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Enhancement of the Water-resistance and Physical Properties of Sodium Alginate Film

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Abstract To improve water-resistance and physical properties of sodium alginate film, effects of sodium alginate and plasticizer concentrations, divalent cation types and concentrations, and immersion time of films into divalent cation solutions on sodium alginate films were evaluated, based on elongation strength (ES), elongation rate (E), water vapor permeability (WVP), and water solubility (WS). Film made from 1.5% sodium alginate solution (w/w) had low WVP and WS, which are optimal characteristics for application of film preparation. Addition of plasticizer increased E and WS. Less than 2% $CaCl_2$ addition and 15min immersion time reduced WVP, WS, and E significantly ($p<0.05$). Sodium alginate films treated with $CuCl_2$, and $ZnCl_2$ solutions had lower WVP and WS, whereas $MgCl_2$ had no influence on improving water resistance of films.

Keywords: Na-aginate film, divalent cations, plasticizer, and immersion time

Introduction

Recently, due to the serious environmental pollution caused by plastic wastes, much interest has been placed by researchers and industries on the environment-friendly packaging, which can be decomposed by soil microorganisms. In particular, researches on various biodegradable films have been actively performed on food packaging with various biodegradable films developed from carbohydrates, proteins, lipids, and their mixtures (1-6).

Carbohydrates such as starch, cellulose and their derivatives, pectin, carrageenan, chitosan, and alginic acid have been widely employed due to their good film-forming ability (7). Among these carbohydrates, alginic acid, which is a hetero-polysaccharide joined together by β-D-manuronic and α-L-guluronic acid, is water-soluble, non-toxic, viscous, and adhesive, and has high ability to form film and strong gel with divalent cations as well as to join metal salts (8-9). Due to these characteristics, it has been used to form biodegradable films (10) and enzyme immobilization beads (11), and to produce fillings and gelling ingredients in food industry (12), and cosmetic and pharmaceutical industries (8-9).

However, the use of biodegradable film based on Na-alginate has limitation due to poor water resistance caused by its hydrophilic nature (2). In addition, due to the rapid reaction of Na-alginate with calcium ions, heterogeneous alginate gel is formed, preventing the casting of film-forming solution (1). Calcium ions generally form a strong, water-insoluble gel with Na-alginate, enhancing the water resistance of the alginate film (13). Pavlath *et al.* (13) reported that insolubility of Na-alginate film was significantly improved by soaking the film in calcium ion solution. Rhim (14) also demonstrated that immersion of Na-alginate film into calcium ion solution resulted in higher water-resistance than with the mixture of Na-alginate and calcium ion solution.

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The objective of this work was to investigate the effects of concentrations of Na-alginate, plasticizer, and calcium ion, immersion time, and divalent cation types on the water-resistance and mechanical properties of Na-alginate film.

Materials and Methods

Materials Na-alginate was obtained from Kanto Chemical Co., Inc (Tokyo, Japan). $CaCl_2$, $MgCl_2$, $CuCl_2$, and KCl were purchased from Sigma Co. (St. Louis, MO, USA), and glycerol as a plasticizer was purchased from Daejung Chemical & Materials Co. Ltd (Seoul, Korea).

Preparation of Na-alginate films A predetermined amount of Na-alginate and glycerol were dissolved in distilled water and heated on a hot plate. The clear film-forming solution was placed in a water bath at 90°C for 30 min to remove foam, and was poured onto a Teflon-coated glass plate (24 × 30 cm). Films were dried at ambient temperature for 48 hr, soaked in 2.0% $CaCl_2$ solution for 5 min, and dried again at ambient temperature about 5 hr. The dried films were cut into 7 × 7 cm pieces for the measurement of water vapor permeability, and elongation strength and rate at break, and into 2 × 2 cm pieces for the measurement of water solubility. All film samples were preconditioned in a constant temperature and humidity chamber (Model JS-THC 3500, Johnsm Co., Seoul, Korea) set at 25°C and 50% RH for 48 hr to adjust the constant moisture content. To investigate the water-resistance and physical properties of Na-alginate films, different concentrations of Na-alginate (0.5-3.0%, w/w) and a plasticizer (0-65%, w/w), various divalent cations (Ca^{2+}, Mg^{2+}, Cu^{2+}, and Zn^{2+}) at different concentrations (1.0-3.0%), and immersion times (5-35 min) were tested.

