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Physical Properties of *Gelidium corneum* Films Treated with Cinnamaldehyde

- Research Note -

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Abstract

Gelidium corneum **films were prepared using cinnamaldehyde as a cross-linking agent and their physical properties were determined. Tensile strength (TS) value of the film containing 0.01% cinnamaldehyde was higher than the control by 8.31 MPa. However, increasing cinnamaldehyde from 0.01% to 0.1% significantly decreased TS from 9.54 MPa to 0.03 MPa, and no film was formed at 1% cinnamaldehyde. On the contrary, when cinnamaldehyde content was increased from 0.01% to 0.1%, % elongation was increased from 1.44% to 2.75%. Water vapor permeability (WVP) of the film containing 0% and 0.01% cinnamaldehyde were 1.64 ng m/m^{2}sPa and 1.42 ng m/m^{2}sPa, respectively. There was no significant difference in Hunter values among treatments. Scanning electron microscopy results revealed that both cinnamaldehyde and control films had similar surfaces. These results suggest that 1.5%** ***Gelidium corneum*** **treated with 0.01% cinnamaldehyde should be the most suitable condition for film formation.**

Key words: *Gelidium corneum*, edible film, cross-linking agent, physical property

INTRODUCTION

Recently, there has been increased concern about disposal of non-biodegradable packaging materials, and food packaging has become the subject regarding waste reduction efforts (1). Food packaging waste has been increasing, and manufacturing packaging materials from natural biopolymers that are biodegradable has been studied (2-3). Compared to plastic films, edible film is easily biodegradable and coating of food surface is possible, providing better sensory value by adding nutrient, flavor, and antioxidant properties (4). However, the cost of the edible film has been the main obstacle preventing its use (5). Therefore, development of biodegradable edible film using inexpensive biomaterials is needed.

Gelidium corneum is a type of red algae containing polysaccharides, mainly agar which can be used as a source of food ingredients, pharmaceutical products as well as culture media (6-8). It also has a high amount of dietary fiber, providing various physiological functions when it is taken (8). Recently, the use of red algae pulp using *Gelidium corneum* has been investigated for manufacturing purposes (9). As a byproduct of this processing, an extract of *Gelidium corneum* containing high concentrations of agar is obtained. Therefore, considering that there have been many attempts to manufacture environment-friendly edible films using various biomaterials (3,5), an extract of *Gelidium corneum* can be utilized for the preparation of edible film. However, to manufacture the edible film using *Gelidium corneum* extract, increased physical strength of the film using cross-linking agent is necessary. In our laboratory, cinnamaldehyde has been used to improve tensile strength and water vapor permeability (10).

Therefore, the objectives of this study were to establish the optimal conditions for making *Gelidium corneum* edible films that may be used for packaging of food products, and to determine the physical properties of the films.

MATERIALS AND METHODS

Materials

Gelidium corneum was harvested from Jeju Island. Cinnamaldehyde was purchased from Sigma-Aldrich Chemical Co. (Sigma-Aldrich Chemical Co., St. Louis, MO, USA).

Preparation of film forming solution

Gelidium corneum was washed to remove foreign substances, and bleached using 5% chlorine dioxide at 60°C for 90 min, following treatment with 8.5 g/hr ozone gas. Bleached and dried samples were cut, ground, and screened through a 200 mesh sieve. For making *Gelidium corneum* film, 1%, 1.5%, and 2% of *Gelidium*

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corneum powder was dissolved in a distilled water, and mixed with 0.01, 0.1, 1% cinnamaldehyde (w/v) that was dissolved in a distilled water. Film forming solutions were then conditioned in a water bath at 90°C for 30 min.

