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Properties of Curdlan Film as Influenced by Types and Concentrations of Plasticizers

KEYWORDS: Curdlan, film, plasticizer, physico-chemical properties, microbial polysaccharide

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ABSTRACT *Effect of different types of plasticizers (glycerol, sorbitol and polyethylene glycol-400) on properties of film from curdlan (β-1,3-glucan) was studied. Film without plasticizer was mostly brittle, and became more flexible in the presence of plasticizer. Glycerol showed the highest plasticizing effect, providing the highest film elongation or flexibility, as compared to the others at the same concentration used. Properties of curdlan film added with glycerol at various concentrations (0 - 60% based on curdlan) were also investigated. Tensile strength (TS) of the film generally decreased but elongation at break (EAB) and water vapor permeability (WVP) increased as glycerol content increased ($p<0.05$). The film of curdlan containing glycerol at 50% exhibited the greatest mechanical properties. Therefore, glycerol as plasticizer at appropriate amount could improve flexibility of curdlan film.*

1. INTRODUCTION

In recent years, there is an increasing interest in the development of materials from bio-based resources, which are environmental friendly. Various types of biodegradable films and coatings have been prepared from different renewable or bio-based materials including polysaccharides, proteins and lipids [1]. Among various biopolymers, polysaccharides from microbial, such as xanthan, pullulan, gellan and curdlan, are of interest for various applications including chemical, food and pharmaceutical industries. Those microbial polysaccharides can be used as gelling agents, emulsifiers, stabilizers, binders, film formers, thickening agents and suspending agents [2].

Curdlan is a microbial hydrocolloid polysaccharide consisting of β-1,3-glucan (Fig. 1), produced from *Alcaligenes faecalis* var. *myxogenes* [3].

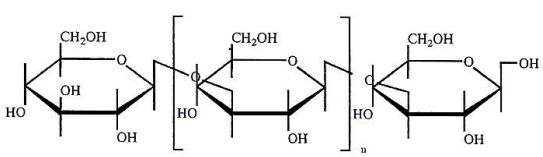

Figure 1: Molecular structure of curdlan [3].

Curdlan generally has high molecular weight so that it is insoluble in water at room temperature but soluble in alkaline solution [3]. Curdlan is known to form gels induced by heat and calcium ions. Curdlan has been used as a thickener and a stabilizer in food engineering and construction engineering and as an anti-cancer drug in pharmaceutics and clinics [3,4]. Gel of curdlan has been used as additive in various foods particularly in meat gels to improve their texture and water-holding capacity [4]. Curdlan gel is tasteless and safe as approved by the US Food and Drug Administration. Thus, curdlan can be used as additive in food products manufactured via retort and freezing processes [3]. To date, however, very limited information is available concerning film formation and the properties of film from curdlan. Preparation of curdlan in the film form could widen the applications of curdlan.

The making of polysaccharide-based films which possess highly molecular interaction generally needs the incorporation of the minimal content of plasticizer to overcome the brittleness and improve the flexibility as well as toughness of the films [5]. The most common plasticizers used are polyols and mono-, di- and oligosaccharides, such as glycerol, sorbitol and polyethylene glycol [6]. As a result, the film properties would depend on type and amount of plasticizer used. Therefore, this work was aimed at studying the preparation and properties of curdlan film. In particular, the effect of types and concentrations of plasticizers on film formation ability and film properties of curdlan was investigated.

2. MATERIALS AND METHODS

2.1 Materials and chemicals

Curdlan was purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan). Glycerol (GLY), sorbitol (SOR), poly(ethylene glycol)-400 (PEG) and sodium hydroxide were procured from Sigma Chemical Co., Ltd. (St Louis, Mo., USA).