Film thickness Film thickness was measured using a Micrometer (Dial Thickness Gauge 7301, Mitutoyo, Japan) with 10 μm accuracy. Film thickness is presented as the average of five measurements.

Water vapor permeability (WVP) The water vapor permeability (WVP) of films was calculated by the following equation:

$$WVP = (WVTR \times L)/\Delta p$$

where WVTR is the water vapor transmission rate ($g/m^2 \cdot s$), L is the average of film thickness (m), and Δp is the difference in partial vapor pressure (Pa) across the two sides of a film (15). WVTR was measured using the slightly modified ASTM standard Method E 96-95 (16). Film specimens were mounted on poly(methylmethacrylate) cups filled with 18 mL distilled water up to 1 cm from the film underside. Cups were placed in a constant temperature and humidity chamber, and weights of cups were recorded every hour for a period of 8 hours. Slopes of the linear portion of weight loss versus time curves were evaluated by linear regression to determine the WVTR. When calculating WVP, the effect of resistance of the stagnant air layer between the film undersides and the surface of water in cups was corrected according to the methods of MuHugh *et al.* (17) and Gennadios *et al.* (18).

Water solubility (WS) Water solubility (WS) of films was measured by the method of Rhim (14). Three film specimens (2 x 2 cm) were first dried at 105°C for 24 hr to determine the initial dry matter. Additional three film specimens were put in a 50-mL beaker with 30 mL distilled water. After sealing with aluminum foil, beakers were placed in a constant temperature chambers set at 5, 25, and 37°C for 24 hours. Subsequently, insolubilized film specimens were dried at 105°C for 24 hours and weighed. WS of films was calculated by the following equation:

$$WS = (S_0\text{-}S)/S_0$$

where S_0 and S are the initial and insolubilized dry matters, respectively.

Elongation strength (ES) and rate (E) at break Elongation strength (ES) and elongation rate (E) were measured using a Rheometer (CR-200D, Sun Scientific, Tokyo, Japan) (Fig. 1(a)). Fixed film specimens were compressed with the adapter No. 2 at 5 mm/min cross-head speed until the film broke. E of film was defined as the ratio of a surface area (A_1, m^2) of the film deformed with a cone to an initial area (A_0, m^2) of the film, and the elongation strength (ES) was calculated as shown in Fig. 1.

Statistical analysis WVP, WS, ES, and E were measured at minimum in triplication. The data were analyzed by Duncan's multiple range tests using SAS (SAS Institute Inc., Cary, NC, USA). The significant difference was established at $p<0.05$ (19).

$$\text{Elongation rate } (\%) = \frac{A_1}{A_0} \times 100$$

$$\text{Elongation strength (MPa)} = \frac{f \times 9.8}{\frac{\cos\theta}{\Delta A}}$$

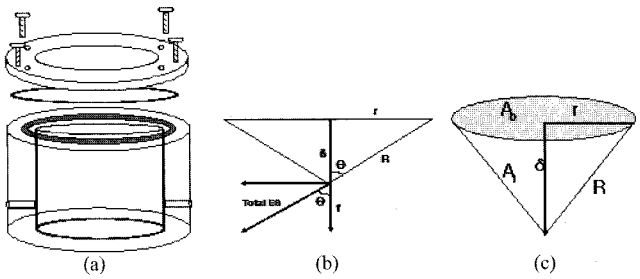

Fig. 1. Cup assembly (a) used to measure the elongation strengtl (ES) and elongation rate (ER) and schematic diagrams to calculat ES (b) and ER (c) at break of alginate films.

