Physicochemical properties of sugar palm starch film: Effect of concentration and plasticizer type

D J Prasetyo¹, W Apriyana¹, T H Jatmiko¹, Hernawan¹, S N Hayati¹, V T Rosyida¹, Y Pranoto², C D Poeloengasih¹
¹Research Unit for Natural Product Technology, Indonesian Institute of Sciences, Yogyakarta, Indonesia 55861
²Faculty of Agricultural Technology, Universitas Gadjah Mada, Yogyakarta, Indonesia 55281
e-mail: crescentianadewi@gmail.com

Abstract. In order to find the best formula for capsule shell production, this present work dealt with exploring physicochemical properties of sugar palm (Arenga pinnata) starch film as a function of different kinds and various concentrations of plasticizers. The films were prepared by casting method at different formula: starch 9-11%, glycerol or sorbitol 35-45% and polyethylene-glycol 400 (PEG 400) 5-9%. Appearance, thickness, retraction ratio, moisture content, swelling behavior and solubility of the film in water were analyzed. Both glycerol and sorbitol are compatible with starch matrix. On the contrary, PEG 400 did not form a film with suitable characteristics. The result reveals that glycerol- and sorbitol-plasticized films appeared translucent, homogenous, smooth and slightly brown in all formulas. Different type and concentration of plasticizers altered the physicochemical of film in different ways. The sorbitol-plasticized film had lower moisture content (≤ 10%) than that of glycerol-plasticized film (≥ 18%). In contrast, film plasticized with sorbitol showed higher solubility in water (28-35%) than glycerol-plasticized film (22-28%). As the concentration of both plasticizers increased, there was an increasing tendency on thickness and solubility in water. Conversely, retraction ratio and swelling degree decreased when both plasticizers concentration increased. In conclusion, the sorbitol-plasticized film showed a potency to be developed as hard capsule material.

1. Introduction

For more than a century, gelatin was adopted as the main material of capsule manufacture due to its excellent characteristic including gelling, film forming and surface active properties. Although gelatin has such a wide range of useful applications, big concerns persist among consumers about its usage. Mad cow disease episode in the 1990s, religious and cultural issues, and nature of gelatin capsule are the main reasons to consider the use of gelatin in food and pharmaceutical field. Consequently, development of gelatin alternative is highly desirable because the global halal market is growing rapidly.

Many researchers have been exploring and developing materials to replace gelatin. Numerous studies have been conducted by using starch from plant sources, such as yam [1], sweet potato [2-3], mungbean [3], cassava [4-5], banana [6], corn [7] and sago [8-11]. Moreover, sugar palm starch (SPS) film also have been successfully developed in the last several years [12-18]. Compared to sago starch, SPS has more suitable properties for producing starch gels or dough because of its abilities to form a firmer and more resistant gels at concentrations above the gel point [19].
Many studies have been conducted to explore film formation from SPS. While earlier studies were focused on developing SPS film with starch concentration of 8-9 % w/w [12-18], this study focuses on developing SPS film with higher starch concentration. Meanwhile, appropriate SPS film for capsule shell formation could be obtained by combining it with plasticizer. The addition of plasticizer would affect physicochemical properties of film, such as appearance, moisture content, and solubility in water. The effects of type and concentration of plasticizer on physicochemical properties of SPS film in high starch concentration were not yet studied. This work focuses on studying the effects of plasticizer type and concentration on physicochemical properties of high starch concentration SPS film to provide an appropriate film formula for hard capsule production.

2. Materials and methods

2.1. Materials

SPS with 47.70 % amylose content and 9.54 % water content was obtained from PT Aren Mulya, an SPS industry in Klaten, Central Java, Indonesia in January 2015. Glycerol, sorbitol and polyethylene-glycol 400 (PEG 400) and magnesium nitrate (Mg(NO₃)₂) were purchased from Merck.