2.2 Preparation of film-forming solution and film from curdlan

Curdlan powder was mixed with 0.3 M NaOH at concentration of 1% (w/w). The mixture was stirred for 15 min to solubilize the curdlan. Plasticizers (GLY, SOR or PEG) were added to curdlan solution at different concentrations (0 – 60% by weight of curdlan) and stirred for 15 min. The obtained film-forming solution (4 g) was cast onto a rimmed silicone plate (5x5 cm^2) and air blown for 12 h at room temperature prior to further drying at 25 °C and 50% relative humidity (RH) for 24 h in an environmental chamber. Finally, the resulting films were manually peeled off and used for analysis.

2.3 Determination of film properties

2.3.1 Film thickness

The thickness of film was measured using a micrometer (Mitutoyo Absolute, Tokyo, Japan). Five random positions of each film of five films were used for thickness determination.

2.3.2 Mechanical properties

Prior to the measurement of mechanical properties, the films were conditioned for 48 h in a ventilated oven at 25 °C and 50±5% RH. Tensile strength (TS) and elongation at break (EAB) of films were determined using a Universal Testing Machine (Lloyd Instruments, Hampshire, UK) equipped with tensile load cell of 100 N and testing at the cross-head speed of 30 mm/min. Ten samples (2x5 cm^2) with initial grip length of 3 cm were used for testing.

2.3.3 Water vapor permeability (WVP)

WVP of conditioned films was determined using a modified

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ASTM D-882 method [7]. The film was sealed on an aluminum cup containing silica gel (0% RH) with silicone vacuum grease and rubber gasket. The cup was placed at 30 °C in a desiccator containing the distilled water (100% RH). The cup was weighed at 1 h intervals over a 10 h period. WVP of the films was calculated as follows:

$$WVP\ (g\ cm^{-1}\ h^{-1}\ mmHg^{-1}) = wlA^{-1}t^{-1}(P_2-P_1)^{-1}$$

Where w is the weight gain of the cup (g); l is the film thickness (cm); A is the exposed area of film (cm^2); t is the time of gain (h); (P_2-P_1) is the vapor pressure difference across the film (mmHg). Five films were used for WVP testing.

3. RESULTS AND DISCUSSION

3.1 Effect of plasticizer types on curdlan film properties

Curdlan films with the thickness of 0.047 - 0.052 mm prepared by using different plasticizers including GLY, SOR and PEG at 40% were analyzed for tensile mechanical performance and water vapor permeability, in comparison with the control film without plasticizer addition.

3.1.1 Mechanical properties

Films from curdlan added with different plasticizers had varying TS and EAB as shown in Fig. 2. Curdlan film without plasticizer addition was rather brittle and less resistant to tensile deformation as indicated by low TS and EAB. This mainly resulted from high intermolecular interaction among curdlan chains especially via hydrogen bonding [3]. Curdlan film plasticized with PEG had higher TS by approximately 3 times than the control film. Films with GLY and PEG did not have significantly different TS ($p>0.05$). Film with SOR showed similar TS to the control film ($p>0.05$). For EAB of curdlan films, those with GLY exhibited the highest EAB ($p<0.05$), which was about 2.6 times higher than that of the control film. Similar EAB of films with GLY and those with SOR was observed ($p>0.05$). Films plasticized with PEG had not significantly different EAB as compared to the control film ($p>0.05$).