Film casting and drying

Film-forming solutions were strained through cheese cloth and cast on flat, Teflon-coated glass plates (24 cm ×30 cm). Uniform film thickness was maintained by casting the same amount of film forming solution on each plate. Plates were dried at 25°C for 48 hr. Dried films were peeled intact from the casting surface. Film specimens were conditioned in an environmental chamber at 25°C and 50% relative humidity (RH) for 2 days. Specimens were cut to size for water vapor permeability (2 cm×2 cm), tensile strength (2.54 cm×10 cm), and color (7 cm×7 cm) measurements.

Measurement of film thickness

Film thickness was measured with a micrometer (Mitutoyo, model No. 2046-08, Tokyo, Japan) at five random positions and the mean value was used.

Measurement of tensile strength and elongation

Film tensile strengths (TS) and elongation at break (E) were determined with an Instron Universal Testing Machine (model 4484, Instron Corp., Canton, MA, USA) according to ASTM Standard Method D882-91 (11). Film specimens were conditioned in an environmental chamber at 25°C and 50% RH for 2 days. Initial grip distance of 5 cm and crosshead speed of 50 cm/min were used. TS was calculated by dividing the maximum load by initial cross-sectional area of a specimen, and elongation was expressed as a percentage of change of initial gauge length of a specimen at the point of sample failure. Five replicates of each film were tested.

Measurement of water vapor permeability

Water vapor permeability (WVP) of the film was determined according to the modified ASTM E 96-95 method (12) at 25°C and 50% RH using polymethylacrylate (13). The cup was filled to 1 cm with distilled water and covered with a film specimen. Film specimens were conditioned in an environmental chamber at 25°C and 50% RH for 2 days. Weight loss of cups with time was measured. A linear regression analysis was performed to calculate a slope. WVP (ng m/m^{2}s Pa) values were then calculated from: $WVP=(WVTR \times L)/\Delta p$
where water vapor transmission rate (WVTR, g/m^{2}s) was calculated by dividing the slope by the open area of the cup. L is mean thickness (m), and Δp is corrected partial vapor pressure difference (Pa) across the film specimen.

Color measurements

Color values of *Gelidium corneum* films were measured using a colorimeter (CR-300 Minolta Chroma Meter, Minolta Camera Co., Osaka, Japan). Film specimens (7 cm×7 cm) were placed on a white standard plate and the Hunter L, a, and b color was used to measure color: L=0 (black) to L=100 (white); a=-80 (greenness) to a=100 (redness); and b=-80 (blueness) to b=70 (yellowness). Five measurements were taken at different locations on each specimen (10).

Measurement of film surface

Surfaces of *Gelidium corneum* films were studied using scanning electron microscopy (JEOL, JSM-7000F Japan electron optic, Tokyo, Japan). *Gelidium corneum* films were coated using gold-palladium alloy coater (Baltec Company, Manchester, NH, USA). Coated films were observed at 500× magnification.

Statistical analysis

Analysis of variance and Duncan multiple range tests with significance at $p<0.05$ were performed to analyze the results statistically using a SAS program (SAS Institute, Inc., Cary, NC, USA).

RESULTS AND DISCUSSION

Thickness of each film was measured using a micrometer. Thicknesses of *Gelidium corneum* films containing cinnamaldehyde were not significantly different among treatments because the same amounts of film forming ingredients were used. In the case of *Alaska Pollack* protein films (14), thickness of the films was 77±5 μm, while the thickness of *Gelidium corneum* films prepared in this study was 36.0±0.1 μm. These results represent that *Gelidium corneum* film can can have wider application due to its thinness.

One of the most important physical properties of a film is its tensile strength (TS). TS and % elongation of the films at various concentration of *Gelidium corneum* were presented in Table 1. TS of the film at 1.5% *Gelidium corneum* was 9.54 MPa, whereas the film was not sufficiently stable for determination of TS at 1% and 2% of *Gelidium corneum*. For 1% *Gelidium corneum*, the physical properties of the film were not determined because it was easily torn due to lack of cross-linking, and a film was not even formed with 2% *Gelidium corneum* was not even formed. Therefore, 1.5% of *Gelidium corneum* was the most appropriate concentration for making the film.

