FE-04

IMPROVEMENT OF MECHANICAL PROPERTIES OF EDIBLE CHITOSAN FILMS BY COMBINED USE OF PLASTICIZER AND EMULSIFIER

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ABSTRACT

Edible chitosan films have recently received much attention as an alternative green packaging material. These films, however, possess limitations due mainly to their hard and brittle characteristics. Various plasticizers, including glycerol, are generally added to the film forming solution to help alleviate such a limitation. However, there is still a restriction on the amount of glycerol that can be added to the film forming solution; excessive concentration of glycerol was noted to result in phase separation, rendering the addition of glycerol ineffective. A means to help reduce phase separation by increasing the emulsion stability is desired. In this study, Tween® 20, which is a widely used emulsifier, was added at 0% or 10% (w/w chitosan) to the chitosan/-glycerol film-forming solution system; the glycerol concentration was varied at 25% and 50% (w/w chitosan). Film-forming solution was then homogenized by two-stage high-pressure homogenization at 10/5 MPa. The homogenized chitosan solutions were dried using hot air drying at 40 oC. Physical (thickness and moisture content) and mechanical (tensile strength and percent elongation) properties of the resulting films were investigated and compared. Chitosan film having the best mechanical property (tensile strength of 20 MPa and percent elongation of 44) was obtained from the solution containing 50% (w/w) glycerol and 10% (w/w) Tween® 20.

Keywords: Emulsifier; Hot air drying; Two-stage high-pressure homogenization

INTRODUCTION

In recent years consumers have started to put more attention to naturally biodegradable packagings due both to the health and environmental related reasons [1]. Among many biomaterials that can be used to produce edible packagings, chitosan is one of the most promising. Chitosan is the second most abundant polysaccharide found in nature and is non-toxic, biodegradable, and biocom-patible; chitosan is therefore of great interest for packaging purposes. However, chitosan-based packagings, especially chitosan films, are rigid and brittle. Improvement of the mechanical properties of chitosan films is therefore necessary. A plasticizer is generally added to the film-forming solution to alleviate the brittleness problem. Plasticizers act to reduce intermolecular forces and increase mobility of polymer chains, therefore improving the flexibility and extensibility of the resulting films [2].

Glycerol is widely used to plasticize edible films [3]. However, there is still a restriction on the amount of glycerol that can be added to the film forming solution; excessive concentration of glycerol was noted to result in phase separation, rendering the addition of glycerol ineffective [4]. Hence, a means to help reduce phase separation by increasing the emulsion stability is desired. One of the most common ways to stabilize an emulsion of the film-forming solution is the addition of an emulsifier. Another method to increase the emulsion stability is via homogenization, which leads to reduced size of plasticizer droplets, and hence their increased ability to lubricate the polymer chains.

Since the combined effect of addition of plasticizer and emulsifier, homogenization and

drying of the resulting film-forming solution on the mechanical properties of chitosan-based films has been lacking, the objective of this study was to investigate this combined effect on selected physical (thickness and moisture content) and mechanical (tensile strength and percent elongation) properties of the films obtained at various conditions.

MATERIALS AND METHODS

Materials

Chitosan (molecular weight of 900,000 Da and degree of deacetylation of 90.2%) was purchased from S.K. Profishery Co., Ltd. (Bangkok, Thailand). Glycerol and acetic acid were obtained from Carlo Erba (Val de Reuil, Italy) and Merck (Darmstadt, Germany), respectively. Emulsifier (Tween® 20) was purchased from Chemipan Corporation Co., Ltd. (Bangkok, Thailand).