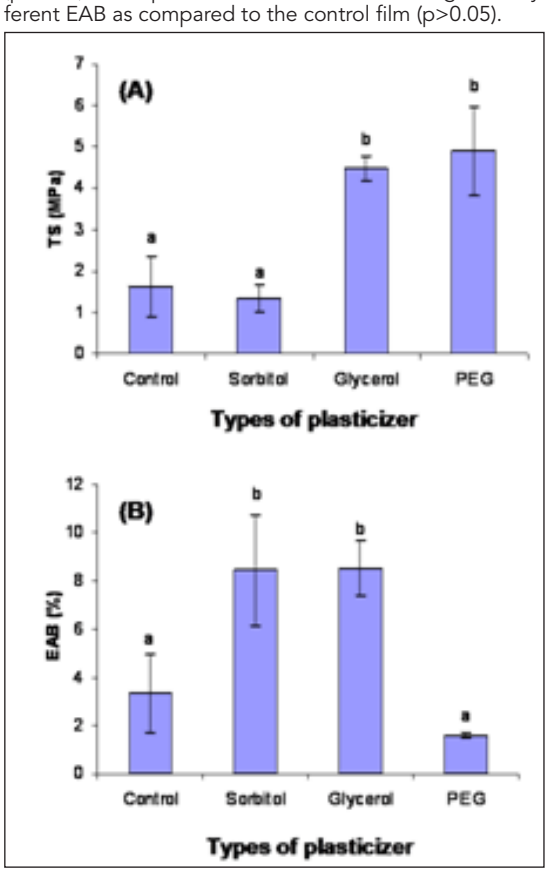

Figure 2: Tensile strength (TS) (A) and elongation at break (EAB) (B) of curdlan films incorporated without and with different plasticizers at 40%. Bars represent the standard deviation (n=3). Different letters on the bars indicate the significant differences ($p<0.05$).

The results indicated that addition of plasticizer could increase flexibility or elasticity of the curdlan film. This suggested the plasticizing effect, mostly resulted from the decrease in inter- and intra molecular attractive forces among polymer chains [8,9]. From the results, use of GLY rendered the curdlan film with greatest flexibility and strength compared to the other plasticizers used. GLY with lower molecular size produced more film plasticization than SOR and PEG which have higher molecular size [9]. Among plasticizer tested, PEG showed the lowest plasticizing effect on curdlan film. This was more likely associated with the lower polarity of PEG compared to the other plasticizers, which likely limited interaction with hydrophilic curdlan molecules and ability to produce flexible film. Similar results were found in plasticized methylcellulose films [10] and b-lactoglobulin films [9].

3.1.2 Water vapor permeability (WVP)

Table 1 shows WVP of curdlan films added with different plasticizers at 40%. Plasticized curdlan films had higher WVP than the control film, regardless of plasticizer types ($p<0.05$). Incorporation of hydrophilic plasticizers could bring about the increased hydrophilicity of the film as well as decreased intermolecular interaction of curdlan. This caused the increase in water vapor adsorption and diffusion and thus increasing WVP of the resulting curdlan film. However, curdlan films added with all plasticizers tested showed no significant differences in WVP ($p>0.05$).

Table 1: Water vapor permeability (WVP) of curdlan films incorporated without and with different types of plasticizers at 40%.

Films	WVP* (x 10^{-7} g/cm/h/mmHg)
Control (no pls.)	0.76 ± 0.01 [a] **
Sorbitol	1.54 ± 0.22 [b]
Glycerol	1.60 ± 0.38 [b]
PEG-400	1.43 ± 0.08 [b]

***Values are given as mean ± SD (n=3).**
****Different superscripts indicate significant differences ($p<0.05$).**

3.2 Effect of glycerol concentrations on curdlan film properties

Among different plasticizers tested, GLY showed the most plasticizing effect and provided curdlan film with better mechanical properties. Therefore, influence of GLY at various concentrations (0, 30, 40, 50 and 60%) on mechanical properties and WVP was further investigated.

3.2.1 Mechanical properties

Figure 3 illustrates TS and EAB of curdlan films incorporated with GLY at various concentrations. Among GLY-plasticized curdlan films, those with 40% GLY had the highest TS while those with 60% GLY showed the lowest TS ($p<0.05$). TS of films trended to decrease with increasing GLY levels ($p<0.05$). GLY has the relatively small molecule with hydrophilic characteristic which could be easily inserted between hydrophilic polymer chains and establish hydrogen bonds with hydroxyl or carbonyl groups of polysaccharide molecules. When GLY was incorporated in the curdlan film network, direct interactions and the proximity between curdlan chains were reduced [11]. The control film of curdlan had lower TS than the films added with GLY at 30-50% ($p<0.05$). This was most likely due to the brittleness of the control film which could be broken easily under tensile deformation, as evidenced by the lowest EAB ($p<0.05$). The EAB of films continuously increased with the increase in GLY level ($p<0.05$). It was noted that film with

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60% glycerol exhibited decreased TS and the sticky surface, indicating the excessive of GLY added.

