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Physical Properties of Chitosan Films as Affected by Concentration of Lactic Acid and Glycerol.

Aishah Bujang[1+], Syarifah Nur 'Adila[1] and Nugraha Edhi Suyatma[2]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2]Faculty of Agricultural Engineering and Technology, Bogor Agricultural University, 16680 Bogor, Indonesia

Abstract. In this study, the physical properties of chitosan film (1% w/v) incorporated with different concentration of lactic acid (1 and 2% w/v) and glycerol (2 4, 6, 8, 10% w/w) were evaluated. Results indicated that the addition of different concentration of glycerol on the chitosan film mixed with 2% lactic acid did not affect the thickness of the film. However, significant reduction in thickness was observed on the chitosan film when mixed with 1% lactic acid at different concentration of glycerol. Similarly, water vapour transmission rate (WVTR) of the chitosan film mixed with 2% lactic acid showed no significant difference in value when different concentrations of glycerol were added. While the chitosan film with 1% lactic acid showed gradual linear increase in WVTR as the concentration of glycerol added was increase. In term of the mechanical properties of the chitosan film, addition of glycerol at different concentration did not affect the tensile strength of the film incorporated with 2% lactic acid. However, chitosan film of the 1% lactic acid showed decrease in tensile strength, as the glycerol concentration added was increase. The unplasticized chitosan film prepared with 1% lactic acid exhibited the highest tensile strength (26.12 ± 4.5236 Mpa). While no significant difference in tensile strength was observed for the 2% lactic acid chitosan films. Percent elongation of the chitosan film mixed with 1% and 2% lactic acid as solvent showed a contrast effect between each other when added with different concentrations of glycerol. An increase in % elongation was observed on the 1% lactic acid chitosan film, as the concentration of glycerol was increase. While for the 2% lactic acid chitosan film, decrease in % elongation was obtained when the concentration of glycerol added was increase.

Keywords: Chitosan, lactic acid, glycerol, chitosan film, plasticized film

1. Introduction

Due to environmental concerns, the development of new biodegradable packaging material films is needed to find alternatives to petroleum-based plastics and reduce the amount of synthetic materials used. Biodegradable films made from natural biopolymers were shown to have tendencies in improving handling properties and able to extend the shelf life of food product. Chitosan is a β-1,4-linked polymer of glucosamine (2-amino-1-deoxy-β-D-glucose) with lower amounts of *N*-acetylglucosamine. It is obtained through deacetylation of chitin, an abundant by-product of the crab and shrimp processing industries. Previous studies showed that chitosan has a potential for a wide range of applications since it can be formed into fibers, films, gels, sponges, beads or nanoparticles [1]. Since chitosan is highly crystalline and intractable material, therefore appropriate solvent system to dissolve and to impart its functionality is an important factor. While plasticizer such as glycerol is commonly used [2] in order to reduce rigidity and to decrease the intermolecular forces of the chitosan biopolymer chains [3].

This study aims to analyze the effect of lactic acid and glycerol concentrations on the physical, barrier and mechanical properties of chitosan film developed.

+ Corresponding author. Tel.: +60133496942.
E-mail address: shah2012@gmail.com

2. Materials and Method

2.1. Materials

Pharmaceutical grade chitosan powder with 85% degree of deacetylation was obtained from Saintifik Zener Sdn. Bhd., Malaysia. Other chemicals including lactic acid, glycerol, silica gel, calcium chloride were also obtained from the same supplier.

2.2. Preparation of Film

Chitosan film was prepared by a casting technique. A 1% w/w chitosan solution was prepared in 1% and 2% lactic acid. After the chitosan was completely dissolved, glycerol was added in the solution and mixed until it is fully dispersed. The solution was degassed using vacuum system in order to prevent the formation of air bubbles in the films when the casting solvent evaporated. Petri dishes were cleaned and then 40 g of film solution were cast in the centre of each plate and spread. The films were dried in cabinet drier at 60 ℃ for approximately 1 day before conditioning in desiccators containing silica gel (RH: 58%) for 1 day prior to analysis. The glycerol contents employed in this study were 2, 4, 6, 8, and 10% w/w of chitosan.

2.3. Film Thickness

Film thickness (T) was measured using the electronic digital micrometer (Mitaka, Tokyo, Japan) with a precision 0.001 mm. The values obtained for each sample at five different locations were averaged.

