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Kinetics of Water Vapor Absorption by Sodium Alginate-based Films

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Abstract

Water vapor sorption by sodium alginate-based films may result in swelling and conformational changes in the molecular structure and affecting the water vapor barrier properties. Sodium alginate film specimens were dried in a vacuum freeze dryer and their moisture content was determined by an air-oven method. The water vapor absorption was determined at two different levels of water activities (0.727 and 0.995) and at three temperatures (10, 20, and 30°C), and kinetics were analyzed using a simple empirical model. Reasonably good straight lines were obtained with plotting of $1/(m\text{-}m_0)$ vs $1/t$. It was found that water vapor absorption kinetics of sodium alginate films were accurately described by a simple empirical model. The rate of water vapor sorption increased with increase in temperature and it showed temperature dependency following the Arrhenius equation. The activation energies varied from 49.18~149.55 kJ/mol depending on the relative humidity.

Key words: sodium alginate films, water vapor absorption, kinetics, barrier property

INTRODUCTION

Alginate has been utilized to develop biodegradable or edible films (1-5) due to its unique colloidal properties such as thickening, stabilizing, suspending, film forming, gel producing, and emulsion stabilizing properties (6,7). Alginate is a natural polysaccharide extracted from marine brown algae. It consists of linear copolymers composed of (1,4)-β-D-mannuronic acid (M) and (1,3)-α-L-guluronic acid (G) with varying proportions of M and G units (5). Sodium alginate (Na-Alg), a polyelectrolyte having a rigid molecular chain, forms strong films (5) and has been extensively investigated for biomedical applications as a drug carrier (8-10) and haemostatic materials (11). Na-Alg occurs in white to yellowish brown filamentous, grainy, and granular or powdered forms, and has been widely used as a stabilizer, thickener, gelling agent, and emulsifier (12).

Despite the good film forming ability of Na-Alg, it exhibits a poor water resistance due to its hydrophillic nature. The water vapor barrier properties of hydrophilic bioploymer-based films, like Na-Alg films, are significantly influenced by the presence of moisture (13, 14), which limits their applications. To solve this problem, various methods have been developed to improve the water or water vapor resistance property of alginate-based films such as compositing with hydrophobic materials like fatty acids (15) or inducing a crosslink with multivalent ions like Ca^{2+} and Cu^{2+} (1,2,4,15).

Sorption of water vapor plays a very important role in film stability, especially in hydrophilic polymer-based films. Therefore an understanding of the water sorption properties of biopolymer-based films is essential for their application in food packaging systems. In the sorption process, water molecules distribute themselves between the vapor phase and the film surface until a state of equilibrium has been reached. This process may be studied by measuring either the equilibrium condition or the rate of approach to equilibrium (15). The equilibrium condition can be evaluated by determining the water absorption isotherm, however, isotherm only explains the final equilibrium condition, but it does not explain sorption of water vapor in the middle of the process. Kim and Rhim (16) provided a method for testing the water vapor sorption behavior of sweet potato starch-based films using a simple relationship of water sorption rate instead of determining time-consuming equilibrium moisture content of the films.

The objectives of this study were to provide reliable experimental data regarding water vapor sorption behavior of $CaCl_2$ treated Na-alginate films and to identify and test simple relationships to characterize the water vapor absorption kinetics at different temperatures and relative humidities.

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MATERIALS AND METHODS

Materials

Commercial grade Na-alginate (Product No.: 37094-01) was purchased from Kanto Chemical Co. (Tokyo, Japan) and glycerin was obtained from Mallinckrodt Baker Chemical (Phillipsburg, NJ, USA).

