FE001

Improvement of Mechanical and Heat Sealing Properties of Chitosan Films via the Use of Glycerol and Gelatin Blends in Film-Forming Solution

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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 poor mechanical properties and ability to be sealed. Various plasticizers, including glycerol is generally added to the film forming solution in order to help alleviate the mechanical property-related limitation. A means to help increase the seal strength is still nevertheless desired. In this study, combined use of glycerol and gelatin as a co-polymer to promote seal strength to prepare a chitosan film-forming solution prior to drying was investigated. Glycerol was added at 0 or 25% (w/w chitosan), while gelatin was added at a concentration of 0 or 10% (w/v). The treated film-forming solution was dried by hot air drying at 40°C to cast a film. The film was then sealed at 100-200°C by a direct heat sealer for 10 s. Mechanical properties in terms of the tensile strength and percent elongation of the films were assessed. Heat seal strength and color of the film were also measured. A film with the best mechanical properties (tensile strength of 51.7 MPa and percent elongation of 38.3) was derived from the solution that contained 25% (w/w) glycerol and 10% (w/v) gelatin. The film, which was sealed at a temperature higher than 180°C showed the peeling-mode failure, indicating a good seal strength; the highest seal strength value was 110.7 N/m. Total color difference of the film with glycerol and gelatin (as compared to the color of the commercially available plastic film) was lower than that of the film prepared from the chitosan solution with only glycerol added by 7.6 and 11.3, respectively.

Keywords: Elongation, Gelatin, Glycerol, Heat seal strength, Hot air drying, Tensile strength.

1. Introduction

Since commercial plastic packagings are known to be associated with health issues and environmental problems, development of biodegradable packagings, in particular, packaging films, from bio-based materials has gained increasing interest (Leceta et al., 2013). Among biomaterials available for such a purpose, chitosan, which is a polysaccharide-based biopolymer, has widely been used owing to its non-toxicity, biodegradability and good film-forming ability (Elsabee and Abdou, 2013; Hamed et al., 2016). Unfortunately, chitosan films are not thermoplastic, and hence cannot be heat-sealed like conventional thermoplastic packaging polymers (van den Broek et al., 2015). A means to increase the sealing ability of chitosan is therefore desired.

Plasticizers such as glycerol have been noted to help increase the seal strength of a polymer by adding hydroxyl groups to the polymer structure (Abdorreza et al., 2011). This addition could enhance thermal motion of the chain segments, leading to increased polymeric diffusion across the film interface. This is then followed by recrystallization of the polymer structure, which eventually results in increased seal strength (Das and Chowdhury, 2016).

Another means that can be used to increase sealability and seal strength of a biopolymer is to add an appropriate co-polymer to a base polymer. Gelatin is a common co-

polymer that can be added to alter functional groups such as hydrogen and covalent bondings within the base polymer structure to increase film strength (Abdelhedi et al., 2017). Upon heat sealing, gelatin helps to promote molecular interdiffusion, which stabilizes the bonds and results in enhanced melting properties and hence sealability. In addition, gelatin could help form thermo-reversible gels (Cao et al., 2009), which in turn, assists sealed joint formation between the surfaces, allowing them to achieve high interfacial strength and hence improved sealing ability.

Despite numerous research investigations evaluating gelatin as a heat sealing adhesive for edible films, no study has attempted to produce and test the films prepared from a chitosan solution with added glycerol and gelatin. Since a study on the combined use of plasticizer and gelatin to prepare a chitosan film-forming solution and on the properties, especially the sealing properties, of the resulting films is lacking, the objective of this work was to investigate the effects of the above-mentioned film-forming solution preparation procedures on the mechanical properties (tensile strength and percent elongation) and heat seal strength of the obtained films. Color values of the films were also measured.