Methods

Chitosan films were prepared following the steps outlined in Figure 1. First, chitosan film-forming solution was prepared by dissolving 1.5% (w/v) chitosan in 1% (v/v) acetic acid under constant stirring via the use of a magnetic stirrer (Framo Gerätechnik, model M21/1, Eisenbach, Germany) at 700 rpm at room temperature for 6 h [5]. Then, glycerol was added at either 25% or 50% (w/w chitosan), while Tween® 20 was added at either 0% or 10% (w/w chitosan). Stirring then continued at 500 rpm at room temperature for 1 h. After mixing the solution was homogenized by two-stage high-pressure homogenization at 10/5 MPa via the use of a homogenizer (GEA Niro Soavi S.P.A. model NS2006L, Parma, Italy). The homogenized solution was centrifuged at 12,400 rpm for 15 min by a refrigerated centrifuge (Hitachi, model Himac CR21, Ibaraki, Japan) to remove undissolved impurities. The solution was then dried by hot air drying (40 ºC) at an air velocity of 0.25 m/s [5]; chitosan solution (16 g) was poured on an acrylic plate with the dimensions of 13×10 cm to cast a film for drying to obtain the target film thickness of 15 µm.

After drying to a final moisture content of approximately 14% (d.b.) (evaluated using AOAC standard method 934.06), a film sample was conditioned for at least 48 h prior to further property determination in a desiccator containing saturated salt solution of sodium chloride (Ajax Finechem, Seven Hills, NSW, Australia), which produced an RH of 75% (an average relative humidity of the environment in Thailand). Mechanical properties of the films, in terms of tensile strength and percent elongation, were then determined by the use of a texture analyzer (Stable MicroSystem, model TA.XT. Plus, Surrey, UK).

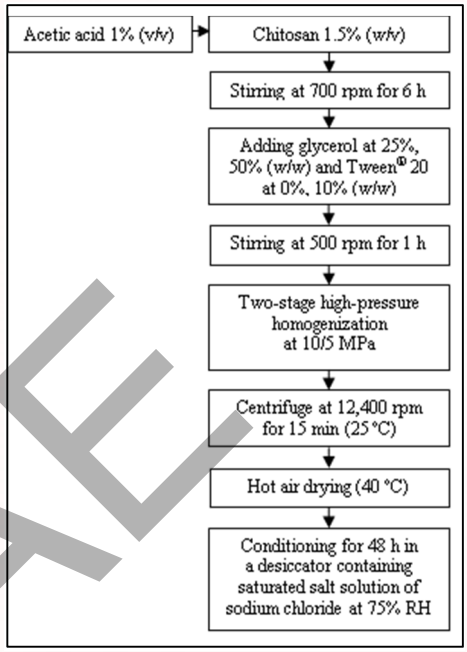

Fig. 1 Chitosan film preparation steps

RESULTS AND DISCUSSION

The moisture content, thickness, tensile strength and percent elongation of chitosan films added with various concentrations of glycerol and Tween® 20, homogenized at 10/5 MPa and prepared by hot air drying at 40 oC are shown in Table 1. At the same glycerol concentration, addition of Tween® 20 did not affect the film thickness. On the other hand, at the same Tween® 20 concen-tration, the concentration of glycerol had a significant effect on the film thickness. After conditioning at 75% RH for 48 hours, the film thickness increased with the glycerol concentration. Since glycerol is a hydrophilic plasticizer, the films with a higher concentra-tion of glycerol adsorbed more moisture (as can be seen in Table 1 in terms of the mois-ture content). Hence, these films swelled to a larger extent.

At the glycerol concentration of 25% (w/w chitosan), addition of Tween® 20 signifi-cantly affected the tensile strength of the films, but did not affect the percent elonga-tion of the films. On the other hand, at the glycerol concentration of 50% (w/w chito-san), addition

of Tween® 20 did not have a statistically significant influence on the mechanical properties of the films.

At the same Tween® 20 concentration, the concentration of glycerol had a significant effect on the mechanical properties of the films. The tensile strength and percent elongation of the films generally decreased and increased with an increase in the concentration of glycerol. This is because the larger number of glycerol droplets helped increasing the plasticization ability. The glycerol droplets penetrated through the polymer matrix and interfered with the chitosan chains, decreasing the intermolecular attraction and increasing polymer mobility, leading the films to be more flexible [4].