Preparation of films

Na-alginate films were prepared according to the method of Rhim (4). A film-forming solution was prepared by slowly adding 4 g of alginate powder with constant stirring to a mixture of 200 mL of distilled water with 2 g of glycerin as a plasticizer. The mixture was heated on a hot plate with stirring until the mixture dissolved completely to become clear. Each solution was strained through eight-layered cheese cloth (grade 40, Fisher Scientific, Pittsburgh, PA) to remove foam and other impurities, and poured onto a leveled Teflon-coated glass plate (24×30 cm). Films were allowed to dry at ambient conditions for about 24 hr, followed by modification of the films through treatment with $CaCl_2$ solution. The modification of Na-Alg films were done by soaking the preformed alginate films with 3% $CaCl_2$ solution (3 g $CaCl_2$/100 mL distilled water). To prevent curling of the films during drying, 100 mL of $CaCl_2$ solution was poured onto the dried alginate films on the rimmed glass plate prior to peeling. After immersing the film for 5 min, the $CaCl_2$ solution was discarded and the treated film was dried at ambient condition for 6 hr.

Water vapor absorption

The film specimens were dried in a vacuum freeze dryer (EYELA vacuum Freeze dryer, FDU-1100, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) at -40°C and 760 mmHg vacuum for 5 days to reduce the initial moisture content. Moisture content of the films was determined by oven drying (Mechanical Convection Oven, DMC-122SP, 021001-03, Daeil Engineering Co., Masan, Korea) at 105°C for 24 hr.

Tests of water vapor absorption of the films were conducted at three different temperatures (10, 20, and 30°C) with water activities from 0.727 to 0.995. One piece (*ca.* 0.05 g) of the film specimen was placed on a perforated stainless steel screen of an Aw Sprint TH-500 apparatus (Aw Sprint TH-500, Novasina Co. Ltd., Talstrasse, Switzerland). The temperature of the test chamber was maintained within ±0.5°C of the indicated temperature. Increase in weight of the film specimens during the water vapor absorption process was recorded during 3 hr and the weight gain in g H_2O/g dry solid was used for the further analysis.

Water activity measurement

The reagent grade salts (NaCl and $K_2Cr_2O_7$) were used to obtain the desired relative humidity. Saturated salt solutions were obtained from the Novasina humidity control standards (Novasina, Axair Ltd., Pfäffikon, Switzerland). Relative humidity after attaining equilibrium with saturated salt solution was determined automatically by Aw Sprint.

Data analysis

Water vapor absorption curves of the films were obtained by plotting increases in weight (*m*) due to water vapor sorption expressed in g H_2O/g dry solid against absorption time. The reaction rate constant was determined by taking inverse of the slope value as the following:

$$\frac{1}{m-m_0}=\frac{1}{k(m_e-m_0)t}+\frac{1}{m_e-m_0} \qquad (1)$$

where m_e and m_0 are the saturation moisture and the initial moisture, respectively, and *k* is the rate constant of the sorption process. The inverse of m-m_0 (*i.e.*, $1/(m-m_0)$) was plotted against inverse of time ($1/t$) following the Eq. (1) to obtain a straight line. The reaction rate constant was determined by taking the inverse of the slope value and multiplying with the intercept value ($1/(m_e-m_0)$). The equilibrium moisture content (m_e) of the film at each condition was also determined from the intercept value of the regression line. The temperature dependency of *k* value was determined by an Arrhenius-type equation as follows:

$$k=k_0\exp(-E_a/RT) \qquad (2)$$

where k_0 is a pre-exponential factor, E_a is the activation energy, *R* is the universal gas constant (8.314 J/mol·K), and *T* is the absolute temperature (K).

RESULTS AND DISCUSSION

Water activity and isosteric heat of sorption

Water activity values of saturated salt (NaCl and $K_2Cr_2O_7$) solutions are shown in Table 1. The water activity values of saturated salt solutions decreased with

Table 1. Water activity values of saturated salt (NaCl and $K_2Cr_2O_7$) solutions at different temperature

	Water activity		
	10°C	20°C	30°C
NaCl (75%)	0.730	0.729	0.727
$K_2Cr_2O_7$ (98%)	0.995	0.981	0.978