2.2. Film Formation

The film forming solution was prepared by dissolving an amount of plasticizers (35-45% for glycerol or sorbitol and 5-9% for PEG 400) in distilled water. The desired amount of SPS (9-11%) was added to the aqueous plasticizer dispersion. The mixture was heated above the gelatinization temperature and maintained under continuous stirring for 30 min. The film solution was degassed to remove the bubbles, spread onto the acrylic plate fitted with rims around the edge and dried overnight at 50°C. Film was allowed to cool to room temperature before removing from the plate. All films were stored in the desiccator under 52% RH at 25°C at least for 48 h before analysis.

2.3. Characterization of Film

Visual test and tactile test were performed to observe the effect of various plasticizers on the appearance of SPS film. Film thickness was measured using a digital micrometer (Mitutoyo, Japan) at nine random positions around the film. The measurement was performed on ten replications. The retraction ratio of films was determined according to a method proposed by The et al., (2009) [5] and calculated as the percentage of film shrinkage from the initial film thickness. The initial film thickness (t₀) was obtained after casting (2 mm), whereas the dry film thickness (t) was obtained after drying the film overnight at 50°C in an air circulated oven. The film retraction ratio was calculated by Equation (1).
Retraction ratio (%) = \frac{t_0 - t}{t_0} \times 100\% (1)

Moisture content of films was determined gravimetrically. The film was cut into 20 mm x 20 mm and the initial weight \( (w_0) \) was measured. The film was conditioned and dried at 105°C until constant weight \( (w) \) was obtained. Ten replicates were obtained for each sample. The percentage of moisture content was calculated by following equation:

\text{Moisture content} (%) = \frac{w_0 - w}{w_0} \times 100\% (2)

The swelling behavior study of film was performed by immersing film sample in distilled water at room temperature following by monitoring the weight change and thickness of film upon soaking in distilled water periodically. Excess water was removed by filtering paper before weighing. Measurements were done in ten replicates. The initial weight \( (w_0) \), final weight \( (w) \), initial thickness \( (t_0) \), and final thickness \( (t) \) were measured. The swelling degree and swelling thickness, expressed in percentage, were calculated according to the following equation:

\text{Swelling degree} (%) = \frac{w - w_0}{w_0} \times 100\% (3)

\text{Swelling thickness} (%) = \frac{t - t_0}{t_0} \times 100\% (4)

Solubility of film in water was studied and a method proposed by Shih [20] was adopted with slight modification. A film sample was weighed and immersed in 50 mL distilled water. The flask was stored in an orbital incubator at 37°C for one hour with mild agitation at 175 rpm. The specimen was then collected by filtration and dried again in an air-circulating oven at 105°C for 24 h. Ten replicate measurements were taken for each type of film. The initial dry weight \( (w_0) \) and final dry weight \( (w) \) of film were measured, then solubility of film was calculated by following formula:

\text{Solubility} (%) = \frac{w_0 - w}{w_0} \times 100\% (5)
3. Results and Discussion

3.1. Visual and Tactile Test

SPS with PEG 400 as plasticizer did not form film with suitable characteristics. There were many white opaque spots on the film that might be due to the incompatibility of both polymers. It has been referred as blooming or blushing phenomenon. Hence, this film did not characterize during this study.

![Visual appearances of homogeneous (a) and brittle-cracked (b) film](image)

**Figure 1.** Visual appearances of homogeneous (a) and brittle-cracked (b) film

Table 1 summarizes the visual observation of films. It was found that both glycerol and sorbitol are compatible with SPS matrix. For glycerol-plasticized film, it was visible that all developed formulas were able to form films with suitable characteristics. However, sorbitol-plasticized films gave different results. It was showed that to produce intact film at 10% starch or above, higher concentration of sorbitol was needed. Since some films were brittle and cracked, it was not possible to analyze other properties. Overall, sorbitol-plasticized film had dry appearance. On the other hand, at higher concentration of glycerol, film would become sticky and hard to handle. Therefore each type of plasticizer has optimum concentration to produce film with expected properties.

**Table 1. Appearance of films**

| Starch Concentration (%w/v) | Glycerol | Plasticizer (%w/w) |
|-----------------------------|----------|--------------------|
| 9*                          | a        | a                  |
| 10                          | a        | a                  |
| 11                          | a        | a                  |

*Homogeneous, translucent with smooth surface, no tear after peeled, visually looked wet

*Homogeneous, translucent with smooth surface, no tear after peeled, visually looked dry

Brittle and cracked

*Data of film formula with 9% (w/v) starch were already presented in International Symposium on Frontier of Applied Physics (ISFAP 2015) held on October 5-7th, 2015 in Indonesia.