2. Materials and Methods

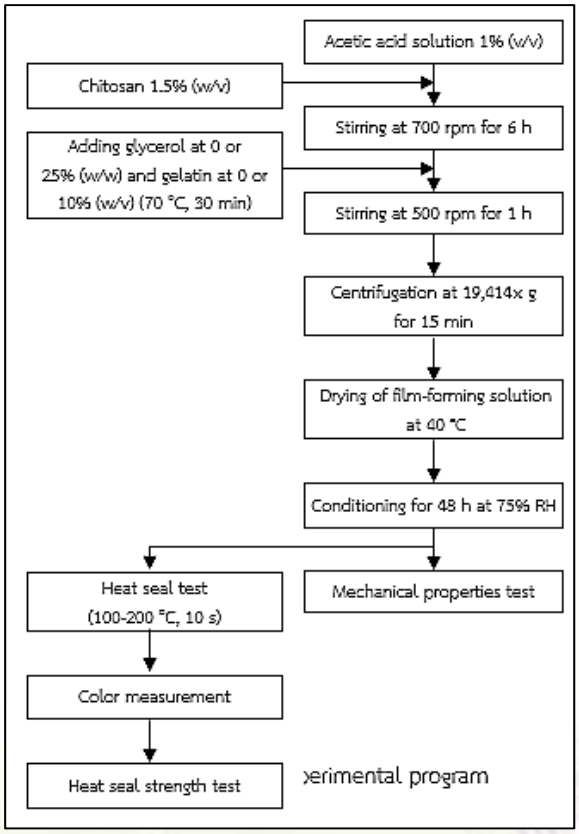
2.1 Materials

Chitosan powder with a molecular weight of 900 kDa and degree of deacetylation of 90.2% was obtained from S.K. Profishery Co., Ltd. (Samut Sakhon, Thailand). Analytical grade glacial acetic acid and glycerol were obtained from Merck (Darmstadt, Germany) and Ajax Finechem Pty Ltd. (Seven Hills, Australia), respectively. Gelatin was purchased from Ruam Chemical 1986 Co., Ltd. (Bangkok, Thailand).

2.2 Preparation of film-forming solutions.

Chitosan film-forming solution was prepared based on the methods of Thakhiew et al. (2015) with appropriate modification as shown 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 Gerätetechnik, model M21/1, Eisenbach, Germany) at 700 rpm at room temperature for 6 h. Glycerol was added to the solution at either 0 (control) or 25% (w/w chitosan). Gelatin solution at 10%(w/v) concentration was prepared following the method of Tongnuanchan et al. (2016) with some modification, by dissolving 1 g of gelatin powder in 10 mL of deionized water and then heating at 70°C for 30 min.

After preparing the chitosan-glycerol mixture, the gelatin solution was added at either 0 or 10% (w/v) to obtain the chitosan-glycerol-gelatin film-forming solutions. The resulting solution was stirred at 500 rpm at room temperature for 1 h. The film-forming solution was centrifuged at 19,414× g for 15 min via the use of a refrigerated centrifuge (Hitachi, Himac CR21, Ibaraki, Japan) to remove undissolved impurities.



2.3 Preparation and mechanical characterization of chitosan films.

Each prepared film-forming solution (16 g) was poured onto an acrylic plate with the dimensions of 13×10 cm to cast a film. Drying was conducted at an air temperature of 40°C and air velocity of 0.25 m/s (Thakhiew et al., 2010) until the film reached a moisture content of approximately 14% (d.b.); moisture content was evaluated via the AOAC Official Method 934.06. Film was then conditioned for at least 48 h prior to

further characterization in a desiccator containing a saturated solution of sodium chloride, which produces a relative humidity of 75% (the average relative climactic humidity in Thailand) (Thakhiew et al., 2010). Mechanical properties of the film, in terms of the tensile strength and percent elongation, were determined by a texture analyzer (Stable MicroSystem, TA.XT. Plus, Surrey, UK) according to the ASTM Standard Test Method D882 (ASTM, 2010).

2.3.1 Heat seal strength determination

A film sample was cut into a 10×2.5 cm strip, which were then placed on top of a 10×2.5 cm strips as shown in Figure 2. A 1-cm width of the seal area was heat-sealed at 100-200 oC for 10 s using an impulse heat sealer (DAKO, TH-13, Bangkok, Thailand). Seal strength of the heat-sealed film was determined by the same texture analyzer according to the ASTM Standard Test Method F88 (ASTM, 2005) with some modification. Each leg of the sealed film was clamped to the texture analyzer and held perpendicularly to the test direction. The maximum force required to cause seal failure is reported as the seal strength in N/m:

2.3.2 Color determination

The color of a film sample was determined by a spectrophotometer (HunterLab, model ColorQuest® XE, Reston, VA) in terms of L* (lightness), a* (greenness-redness) and b* (blueness-yellowness) values. Each film sample was measured at its center and three other positions along the strip; average color values are reported.