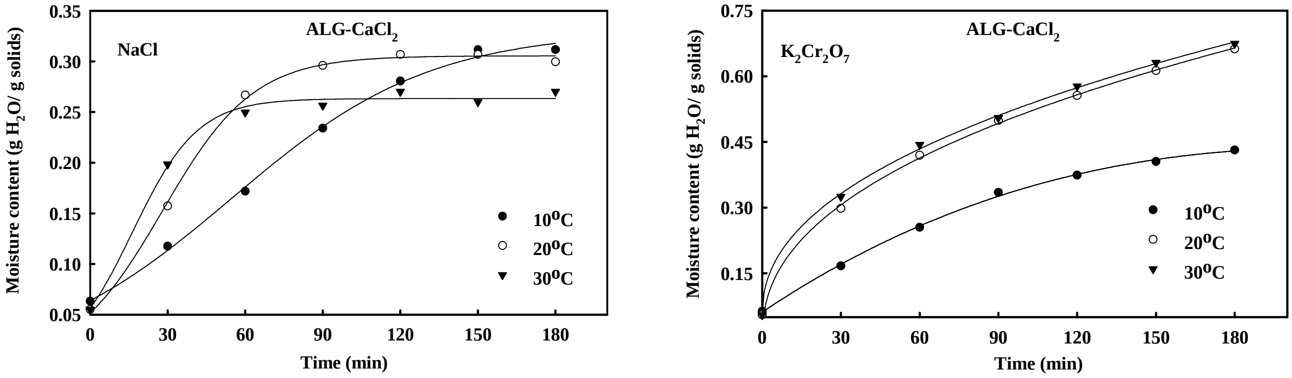

Fig. 1. Water vapor absorption behaviors of Na-Alg films at different temperatures and relative humidities.

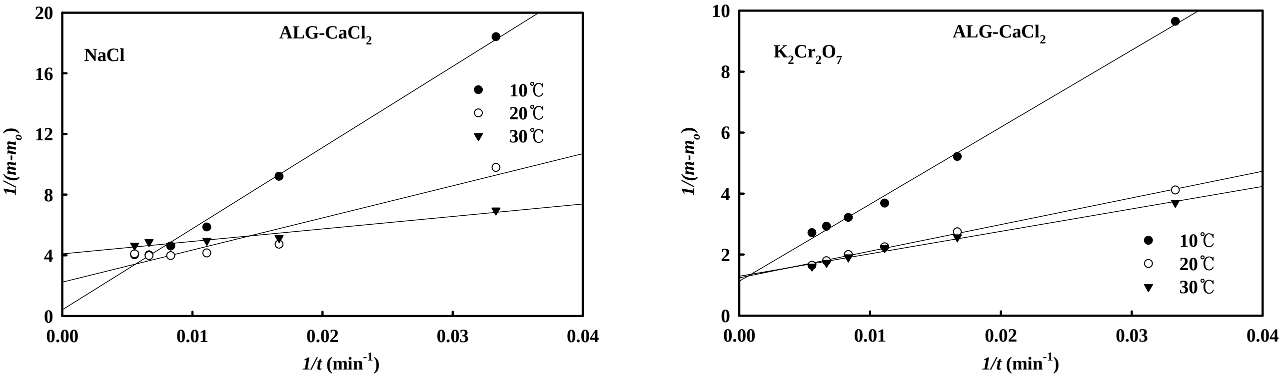

Fig. 2. Absorption kinetics of Na-Alg films determined at different temperatures and relative humidities.

an increase in temperature. The phenomena of decreased water activity of saturated salt solutions with increases in temperature have been frequently observed with other saturated salt solutions (17,18).

Water vapor absorption curves

Water vapor sorption behaviors of Na-Alg films at different temperature and humidity conditions are shown in Fig. 1. The rapid initial moisture sorptions followed by slower absorption at later stages, due to filling of the capillaries of the surface of the films (16,19), were observed for the samples placed in NaCl salt solution at 20 and 30°C. Other samples exhibited gradual increases in moisture content as the sorption process proceeded.