3.2. Thickness and Retraction Ratio

The thickness and retraction ratio of film are presented in Table 2. The thickness of glycerol and sorbitol-plasticized films varied from 0.129 to 0.170 mm and from 0.113 to 0.160 mm, respectively. There was
an increasing tendency of film thickness as plasticizer concentration increased for all starch concentrations because higher starch and plasticizer concentration would increase the total soluble matter of solution so that it increase film thickness. Furthermore, the thickness of film also affected by retraction phenomenon that occurs in film casting technique. This phenomenon was related to the concentration of dry matter of film and shrinkage during drying period [5]. The retraction ratio of glycerol- and sorbitol-plasticized film varied from 91.45 to 93.55% and from 92.00 to 94.35%, respectively. At the same starch and plasticizer concentration, retraction ratio of sorbitol-plasticized films was slightly higher than that of glycerol-plasticized film. Meanwhile, it was found that the retraction ratio decreased as the plasticizer content increased.

Table 2. Comparison of film thickness, retraction ratio and moisture content of SPS film

| Starch concentration (% w/v) | Plasticizer type | Plasticizer concentration (% w/w starch) | Thickness of film (mm) | Retraction ratio (%) | Moisture content (%) |
|------------------------------|------------------|------------------------------------------|------------------------|----------------------|---------------------|
| 9*                           | Glycerol         | 35                                       | 0.129                  | 93.55                | 21.32               |
|                              |                  | 40                                       | 0.136                  | 93.20                | 26.59               |
|                              |                  | 45                                       | 0.141                  | 92.95                | 33.34               |
|                              | Sorbitol         | 35                                       | 0.113                  | 94.35                | 8.74                |
|                              |                  | 40                                       | 0.125                  | 93.75                | 8.30                |
|                              |                  | 45                                       | 0.134                  | 93.30                | 8.13                |
| 10                           | Glycerol         | 35                                       | 0.150                  | 92.50                | 18.46               |
|                              |                  | 40                                       | 0.156                  | 92.20                | 23.61               |
|                              |                  | 45                                       | 0.171                  | 91.45                | 29.33               |
|                              | Sorbitol         | 35                                       | NA                     | NA                   | NA                  |
|                              |                  | 40                                       | 0.140                  | 93.00                | 9.56                |
|                              |                  | 45                                       | 0.152                  | 92.40                | 10.10               |
| 11                           | Glycerol         | 35                                       | 0.152                  | 92.40                | 21.35               |
|                              |                  | 40                                       | 0.166                  | 91.70                | 24.82               |
|                              |                  | 45                                       | 0.170                  | 91.50                | 30.52               |
|                              | Sorbitol         | 35                                       | NA                     | NA                   | NA                  |
|                              |                  | 40                                       | NA                     | NA                   | NA                  |
|                              |                  | 45                                       | 0.160                  | 92.00                | 10.20               |

NA : not available
*Data of film formula with 9% (w/v) starch were already presented in International Symposium on Frontier of Applied Physics (ISFAP 2015) held on October 5-7th, 2015 in Indonesia.

3.3. Moisture Content

Table 2 summarizes the average value of moisture content of the films. Moisture content of films was affected by type of plasticizer. Glycerol-plasticized films had higher moisture content than sorbitol-plasticized films because glycerol is hygroscopic material and can behave as water holding agent. Therefore, moisture content of glycerol-plasticized films would increase as glycerol content increase. On the contrary, sorbitol affected plasticized film differently. Sorbitol-plasticized films had low moisture content, even in film with 9 % of starch concentration there is slightly decreasing tendency as sorbitol
concentration increase. Both glycerol (molecular weight 92.09 g/mol) and sorbitol (182.17 g/mol) are polyols which have a similar straight-chain molecule and own molecular structure of glucose. Sorbitol contains more hydroxyl group than glycerol, so its chance to react with starch chain is higher than glycerol. As a result, sorbitol offers higher intermolecular forces with starch molecule thus only fewer hydroxyl groups which are available to interact with water molecules. Hence, sorbitol-plasticized films have lower moisture content than glycerol-plasticized films. This result is in line with the previous study by Godbillot et al., (2006) [21] that film composition affects its moisture content. Meanwhile, by visual observations, there were no differences in opacity among the films. Since in this work the films were only produced of only SPS, this results is in line with the previous study by Fakhouri et al., (2007) [22] that film opacity was affected by amylose content of the starches.