2.4. Water Vapour Transmission Rate (WVTR)

WVTR was determined gravimetrically using the cup method based on the American Society for Testing and Materials No. E96-95 [4]. Film samples were mounted on the stainless steel cans to expose the coated face to the outside of the cans filled with 50 g of calcium chloride. The area of the films was measured and the initial weight of the can was recorded. The weight loss of the cans was monitored by weighing every 24 hours for a period of 7 days. The setup was subjected to a temperature and relative humidity of 25 ℃ and 90%, respectively. Slopes of the steady-state portion of weight loss versus time curves were determined by linear regression to estimate water vapour transmission rate using the equation,

$$\text{WVTR} = \frac{\text{Slope}}{\text{Film Area } (\text{m}^2)} \tag{1}$$

2.5. Mechanical Properties

Tensile strength and elongation percentage was measured by using texture analyser (TA.XT*plus*, Stable Micro System Material Test, United Kingdom). Before the measurements, the film is conditioned in desiccators with 58% RH for 3 days. The tensile strength is determined based on maximum load at the time of film rupture and elongation percentage is based on the elongation of the film when the film broke. Percent elongation is calculated by comparing the length of film at break and the length of the film before drawn by the appliance.

3. Results and Discussion

3.1. Thickness

The thickness measurement of the chitosan films dissolved at different concentration of lactic acid and plasticize using different concentration of glycerol is shown in Figure 1. Chitosan film made by 2% lactic acid solvation showed increase in the film thickness compared to the use of 1% lactic acid. The incorporation of glycerol at different concentration in the chitosan films showed no significant difference ($P < 0.05$) on the thickness of 2% lactic acid chitosan films. While the 1% lactic acid chitosan film was affected by the concentration of glycerol added. No significant difference was observed between unplasticized and 4% addition of glycerol on the film thickness. While the thickness value of the 2%, 6% and 10% glycerol addition also showed no significant difference on the 1% lactic acid chitosan film. The 2%, 4% and 10% glycerol addition on the 1% lactic acid chitosan film also showed no significant difference among each other.

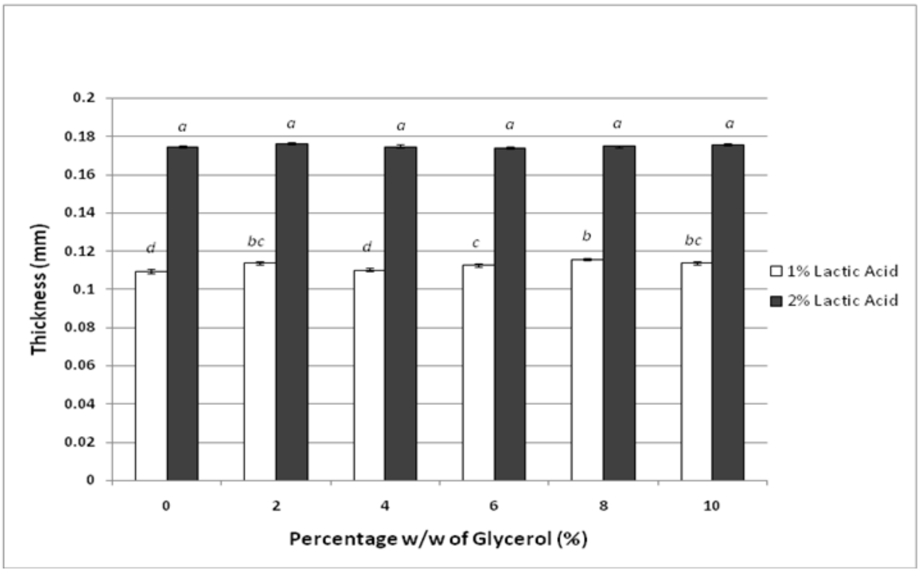

Fig. 1: Effect of lactic acid and glycerol concentration on thickness of chitosan films

3.2. Water vapour transmission rate of chitosan film

Unplasticized chitosan films prepared with 1% lactic acid showed the lowest WVTR when compared with other films as shown in Figure 2. This observation is different from previous result of 'Adila *et al.* [5] in which the addition of glycerol was found able to retain the moisture from the outside and subsequently lower the WVTR of plasticized chitosan film. The result also shows an increase in WVTR for 1% lactic acid chitosan film when the concentration of glycerol was increase.