The maximum attainable water vapor absorption was influenced by the relative humidity during the test. The maximum increases in moisture content due to water vapor absorption were obtained with 2.527 g H_2O/g dry solid at 10°C saturated with NaCl salt solution and 0.950 g H_2O/g dry solid at 10°C saturated with $K_2Cr_2O_7$ salt solution.

Water vapor sorption rate

As shown in Fig. 1, water vapor sorption rate varied depending on temperature. Water vapor sorption rate constant and equilibrium moisture content of the film were determined by plotting $1/(m-m_0)$ against $1/t$ using Eq. (2). Fig. 2 shows typical kinetic plot lines for water vapor sorption of Na-Alg films. Reasonably good

Table 2. Reaction rate constants for water vapor absorption of Na-Alg films at different temperature and humidity

Saturated salt solution	Temp. (°C)	k ($\times 10^{-3}$ g H_2O/g dry solid/min)	m_e (g H_2O/g dry solid)	R^2
NaCl	10	0.759	2.527	0.995
	20	10.533	0.503	0.920
	30	49.628	0.300	0.946
$K_2Cr_2O_7$	10	4.466	0.950	0.996
	20	14.122	0.865	0.997
	30	17.542	0.829	0.991

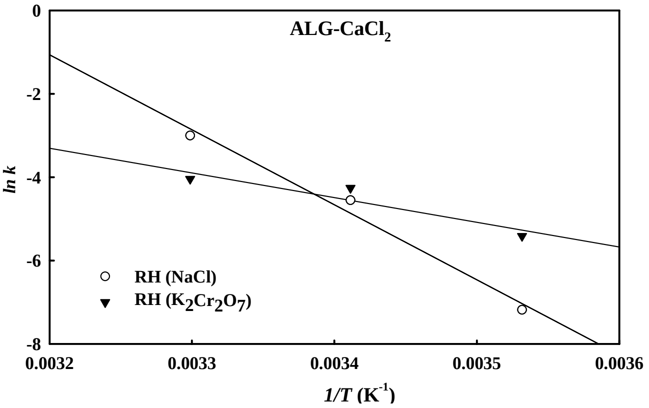

Fig. 3. Temperature dependency of water vapor absorption of Na-Alg films at different relative humidities.

Table 3. Kinetic parameters for water vapor absorption of Na-Alg films

Saturated salt solution	k_o (g H_2O/g dry solid/min)	E_a (kJ/mol)	R^2
NaCl	3.435×10^{24}	149.55	0.984
$K_2Cr_2O_7$	6.087×10^{6}	49.18	0.879

straight lines were obtained with a simple plot of 1/(m-m_0) vs. 1/t. Water vapor sorption rate constants were calculated by taking the inverse of the slope value of the lines and multiplying by the intercept value. The reaction rate constants for water vapor sorption and the equilibrium moisture content of Na-Alg films are summarized in Table 2. The water vapor absorption rate increased with temperature regardless of relative humidity conditions, which is in good agreement with the finding of other researchers (16). The equilibrium moisture content, which is the maximum attainable moisture content of the film, varied depending on temperature and saturated salt solution used. Generally, the equilibrium moisture content of the film decreased with increases in temperature; temperature dependency of the equilibrium moisture content was more pronounced in lower Aw conditions.

Effect of temperature

The temperature dependency of the water vapor sorption rate of alginate films was tested using the Arrhenius equation (Eq. 3). Fig. 3 shows the result of an Arrhenius plot of water vapor absorption rate of Na-Alg films. A reasonably good linear relationship was obtained with high R^2-values of 0.984 and 0.879 for the films at different relative humidities. The linear relationship observed indicates that the temperature dependence of the sorption rate of the films can be properly described by the Arrhenius model. The Arrhenius kinetic parameters, the activation energy (E_a) and the pre-exponential factor (k_0) for the water vapor absorption by the films were determined by linear regression and the results are summarized in Table 3. The activation energies varied from 49.18-149.55 kJ/mol depending on the relative humidity.

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