3.4. Swelling Degree and Swelling Thickness
The visual appearances of original and swelled film were shown in Figure 2. The results showed that swelled film had opaque appearances and the original film had transparent appearances.

![Visual appearances of original (a) and swelled (b) film](image)

**Figure 2.** Visual appearances of original (a) and swelled (b) film

The average value of swelling degree and swelling thickness of the films is presented in Table 3. The results showed that absorption of water was fast at an early stage of immersion and slowly decreased as time increased. Swelling degree and swelling thickness were affected by starch and its interaction in the film matrix. Starch with high amylopectin and low amylose content will produce films with a high swelling degree [23]. Various molecule interaction occurred in film matrix, *i.e.* starch-starch, starch-plasticizer, and plasticizer-plasticizer. As swelling degree affected by the interaction of starch molecule with water molecule, film with less interaction involving starch molecule with others will have high swelling degree. The previous study by Poeloengasih et al., (2016) [16] showed that unplasticized SPS
A film possessed the highest swelling degree compared to other plasticized SPS films. As higher plasticizer content in starch films causes fewer free starch molecules to interact with water, it produces films with lower swelling degrees. Since films with higher swelling degrees absorb more water, there is a higher change in film dimensions, which is shown as a change in film thickness. As swelling degree of the film increases, the swelling thickness also increases. Meanwhile, glycerol-plasticized film had a higher swelling degree and swelling thickness than sorbitol ones because in glycerol-plasticized film, there is less starch molecule that interacts with plasticizer than in sorbitol plasticized film.

### Table 3. Comparison of swelling degree and swelling thickness of SPS film

| Starch concentration (%) w/v | Plasticizer type | Plasticizer concentration (%) w/w starch | Swelling degree (%) 30 min | Swelling degree (%) 60 min | Swelling thickness (%) |
|-----------------------------|-------------------|-------------------------------------------|-----------------------------|------------------------------|------------------------|
|                             |                   |                                           |                             |                              |
| 9*                          | Glycerol          | 35                                        | 130.03                      | 135.87                       | 97.04                  |
|                             |                   | 40                                        | 104.97                      | 109.31                       | 81.33                  |
|                             |                   | 45                                        | 80.70                       | 81.81                        | 69.23                  |
|                             | Sorbitol          | 35                                        | 101.53                      | 105.20                       | 93.61                  |
|                             |                   | 40                                        | 93.95                       | 98.47                        | 86.17                  |
|                             |                   | 45                                        | 88.74                       | 90.97                        | 82.42                  |
| 10                          | Glycerol          | 35                                        | 112.40                      | 119.25                       | 80.03                  |
|                             |                   | 40                                        | 92.58                       | 95.92                        | 63.27                  |
|                             |                   | 45                                        | 70.91                       | 73.28                        | 54.71                  |
|                             | Sorbitol          | 35                                        | NA                          | NA                           | NA                     |
|                             |                   | 40                                        | 93.67                       | 96.77                        | 93.34                  |
|                             |                   | 45                                        | 86.00                       | 89.41                        | 83.46                  |
| 11                          | Glycerol          | 35                                        | 114.67                      | 118.85                       | 97.91                  |
|                             |                   | 40                                        | 94.37                       | 96.73                        | 82.82                  |
|                             |                   | 45                                        | 76.22                       | 78.35                        | 62.35                  |
|                             | Sorbitol          | 35                                        | NA                          | NA                           | NA                     |
|                             |                   | 40                                        | NA                          | NA                           | NA                     |
|                             |                   | 45                                        | 89.26                       | 91.06                        | 97.24                  |

**NA**: not available

*Data of film formula with 9% (w/v) starch were already presented in International Symposium on Frontier of Applied Physics (ISFAP 2015) held on October 5-7th, 2015 in Indonesia.