This result agrees with Chillo *et al.* [6] and Ziani *et al.* [3] which proposed that glycerol could be inserted between adjacent polymeric chains, reducing the rigidity and decreasing the intermolecular attractions, thus, allowing a higher water vapour diffusion through their structure. Souza *et al.* [7] stated that compounds with high hydrogen bonding generate films that are susceptible to water vapour. However, 2% lactic acid chitosan films showed no significant difference ($P < 0.05$) in WVTR values until 8% w/w glycerol content. This observation is similar with the previous findings by Cissé et al. [8] who reported that addition of glycerol did not affect the water vapour permeability. The differences in glycerol action on WVTR of lactic acid chitosan film may be due to the intrinsic chemical nature of chitosan and also to the way blend films are prepared. Concentration of lactic acid had a significant effect on WVTR of chitosan films. The solvent used to dissolve the chitosan powder are critical in water transmission. Chitosan possessing high cationic and being hydrophilic in nature, leads to higher interaction with water molecules, which increases the permeation of water vapour.

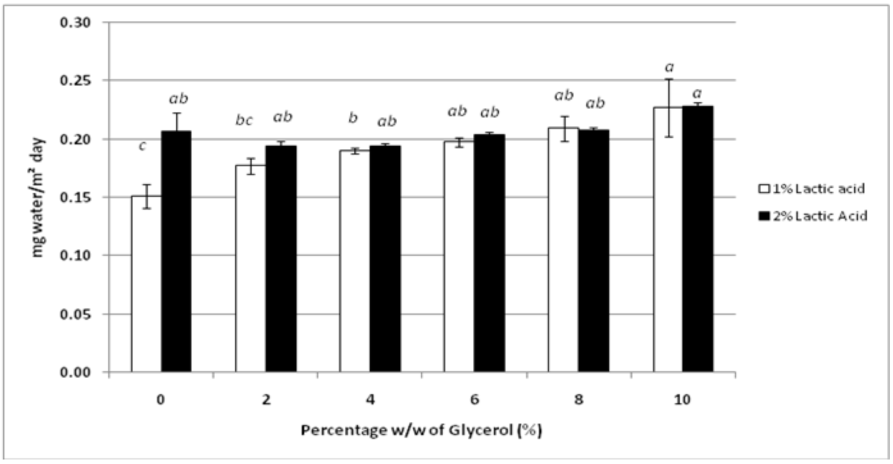

Fig. 2: Effect of lactic acid and glycerol concentration on water vapour transmission rate of chitosan films

3.3. Mechanical properties of chitosan film

The tensile strength and elongation at break of lactic acid chitosan films were displayed in Figure 3 and 4. The result shows that the tensile strength of chitosan film prepared with 1% lactic acid decrease when the concentration of glycerol increase. Addition of glycerol reduces the tensile strength of the film. Similar finding was also observed by Ziani *et al.* [3], they stated that the presence of glycerol resulted in less resistant, more elastic and more permeable films. However, no significant difference ($P < 0.05$) was shown for chitosan films prepared with 2% lactic acid. This indicates that concentration of glycerol does not affect the tensile strength of the 2% lactic acid chitosan films. It is known that lactic acid contained hydroxyl group instead of hydrogen in their structure. Thus, when the counter ion, such as lactate, was larger, the film lost its strength [9]. The highest tensile strength exhibited by unplasticized chitosan film prepared with 1% lactic acid was 26.12 $\pm$4.5236 MPa.

For the percent elongation at break, unplasticized chitosan film prepared with 1% lactic acid showed the lowest elongation even though it had the highest tensile strength. Percent elongation of chitosan films prepared with 1% lactic acid was found to increase with the increase of glycerol concentration. However, the 2% lactic acid chitosan films showed an inverse result. Plasticizer interfere with chitosan chain by decreasing the intermolecular forces, soften the rigidity of the film's structure and increase the polymer mobility [10], thus decrease the tensile strength and increase the percent elongation.

