R^2) and the relative deviation (%P) of the Peleg, GAB, BET and Oswin models for moisture sorption isotherms of P/AG/ZnO-NPs films at 25± 0.5°C*

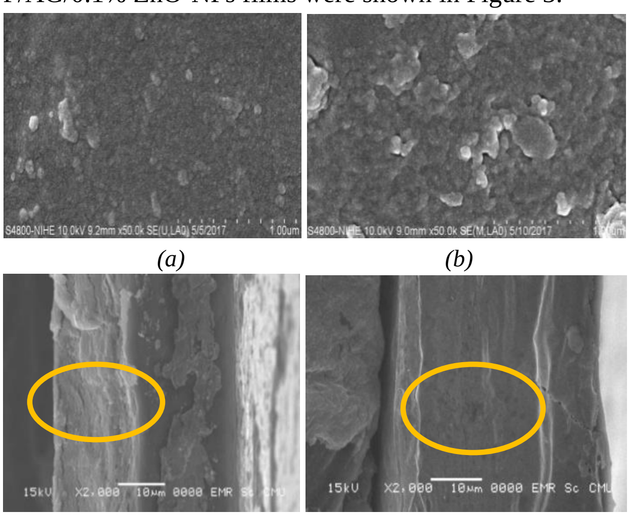
Models	Parameters	P/AG/ZnO-NPs (g ZnO-NPs/100g of solution P/AG)				
		P/AG	P/AG 0.01	P/AG 0.05	P/AG 0.1	P/AG 0.5
Peleg	a	324.39	284.42	32.16	34.60	31.22
	b	16.92	22.85	0.66	0.77	0.85
	c	45.75	32.24	354.27	198.79	5455.07
	d	0.78	0.62	26.83	25.41	73.65
	P	9.09	6.62	9.07	9.08	9.32
	R^2	0.99	1.00	1.00	1.00	1.00
	Chi^2	29.82	4.08	3.35	2.46	0.34
GAB	M	10.37	7.56	7.18	8.62	7.12
	C	5.28 E+45	-5.11 E+45	2.01 E+45	-1.18 E+45	-1.25 E+46
	k	0.99	0.98	0.98	0.93	0.93
	P	7.60	15.08	17.86	12.07	24.53
	R^2	0.99	0.96	0.95	0.96	0.92
	Chi^2	21.51	35.05	41.94	20.79	31.06
BET	Xm	9.75	6.10	5.81	4.97	4.22
	C	4.66 E+45	3.17 E+44	-2.52 E+45	-1.70 E+45	-9.94 E+44
	P	10.57	23.65	25.25	29.58	43.96
	R^2	0.99	0.95	0.93	0.81	0.80
	Chi^2	20.30	40.80	45.15	76.77	62.43
Oswin	k	19.20	15.36	14.85	17.29	14.53
	C	0.75	0.64	0.63	0.49	0.49
	P	9.27	10.41	9.92	10.17	9.94
	R^2	0.98	0.94	0.93	0.97	0.94
	Chi^2	50.81	43.48	46.44	13.52	19.06

Peleg, GAB, BET and Oswin models are popularly used to model moisture sorption isotherms for food and edible materials. To model successfully, any equation should fit as much as possible to experimental data over a range of water activity using a minimum of adjustable constants. The high coefficient of determination (> 0.9) and the low value of the relative deviation (%P) showed good fitting of the models to the experimental value. The results in Table 2 show that the correlation coefficient (R^2) of all films was higher than 0.9. For the Peleg model, R^2 value of all films are more than 0,99 and %P value of all films are less than 10%. This indicated that the Peleg model confirmed the best descriptions of the moisture isotherms with the range of examined water activities. In the GAB models, films without ZnO-NPs showed the highest monolayer value (10.37g water/100g solids) while the lowest monolayer value (7.12g water/100g solids) were observed for P/AG/0.5% ZnO-NPs film. The results showed that the maximum %P value was obtained for the GAB model and BET model, which were 24.53% and 43.96% for the P/AG film incorporated with 0.5% ZnO-NPs at 25°C, respectively. The %P values of GAB and BET models were much higher than 10% so that they were not suitable for EMC description of P/AG/0.5% ZnO-NPs films. In conclusion, the Peleg model was the most suitable to predict the EMC of all P/AG/ZnO-NPs films. These results were due to more adjustable parameters compared to GAB, BET and Oswin models.

The results of the above section showed that the adding of ZnO-NPs into pectin/alginate matrices led to an improvement of hydration properties. The change is the most effective when adding 0.1g ZnO-NPs of 100g solution into P/AG films.

3.4. Morphology of Pectin/ Alginate film and Pectin/ Alginate/ 0.1% ZnO-NPs film

Scanning electron microscopy (SEM) micrographs were conducted to evaluate better visualization about the homogeneity and the microstructure of films. The surface and cross section morphology of the P/AG films and P/AG/0.1% ZnO-NPs films were shown in Figure 3.



(a) *(b)* *(c)* *(d)*

Figure 3. *SEM of surface (a) and cross section (c) Pectin/Alginate film; SEM of surface (b) and cross section (d) Pectin/Alginate/0.1% ZnO-NPs film*

The P/AG film and P/AG/0.1% ZnO-NPs film had a smooth and compact surface. This implicated that ZnO-NPs were uniformly distributed throughout the films and no aggregation of particles was seen. From the images, the P/AG/ZnO-NPs film had smoother cross-section than the P/AG film. It could be because the ZnO nanoparticles were packed closely and well-distributed in the matrix. There were no voids in the P/AG matrix. This was mainly due to the filling ZnO-NPs in smaller size into micro voids of P/AG matrix. These results approved the strong interactions between the P/AG matrix and 0.1% of the ZnO-NPs. This property was related to the decrease of swelling degree, water vapor permeability of P/AG/0.1% ZnO-NPs film when compared with P/AG film.

4. Conclusion

The hydration properties of all films were studied. The experimental results confirm the unique pectin/ alginate/ ZnO-NPs composite structure and the decrease of hydration properties of pectin/ alginate/ ZnO-NPs films. The P/AG films added ZnO-NPs exhibited lower swelling degree, lower water vapor permeability and lower equilibrium moisture content of EMC under all relative humidity conditions. The Peleg model was the best - fit model for P/AG/ZnO-NPs films. These results suggested that it would be favorable to prepare P/AG/ZnO-NPs film by using ZnO-NPs at the amount of 0.1 g/100g solution for the development of films for food preservation. These films should be used at lower than 86% RH.

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