### 3.5. Solubility in Water

Figure 3a and 3b illustrate the variation in solubility of films for glycerol- and sorbitol-plasticized film respectively (data of film formula with 9% (w/v) starch were already presented in International Symposium on Frontier of Applied Physics held on October 5-7th, 2015 in Indonesia). As the concentration of plasticizer increased from 35 to 45%, solubility of film increased. Both plasticizers reached the highest solubility at 9% of starch and 45% of plasticizer, i.e. 28.22% for glycerol and 34.72% for sorbitol. Since film with formula of 10% starch-35% sorbitol, 11% starch-35% sorbitol, and 11% starch-40% sorbitol were brittle and cracked, the solubility data of those film were not available. This result was in line with the report by Ghasemlou et al., (2011) [24] that higher concentration of plasticizer...
can increase solubility of the film. Meanwhile, sorbitol-plasticized film showed higher solubility than glycerol-plasticized film.

![Figure 3. Solubility of glycerol- (a) and sorbitol-plasticized (b) films at different starch concentration](image)

4. Conclusion
Sugar palm starch is successfully developed as a material for the preparation of a film by combining it with plasticizer. Regardless of type, increasing of plasticizer concentration leads to the increasing of thickness and solubility in water. On the contrary, retraction ratio and swelling degree tend to decrease as plasticizer concentration increase. Meanwhile, glycerol and sorbitol affected physicochemical properties in different ways. It is found that sorbitol-plasticized film had lower moisture content and higher solubility in water than glycerol-plasticized film. In conclusion, sorbitol-plasticized film has more potency than glycerol-plasticized to be hard capsule material.

Acknowledgments
This work was funded by Indonesian Institute of Sciences through Riset Unggulan 2016 program. The authors are grateful to Deputy of Engineering Sciences–Indonesian Institute of Sciences for the support.

References
[1] Mali S et al 2005 Food Hydrocolloids 19 157-64.
[2] Zhu F and Wang S 2014 Trends Food Sci.Tech. 36 68-78.
[3] Bae H J et al 2008 Food Chem. 106 96-105.
[4] Fama L et al. 2007 Carbohyd. Polym. 70 265-73.
[5] The D P et al. 2009 J. Food Eng. 90 548-58.
[6] Pelissari F M et al 2013 Food Hydrocolloids 30 681-90.
[7] Bertuzzi M A et al 2007 J. Food Eng. 82 17-25.
[8] Abdorreza M N et al 2011 Food Hydrocolloids 25 55-60.
[9] Singhal R S et al 2008 Carbohyd. Polym. 72 1-20.
[10] Fakharian M H et al 2015 Carbohyd. Polym. 132 156-63.
[11] Poeloengasih C D and Anggraeni F D 2014 Starch/Starke 66 1103-8.
[12] Sanyang M L et al 2015 Polymers 7 1106-24.
[13] Sahari J et al 2013 Carbohyd. Polym. 92 1711-6.
[14] Sahari J et al 2014 Asian J. Chem. 26 955-9.
[15] Sahari J et al 2012 Procedia Chem. 4 254-9.
[16] Poeloengasih C D et al 2016 AIP Conf. Proc. 1711 080003.
[17] Jatmiko T H et al 2016 AIP Conf. Proc. 1711 080004.
[18] Apriyana W et al 2016 AIP Conf. Proc. 1755 150003.
[19] Adawiyah D R et al 2013 Carbohyd. Polym. 92 2306-13.
[20] Shih F F 1996 Cereal Chem. 73 406-9.
[21] Godbillot L et al 2006 Food Chem. 96 380-6.
[22] Fakhouri FM et al 2007 Cien. Tecnol. Aliment. 27 369-75.
[23] Chen C H, Kuo W S and Lai L S 2009 Food Hydrocolloids 23 2132-40.
[24] Ghasemlou M et al 2011 Carbohyd. Polym. 84 477-83.