The appearances of the films added with various concentrations of glycerol and Tween® 20 are shown in Figure 2. At the same Tween® 20 concentration, the film with a glycerol concentration of 50% (w/w chitosan) was stickier than the film with a glycerol concentration of 25% (w/w chitosan). At the same glycerol concen-tration, addition of Tween® 20 helped the films to peel more easily.

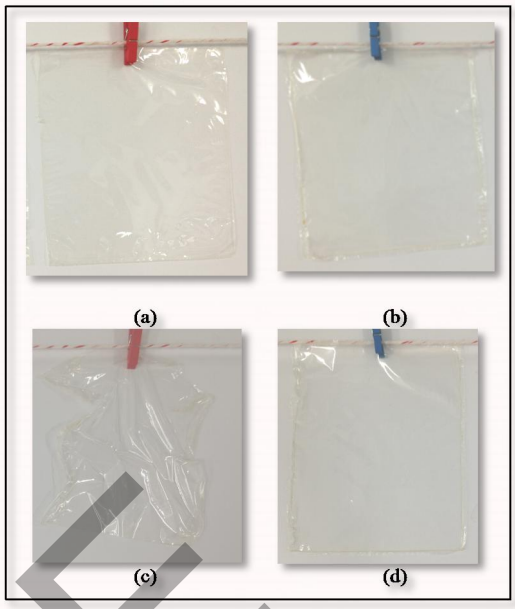

Fig. 2 Edible chitosan films (a) with 25% (w/w) glycerol and 0% (w/w) Tween® 20; (b) with 25% (w/w) glycerol and 10% (w/w) Tween® 20; (c) with 50% (w/w) glycerol and 0% (w/w) Tween® 20; (d) with 50% (w/w) glycerol and 10% (w/w) Tween® 20

Table 1 Moisture content, thickness, tensile strength and percent elongation of edible chitosan films

Glycerol concentration (%w/w chitosan)	Tween® 20 concentration (%w/w chitosan)	Moisture content (%d.b.)		Thickness (μm)		Tensile strength (MPa)	Percent elongation (%)
		Before conditioning at 75% RH	After conditioning at 75% RH	Before conditioning at 75% RH	After conditioning at 75% RH		
25	0	14.4±0.4^{a}	19.8±0.7^{a}	15.8±0.5^{a}	16.6±0.7^{a}	60.0±3.3^{c}	32.8±3.1^{a}
25	10	13.3±0.8^{a}	18.0±0.1^{a}	15.7±0.7^{a}	16.7±1.1^{a}	52.5±0.4^{b}	37.5±1.1^{ab}
50	0	14.9±0.1^{a}	28.0±0.5^{b}	24.3±1.8^{b}	25.1±0.7^{b}	20.8±2.1^{a}	40.0±1.4^{bc}
50	10	14.3±0.1^{a}	26.5±1.4^{b}	24.8±0.4^{b}	26.1±0.4^{b}	20.9±0.7^{a}	44.0±2.8^{c}

Same letters in the same column mean that the values are not significantly different at 95% confidence level ($p > 0.05$)

CONCLUSIONS

Possible improvement of the mechanical properties of chitosan films by adding glycerol (at a concentration of 25 or 50% w/w chitosan) and Tween® 20 (at a concentration of 0 or 10% w/w chitosan), homogenization at 10/5 MPa and hot air drying at 40 oC was investigated. The percent elongation and tensile strength of the films increased and decreased with the concentration of glycerol. The film with glycerol and Tween® 20 at the concentrations of 50% and 10% (w/w chitosan), respectively, had the highest percent elongation (about 44) and moderate tensile strength (about 20 MPa). Besides, addition of Tween® 20 helped the films to peel more easily compared with control films.

ACKNOWLEDGEMENTS

This study was financially supported by the Research Chair Grant of the National Science and Technology Development Agency (NSTDA), Thailand.

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