Results and Discussion

Effect of the concentration of Na-alginate on Na-alginate films The characteristics of films made from 1.5 to 2.5% (w/w) Na-alginate solutions were examined (Table 1). A preliminary study showed 0.5% Na-alginate solution was not suitable for the film-casting application due to a low viscosity, while 3% Na-alginate solution was too high. Film thickness significantly increased from 32.82 to 64.21 μm as the concentration of Na-alginate solution increased. ES and E increased from 7.80 MPa and 0.99% to 11.31 MPa and 1.40%, respectively. However, at 1.5 and 2.0% (w/w) concentrations, no significant differences were observed between ES and E. WVP ranged from 0.81 to 1.17 ng·m/m^2·s·Pa, with the film made from 1.5% (w/w) Na-alginate solution showing the lowest WVP, 0.81 ng·m/m^2·s·Pa. Increases observed in both film thickness and WVP with increasing Na-alginate concentration might be due to the huge network structure caused by high alginate concentration and also because Na-alginate at low concentration could not react sufficiently with the calcium ions (18). WS of 1.5% (w/w) Na-alginate film was the lowest at the entire temperature range examined (5-37°C). Therefore, based on these results, the optimum concentration for the Na-alginate film-formation was determined to be 1.5% (w/w).

Effect of the concentration of plasticizer on Na-alginate films Influences of various concentrations of glycerol (0-

Table 1. Change in physical properties and water-resistance of Na-alginate films with various Na-alginate concentrations[1)]

Films		1.0%	1.5%	2.0%	2.5%
Thickness (μm)		32.82±0.53^d	44.71±0.26^c	55.60±1.43^b	64.21±1.67^a
ES (MPa)		7.80±0.98^b	10.76±0.66^a	10.42±0.33^a	11.31±0.31^a
E (%)		0.99±0.01^c	1.10±0.02^b	1.43±0.01^a	1.40±0.01^a
WVP (ng · m/m^2·s·Pa)		0.98±0.03^c	0.81±0.08^d	1.08±0.07^b	1.17±0.22^a
WS (%)	5°C	5.67±0.06^c	4.82±0.09^d	6.40±0.10^a	6.19±0.20^b
	25°C	6.35±0.11^c	5.02±0.13^d	7.14±0.10^b	7.18±0.14^a
	37°C	6.92±0.09^c	6.00±0.10^d	7.48±0.05^b	7.89±0.12^a

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly ($p>0.05$) different by Duncan's multiful range test.

Table 2. Change in physical properties and water-resistance of Na-alginate films with various glycerol concentrations[1)]

Films		0	20%	35%	50%	65%
Thickness (μm)		45.53±0.05[a]	42.40±0.09[b]	42.21±0.04[b]	42.27±0.06[b]	41.87±0.02[b]
ES (MPa)		10.66±0.21[a]	7.73±0.33[b]	5.91±0.19[c]	4.74±0.12[d]	3.71±0.12[d]
E (%)		1.08±0.02[a]	1.38±0.03[b]	1.83±0.06[c]	2.74±0.04[d]	3.06±0.04[e]
WVP (ng·m/m^2·s·Pa)		0.81±0.02[a]	0.79±0.01[b]	0.75±0.01[c]	0.71±0.01[d]	0.68±0.01[e]
WS (%)	5°C	5.45±0.14[e]	8.33±0.11[d]	10.59±0.12[c]	11.36±0.07[b]	16.06±0.15[a]
	25°C	6.00±0.16[e]	8.40±0.07[d]	10.74±0.05[c]	12.49±0.30[b]	16.50±0.08[a]
	37°C	6.31±0.13[e]	8.54±0.12[d]	11.25±0.22[c]	13.67±0.14[b]	16.89±0.07[a]

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly ($p>0.05$) different by Duncan's multiful range test.