2.4 Statistical analysis

All data were subject to the analysis of variance (ANOVA) using SPSS® software (version 17; SPSS Inc., Chicago, IL) and are presented as mean values with standard deviations. Differences between mean values were established using Duncan's new multiple range tests at a confidence level of 95%. All experiments were performed in triplicate.

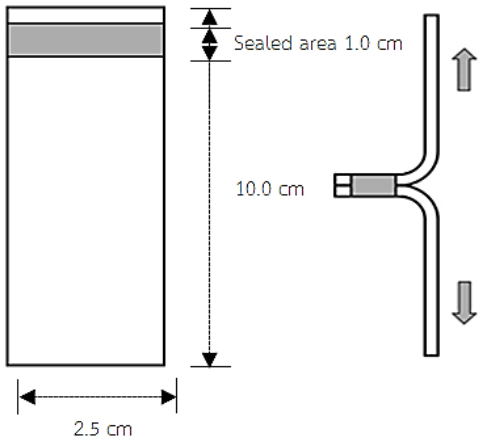


Figure 2 Simplified illustration of test specimen dimensions and testing direction for peel test. (a) Film sample and (b) peel testing direction.

3. Results and Discussion

Tensile strength, percent elongation, heat seal strength as well as color values of the prepared films are listed in Table 1.

3.1 Film mechanical properties

As shown in Table 1, the control film exhibited the highest tensile strength and lowest percent elongation. The tensile strength of the film prepared from the solution with added glycerol was lower, while the percent elongation was higher than those of the control film. This observation was expected because glycerol could help increase spacing between chitosan chains and probably reduce chain-to-chain hydrogen bonding attraction, resulting in facilitated chain movement and weaker chain structure and thus the increased flexibility of the resulting film (Cerqueria et al., 2012; Kang and Min, 2010).

Tensile strength and percent elongation of the film prepared from the solution with combined addition of glycerol and gelatin was higher than that of film prepared from the solution with only added glycerol. This might be because the carboxyl groups of gelatin could break the hydrogen bonds between hydroxyl groups and amino groups in the chitosan chains, thus weakening the interaction between the polymer chains (Dammak et al., 2017; Ning et al., 2015; Palma et al., 2016). Glycerol also led to increased molecular mobility of gelatin chains due to the higher free volume within the film matrix and by interpenetrating between the polymer chains, resulting in

an improvement in the stretchability of the films (Liu et al., 2017). Tensile strength of the film was higher due to probably the formation of polyanion-polycation complexes between gelatin and chitosan (Bonilla and Sobral, 2016).

Film prepared from the solution with 25% (w/w) glycerol and 10% (w/v) gelatin exhibited the best mechanical properties, with tensile strength of 51.7 MPa and percent elongation of 38.2.

3.2 Effects of glycerol and gelatin on heat seal strength

Table 1 also lists the maximum achievable heat seal strength values of the film samples. The films sealed at above 180 oC showed peeling mode failure of the seal, indicating the optimum seal strength. The control film proved difficult to heat sealed. This might be due to its rigid crystalline nature and the occurrence of strong inter- or intra-molecular hydrogen bonding, leading to restricted mobility of chitosan chains during thermal degradation, resulting in lower molecular interdiffusion at the surface of the films (Mittal et al., 2017).

In general, functional groups such as hydroxyl (OH), carboxyl (COOH) and aldehyde (CHO) are responsible for the adhesion strength of a film. Adding glycerol to the film solution increased the seal strength of the films, probably because glycerol contains three CHOs, which enhanced chain interactions via hydrogen bonding, resulting in higher seal strength. It has indeed been reported that plasticizers such as glycerol could act as heat-sealing promoters through the contact surface of glycerol-plasticized films (Farhan and Hani, 2017; Tongnuanchan et al., 2016).

Combined addition of glycerol and gelatin led to the highest seal strength. This might be because of the larger number of hydrogen and covalent bonds involving CHO and N-C within the gelatin structure, leading to major forces responsible for seal formation. During sealing, combined use of glycerol and gelatin could help enhance molecular interdiffusion, stabilized mainly by hydrogen bonding between chains (Tongnuanchan et al., 2016), thus, resulting in better melting and hence the sealing behavior.

The highest seal strength obtained in this study was 110.7 N/m for the film prepared from the solution with 25% (w/w) glycerol and 10% (w/v) gelatin; this value is lower than that of heat-sealed synthetic polymer (678 N/m, for LDPE) (Farhan and Hani, 2017; Tongnuanchan et al., 2016). However, all film samples had higher seal strength than the films prepared from sago starch films with different concentrations of glycerol (10-70 N/m) (Abdorreza et al., 2011).