Table 1. Physical properties of *Gelidium corneum* films containing different levels of *Gelidium corneum*[1)]

Gelidium corneum (%)	TS (MPa)	E (%)
1.0	ND[2)]	ND
1.5	$9.5\pm2.0^{a3)}$	1.5 ± 0.2^{b}
2.0	ND	ND

[1)]All the films contained 0.01% cinnamaldehyde.
[2)]Not determined.
[3)]Means of five replications±standard deviations. Any means in the same column followed by different superscripts are significantly different ($p<0.05$) by Duncan's multiple range test.

Table 2. Physical properties of *Gelidium corneum* films containing different levels of cross-linking agents

Gelidium corneum powder (%)	Cinnamaldehyde concentration (%)	TS (MPa)	E (%)
1.5	0	$1.2\pm0.4^{b1)}$	5.1 ± 1.9^{b}
	0.01	9.5 ± 2.0^{a}	1.4 ± 0.2^{a}
	0.1	0.03[2)]	2.75
	1	ND[3)]	ND

[1)]Means of five replications±standard deviations. Any means in the same column followed by different superscripts are significantly different ($p<0.05$) by Duncan's multiple range test.
[2)]TS value was too low to determine.
[3)]Not determined.

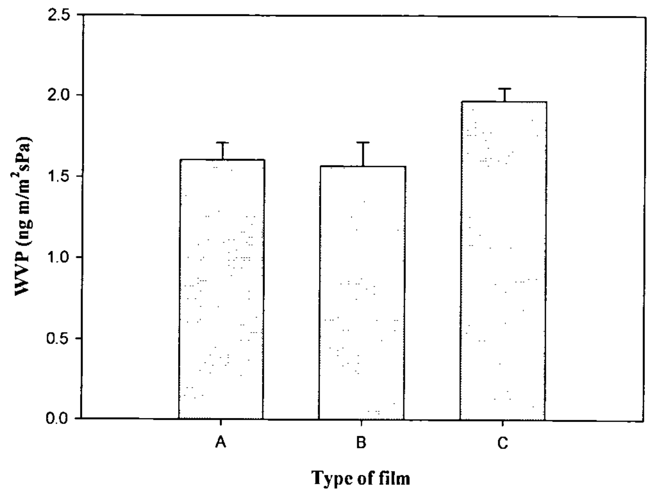


Fig. 1. Effect of different concentrations of cinnamaldehyde on the water vapor permeability (WVP) of *Gelidium corneum* films. A: 0% cinnamaldehyde, B: 0.01% cinnamaldehyde, C: 0.1% cinnamaldehyde.

TS value of the film containing 0.01% cinnamaldehyde was higher than the control by 8.31 MPa (Table 2). Mok et al. (14) reported that new cross-linking between cross-linking agents and biopolymer molecules improved the physical properties of the films. When *Gelidium corneum* films were compared with other edible films, TS value of the film was better than the 2.58 MPa of the blue marlin (*Makaira mazara*) muscle protein (15) and 1.03~4.78 MPa. of soy protein isolate films (16). However, increasing cinnamaldehyde from 0.01% to 0.1% decreased TS significantly from 9.54 MPa to 0.03 MPa, and the film was not formed at 1% cinnamaldehyde. This can be explained by the excess amount of cinnamaldehye affecting formation of cross-links, resulting in irregular network among agar molecules.

On the contrary, when cinnamaldehyde content increased from 0.01% to 0.1%, % elongation increased from 1.44% to 2.75%. A similar result was also observed in the study of starch based edible films (17).

