

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 ($\leq 10\%$) than that of glycerol-plasticized film ($\geq 18\%$). 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 focus 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 ($\text{Mg}(\text{NO}_3)_2$) 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 (t_0) 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).

$$\textbf{Retraction ratio}(\%) = \frac{t_0 - t}{t_0} \times 100\% \quad (1)$$

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:

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

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:

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

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

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:

$$\textbf{Solubility}(\%) = \frac{w_0 - w}{w_0} \times 100\% \quad (5)$$

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.

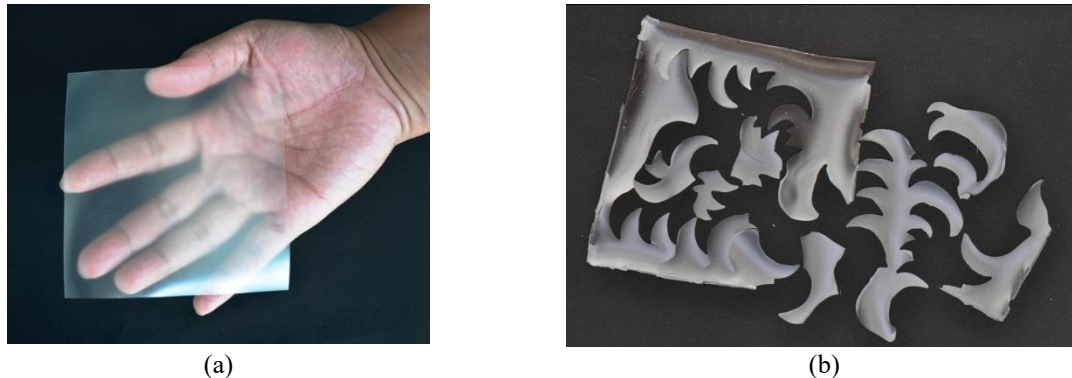


Figure 1. Visual appearances of homogeneous (a) and brittle-cracked (b) film

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)	Plasticizer (%w/w)					
	35	Glycerol 40	45	35	Sorbitol 40	45
9*	a	a	a	b	b	b
10	a	a	a	c	b	b
11	a	a	a	c	c	b

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

^bHomogeneous, translucent with smooth surface, no tear after peeled, visually looked dry

^cBrittle 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
	Glycerol	35	0.150	92.50	18.46
		40	0.156	92.20	23.61
		45	0.171	91.45	29.33
10	Sorbitol	35	NA	NA	NA
		40	0.140	93.00	9.56
		45	0.152	92.40	10.10
	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.

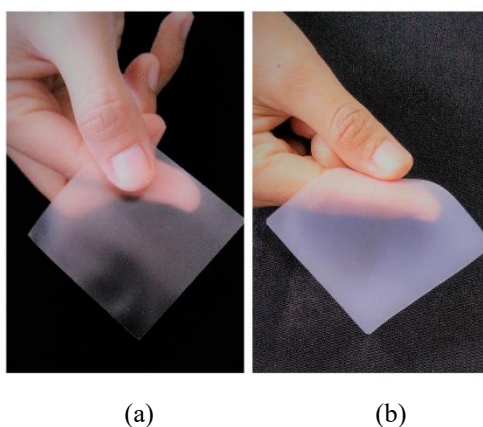


Figure 2. Visual appearances of original (a) and swelled (b) film

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

film possessed highest swelling degree compare to other plasticized SPS films. As higher plasticizer content in starch film cause lesser free starch molecules interact with water so it would produce film with lower swelling degree. Since film with higher swelling degree absorbed more water, there is a higher change in film dimension which was shown as a change of film thickness. As swelling degree of film was increased, the swelling thickness also increased. Meanwhile, glycerol-plasticized film had 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 (%)		Swelling thickness (%)
			30 min	60 min	
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.

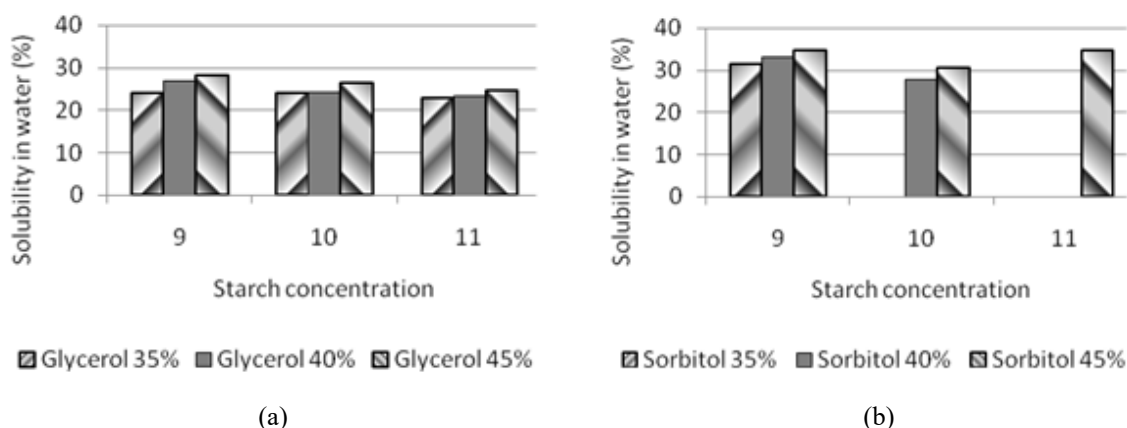


Figure 3. Solubility of glycerol- (a) and sorbitol-plasticized (b) films at different starch concentration

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 *Carbohydr. 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 *Carbohydr. Polym.* **72** 1-20.
- [10] Fakharian M H *et al* 2015 *Carbohydr. 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 *Carbohydr. 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 *Carbohydr. 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 *Cienc. 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 *Carbohydr. Polym.* **84** 477-83.