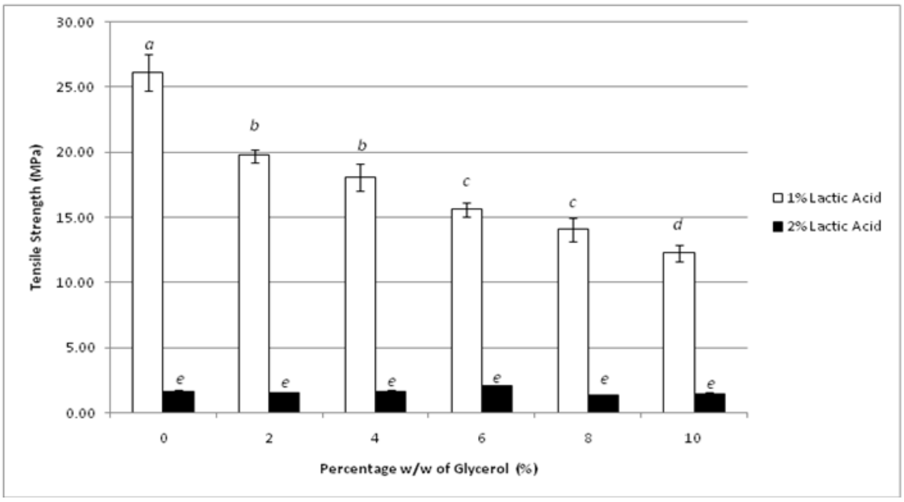

Fig. 3: Effect of lactic acid and glycerol concentration on tensile strength of chitosan films

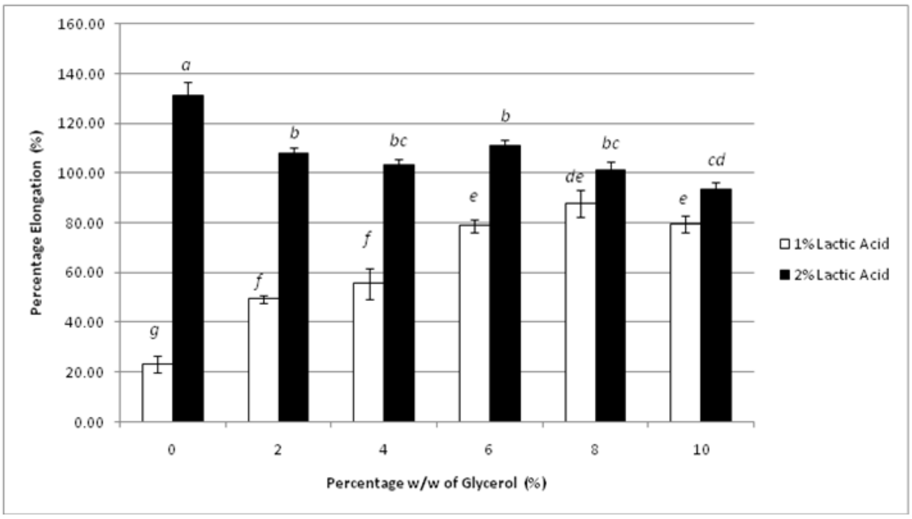

Fig. 4: Effect of lactic acid and glycerol concentration onelongation at break of chitosan films

4. Conclusion

In general, the characteristics of chitosan film developed are affected by the concentration of lactic acid and glycerol used as solvent and plasticizer. The results indicated that the thickness of the chitosan film was only slightly affected by the difference in glycerol concentration but was affected by the concentration of lactic acid used. The difference in WVTR of 1% and 2% lactic acid were observed when the concentration of glycerol added is below 4% while at higher glycerol concentration (6 to 10%), no significant difference in WVTR was observed. Similar with film thickness, the tensile strength of the film was greatly reduced when 2% lactic acid was used as compared to the 1% lactic acid chitosan film. No significant difference was shown by the 2% lactic acid chitosan film at different concentration of glycerol. For the 1% lactic acid chitosan film, the tensile strength decreases as the gylcerol concentration increases. Elongation percentage was found to increase with the increase of glycerol concentration for the 1% lactic acid chitosan film. However, the increase of glycerol concentration has the opposite effect on the 1% lactic acid chitosan film. This study shows that manipulation of solvent and plasticizer used will determine the physical, mechanical and barrier properties of the chitosan film developed.

5. Acknowledgement

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