3.3 Color of films

The color of commercial stretch film (M WrapTM) and that of chitosan films with glycerol as well as with glycerol and gelatin after heat sealing are shown in Table 1. In all cases, chitosan films had lower lightness (L*) and higher greenness (a*) and yellowness (b*) than the commercial stretch film.

In terms of lightness, the films with glycerol exhibited decreased lightness when compared to the value of the control film. On the other hand, the films with combined glycerol and gelatin exhibited significant increased lightness. In terms of redness, films with glycerol had increased greenness, while films with glycerol and gelatin had similar greenness to the control film. In the case of yellowness, films with glycerol exhibited significantly increased yellowness than the control film and films with glycerol and gelatin.

Total color difference (ΔE*) of the films increased significantly according to the higher a* and b* values when compared to the color of the control film. ΔE* of the films was the highest at 11.3. On the other hand, control film and films with combined glycerol and gelatin had significantly lower ΔE* values than the films with only glycerol.

Table 1 Tensile strength, percent elongation, heat seal strength and color of different films.

Film type	Tensile strength (MPa)	Percent elongation (%)	Heat seal strength (N/m)	Color value			
				L^*	a^*	b^*	ΔE^*
Control (Chitosan)	60.9 ± 2.8^{C}	15.6 ± 1.8^{A}	5.5 ± 0.2^{A}	92.8 ± 0.2^{B}	-0.7 ± 0.0^{B}	6.1 ± 0.5^{A}	7.2 ± 0.5^{A}
Chitosan-Glycerol	38.2 ± 2.7^{A}	31.8 ± 2.2^{B}	76.5 ± 2.5^{B}	92.3 ± 0.1^{A}	-1.2 ± 0.2^{A}	10.4 ± 0.1^{B}	11.3 ± 0.2^{B}
Chitosan-Glycerol-Gelatin	51.7 ± 3.1^{B}	38.3 ± 2.7^{C}	110.7 ± 2.1^{C}	92.6 ± 0.2^{B}	-0.8 ± 0.1^{B}	6.6 ± 0.1^{A}	7.6 ± 0.1^{A}

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

4. Conclusions

Improvement of mechanical properties and seal strength of chitosan-based films by addition of glycerol at a concentration of 0 or 25% (w/w chitosan) and gelatin at a concentration of 0 or 10% (w/v) was investigated. Percent elongation of the films increased with the combined addition of glycerol and gelatin. The film prepared with 25% (w/w) glycerol and 10% (w/v) gelatin exhibited the best mechanical properties, with the tensile strength of 51.7 MPa and percent elongation of 38.3. Such a film also had the highest seal strength of 110.7 N/m. Films with combined glycerol and gelatin exhibited significantly increased lightness and decreased greenness and yellowness when compared with the film with only added glycerol, the color was nevertheless not significantly different from that of the control film.