Fig. 1 shows WVPs of *Gelidium corneum* films treated with cinnamaldehyde. WVP is an important factor in determining suitability of a food packaging material because it affects the shelf life of processed food. WVP of the film containing 0.01% cinnamaldehyde was 1.42 ng · m/m^2sPa, compared to 1.64 ng · m/m^2sPa of the control. This can be explained by the decrease of diffusion of water molecules due to new cross-linking between cinnamaldehyde and biopolymers (10). However, increasing cinnamaldehyde to 0.1% increased WVP to 2.05 ng · m/m^2sPa, because excess cinnamaldehyde affects the microstructure of the film. Our results are in good comparison with the result of *Undaria pinnatifida* film treated with $CaCl_2$, where WVP is 5.21 ng · m/m^2sPa (5), and this implies that the *Gelidium corneum* film is a good candidate as a food packaging material due to its low WVP. In particular, *Gelidium corneum* film had 1.42 ng · m/m^2sPa, which was better than WVP of the cassava starch film, 2.40 ng · m/m^2sPa~4.90 ng · m/m^2sPa (18).

Color of protein film might be an important property because it could affect consumer acceptance of the packaged foods. Table 3 shows Hunter L, a, and b values of *Gelidium corneum* film. There was no significant difference in Hunter L, a, and b values between the control and the film treated with 0.01% cinnamaldehyde. These results show that addition of 0.01% cinnamaldehyde did not affect the color of *Gelidium corneum* film. The same trend was also observed in the study of the physical properties of silk fibroin films (19).

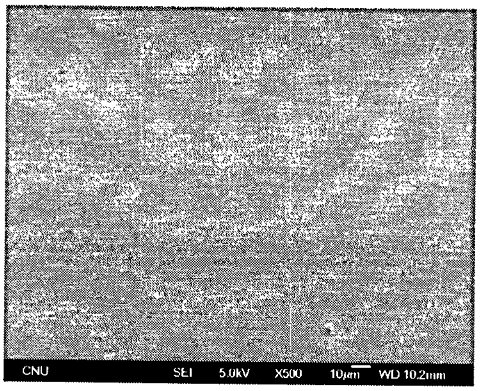
Film surface was studied using scanning electron microscopy. The film treated with cinnamaldehyde had a similar surface compared with the control, but was a little less smooth (Fig. 2). This difference might be explained by the slight difference in terms of the microstructure of the film.

In summary, the optimal conditions for *Gelidium corneum* film formation were 1.5% *Gelidium corneum* and 0.01% cinnamaldehyde, considering the physical properties of the film, addition of cinnamaldehyde should improve the physical properties of the film.

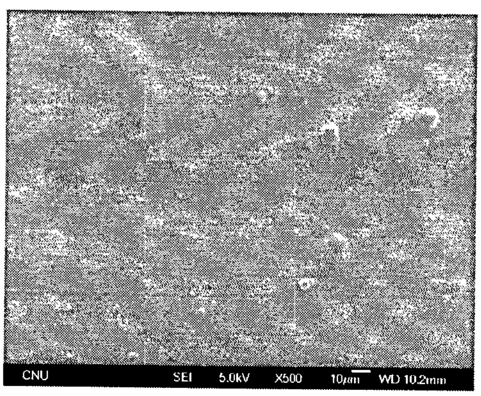
Table 3. Hunter L, a, b values of *Gelidium corneum* films containing different levels of cross-linking agents

Gelidium corneum powder (%)	Cinnamaldehyde concentration (%)	L	a	b
1.5	0	96.24±0.11[a1)]	-0.19±0.33[a]	4.28±0.58[b]
	0.01	96.19±0.07[a]	-0.29±0.03[a]	3.98±0.12[b]
	0.1	95.71±0.49[b]	-0.47±0.08[b]	5.10±0.48[a]
	1	ND[2)]	ND	ND

[1)]Means of five replications±standard deviations. Any means in the same column followed by different superscripts are significantly different ($p<0.05$) by Duncan's multiple range test.
[2)]Not determined.



A



B

Fig. 2. Microstructure of *Gelidium corneum* film (500× magnification). A: 1.5% *Gelidium corneum* powder, B: 1.5% *Gelidium corneum* powder+0.01% cinnamaldehyde.

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