3.2.2 Water vapor permeability (WVP)

WVP of curdlan films containing GLY at different levels is shown in Table 2. As expected that plasticized curdlan films showed higher WVP than the control film ($p<0.05$). Generally, WVP of films increased with increasing GLY concentration ($p<0.05$). Glycerol, a small straight chain hydrophilic plasticizer consisting of 3 hydroxyl groups, is able to attract water to the plasticized hydrophilic polymer system due to its high hygroscopic character [9]. The increase in water vapor transmission rate of films was possibly caused by an increase in free volume of system which enhanced the mobility of the polymeric chains, due to the insertion of glycerol between protein molecules. Consequently, the network structure of films became less dense and more permeable [6,12]. This led to the increase in the rate of water diffusion and thus increased WPV of the film matrix.

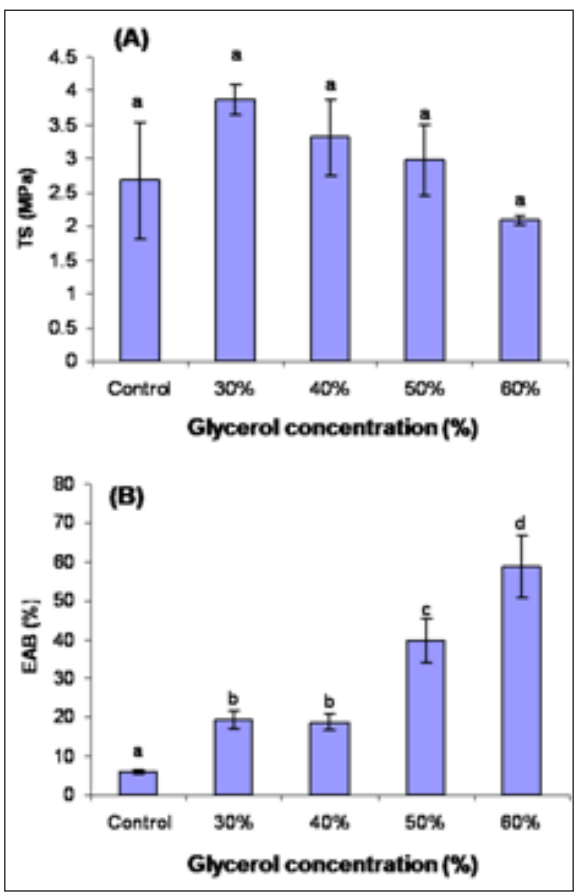

Figure 3: Tensile strength (TS) (A) and elongation at break (EAB) (B) of curdlan films incorporated without and with glycerol at various concentrations. Bars represent the standard deviation (n=3). Different letters on the bars indicate the significant differences ($p<0.05$).

Table 2: Water vapor permeability (WVP) of curdlan films incorporated without and with glycerol at various concentrations.

Films	WVP* (x 10^{-7} g/cm/h/mmHg)
Control (no GLY)	0.86 ± 0.03 [a] **
30%	2.35 ± 0.27 [b]
40%	2.46 ± 0.26 [b]
50%	3.10 ± 0.09 [c]
60%	3.66 ± 0.26 [d]

***Values are given as mean ± SD (n=3).**
****Different superscripts indicate significant differences ($p<0.05$).**

4. CONCLUSIONS

Film from curdlan could be prepared by casting of the solution of curdlan in 0.3M NaOH. Plasticizer of appropriate type and concentration was required to obtain sufficient flexible curdlan film. Types of plasticizers tested affected properties of curdlan films differently. Generally, glycerol showed the most plasticizing effect on curdlan film. TS of glycerol-plasticized curdlan films decreased but EAB and WVP increased with increasing glycerol content.

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