5. Acknowledgements

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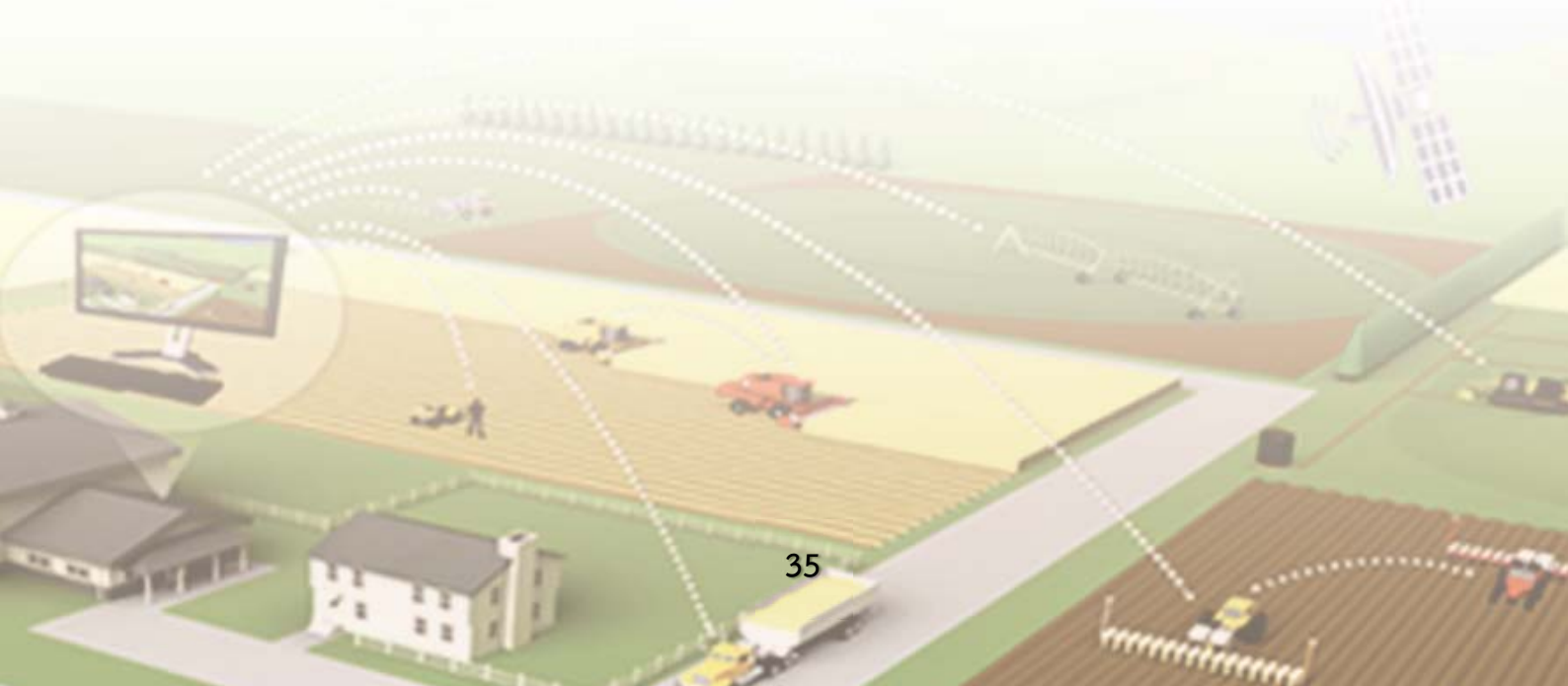

Results show that glycerol quantities used in film forming solutions were responsible for films composition; while polymer/total plasticiser ratio in the solution determined the thickness (and thus structure) of the films. These results were confirmed by TEM. NMR allowed understanding the films molecular rearrangement. Two different behaviours for the two components analysed, water and glycerol were observed: the first is predominantly moving free in the matrix, while glycerol is mainly bounded to the chitosan chain. The chitosan-glycerol films turned out to be systems of high transparency and their properties depended on the plasticizer content, obtaining homogeneous systems for concentrations up to 10% w/w. In addition, the films were found to be more hydrophilic than the reference material, with smaller contact angle and greater water absorption values, obtaining more flexible films in view of their mechanical properties. Export citation Request permission. Copyright.Â Mechanical and barrier properties of nanocrystalline cellulose reinforcedchitosan based nanocomposite films. Carbohydrate Polymers, 90: 1601â€“1608. [20]Dehnad, D., Emam-Djomeh, Z., Mirzaei, H., Jafari, S-M., Dadashi, S. (2014). Uses for chitosan films have been limited because of their high moisture permeability and mechanical problems. However, the properties of chitosan films can be modified to improve barrier and mechanical properties by changing pH or solvent. Kienzle-Sterzer and others (1982) evaluated the effect of chitosan con-. centration and type of solvent on the mechanical properties of chitosan films. Chitosan possesses great potential for use in films, coatings, and encapsulation. Application in edible and degradable films or coatings and encapsulation may be possible only after the proper-ties of chitos... This work characterizes biological, physical, and chemical properties of films formed from an aqueous solution of hydroxypropyl methylcellulose (HPMC), with different concentrations of chitosan (CH) and bioactive cystatin/lysozyme preparation (C/L). The properties of biocomposites were examined by Dynamic Mechanical Analysis (DMA), Fourierâ€™s transfer infrared spectroscopy (FTIR), water vapour permeability (WVP), and tensile.Â Twelve mL of film forming solutions was then cast on leveled, coated by Teflon glass plate on an area of 66 Ã— 77 mm, and dried at 25â˚C and 60% RH for 48 hours. The dried biocomposites were peeled from plates and cut into pieces for the measurements of thermal and mechanical properties.Â Table 2: Mechanical properties of films.