65%, w/w) as a plasticizer on Na-alginate film are shown in Table 2. Thickness of films with glycerol addition ranged from 41.87 to 45.53 μm, with no significant differences observed depending on the concentration of glycerol. As glycerol concentration increased, ES decreased from 10.66 to 3.71 MPa, and E increased from 1.08 to 3.06% (Table 2). This phenomenon probably occurred because a hydrogen bond between Na-alginate and glycerol might have loosened the intra-molecular attraction between Na-alginate and calcium ions (18). As the concentration of glycerol was increased, WVP decreased from 0.81 to 0.68 ng·m/m^2·s·Pa, whereas WS increased 1.57-2.67 times compared to the control. WS also increased with increasing temperatures. This may be due to the high hydrophilic property of glycerol (20). Results showed 50% (w/w) glycerol based on the weight of Na-alginate was suitable for film-manufacturing application, even though glycerol had a negative influence on the water-resistance of Na-alginate film.

Effect of the concentration of $CaCl_2$ immersion solution on Na-alginate films Mechanical and physical properties of Na-alginate film depending on the concentration (1.0-3.0%) of $CaCl_2$-immersion solution are shown in Table 3. As the concentration of $CaCl_2$-immersion solution increased, ES increased 14-16 times and E decreased 4.4-4.8 times compared to the control. Film thickness significantly increased from 42.51 to 52.59 μm. WVP and WS decreased 1.43-1.83 times with increasing $CaCl_2$ concentration; however, at over 2.0%, WVP did not show significant differences. The lowest WS occurred in the film treated with 2.0% $CaCl_2$ solution, while the alginate film not treated with $CaCl_2$ solution completely dissolved during immersion. Pavlath *et al* (13) suggested that, when Na-alginate film was soaked in $CaCl_2$ solution, two competing reactions, dissolution of Na-alginate by the solution, and insolubilization of the films by cross-linking between calcium ion and carboxyl group on the surface of alginate films (10), occurred. They also reported that the insolubilization rate of Na-alginate increased as the concentration of $CaCl_2$ increased. Therefore, based on these results, 2.0% $CaCl_2$ immersion solution was determined to be more effective for improving the mechanical and water-resistant properties of Na-alginate film.

Effect of different immersion times in $CaCl_2$ solution on Na-alginate films Table 4 illustrates the changes in the characteristics of the Na-alginate film according to the immersion time in $CaCl_2$ solution. Increase in the immersion times caused a dramatic decrease of the film thickness from 51.45 to 41.08 μm, and ES increased 16.6-27.6 times and E decreased 4.7-8.7 times compared to the control. WVPs of all Na-alginate films subjected to the immersion process were below that of the control film, but increased from 0.74 to 0.85 ng·m/m^2·s·Pa with increasing immersion time. WS decreased at the entire temperature range examined as the immersion time increased as similarly reported by Pavlath *et al.* (13) that WS of Na-alginate film decreased as the $CaCl_2$ concentration and immersion time increased. However, immersion time over 30 min had negative influence on the mechanical properties by decreasing E. Therefore, based on the results of this study, 15 min immersion time was determined to be appropriate for achieving optimal WS and WVP as well as mechanical properties of Na-alginate film.

Effect of different divalent cations on Na-alginate films Characteristics of Na-alginate films treated with various divalent cations such as Ca^{2+}, Mg^{2+}, Cu^{2+}, and Zn^{2+} are shown in Table 5. Treatment with Zn^{2+} produced the thinnest film, whereas the highest ES was achieved by Cu^{2+} (5.51 MPa) and by Mg^{2+} (3.96 MPa) treatments. On the other hand,

Table 3. Change in physical properties and water-resistance of Na-alginate films with various $CaCl_2$ solution concentrations[1)]

Films		Control	1%	2%	3%
Thickness (μm)		51.79±0.09[b]	42.51±0.10[d]	46.33±0.07[c]	52.59±0.14[a]
ES (MPa)		0.29±0.42[d]	4.07±0.51[c]	4.49±0.29[b]	4.63±0.22[a]
E (%)		12.25±0.39[a]	2.78±0.21[b]	2.74±0.17[c]	2.53±0.10[d]
WVP (ng·m/m^2·s·Pa)		1.32±0.02[a]	0.92±0.01[b]	0.73±0.01[c]	0.72±0.01[c]
WS (%)	5°C	100±0.00[a]	22.78±1.04[b]	12.41±0.44[d]	14.52±0.37[c]
	25°C	100±0.00[a]	25.30±1.10[b]	13.59±0.38[d]	15.95±0.38[c]
	37°C	100±0.00[a]	28.02±1.13[b]	14.34±0.57[d]	17.50±0.56[c]

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly ($p>0.05$) different by Duncan's multiful range test.

Table 4. Change in physical properties and water-resistance of Na-alginate films with various immersion time by $CaCl_2$ solution concentrations[1)]

Films		0	5min	15min	25min	35min
Thickness (μm)		51.45±0.08[a]	46.24±0.20[b]	44.27±1.00[c]	41.23±0.61[d]	41.08±0.55[e]
ES (MPa)		0.25±0.39[e]	4.16±0.30[d]	4.71±0.10[c]	5.11±0.22[b]	6.90±0.51[a]
E (%)		11.58±0.38[a]	2.47±0.13[b]	2.15±0.11[c]	2.06±0.05[d]	1.33±0.07[e]
WVP (ng·m/m^2·s·Pa)		1.38±0.02[a]	0.74±0.02[e]	0.78±0.01[d]	0.80±0.01[c]	0.85±0.02[b]
WS (%)	5°C	100±0.00[a]	13.20±0.52[b]	9.38±0.78[c]	9.34±0.92[d]	8.98±1.10[e]
	25°C	100±0.00[a]	14.11±0.76[b]	9.98±0.65[d]	10.02±0.42[c]	9.23±0.95[e]
	37°C	100±0.00[a]	14.94±0.42[b]	10.30±1.00[d]	10.57±0.75[c]	10.02±1.05[e]

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly ($p>0.05$) different by Duncan's multiful range test.

Table 5. Change in physical properties and water-resistance of Na-alginate films with various divalent cations[1)]

Films		Control	$CaCl_2$	$CuCl_2$	$ZnCl_2$	$MgCl_2$
Thickness (μm)		51.54±0.10[a]	46.43±0.85[d]	47.07±0.30[c]	45.61±0.57[e]	49.55±0.44[b]
ES (MPa)		0.28±0.39[e]	4.83±0.39[c]	5.51±0.47[a]	5.09±0.26[b]	1.95±0.10[d]
E (%)		12.08±0.41[a]	2.21±0.12[c]	2.01±0.20[d]	1.89±0.14[e]	3.96±0.34[b]
WVP (ng·m/m^2·s·Pa)		1.32±0.03[a]	0.78±0.01[c]	0.77±0.01[d]	0.73±0.01[e]	1.12±0.01[b]
WS (%)	5°C	100±0.00[a]	9.15±0.23[b]	8.08±0.30[d]	8.34±0.21[c]	100±0.00[a]
	25°C	100±0.00[a]	9.89±0.34[b]	8.46±0.38[d]	9.76±0.28[c]	100±0.00[a]
	37°C	100±0.00[a]	10.09±0.44[c]	8.98±0.44[d]	10.19±0.35[b]	100±0.00[a]

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly ($p>0.05$) different by Duncan's multiful range test.

Mg^{2+}-treated film showed the poor ES and WVP, and was completely dissolved during the immersion. The film treated with Zn^{2+} showed better characteristics than Ca^{2+}-treated film, but had the lowest E, resulting in handling problem. WVP and WS of films treated with Cu^{2+} and Zn^{2+} were lower compared to those of Ca^{2+}-treated one. In particular, the film treated with Cu^{2+} showed the lowest WS, and was not affected by temperatures (5-37°C). These results indicate that both Cu^{2+} and Zn^{2+} had roles equal to the reaction between Ca^{2+} and Na-alginate. Therefore, not only Ca^{2+} but also Cu^{2+} and Zn^{2+} could be used to enhance the water-resistance and mechanical characteristics of Na-alginate films.

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