*As. J. Food Ag-Ind.* **2012**, 5(03), 183-192

OPEN ACCESS

*Asian Journal of Food and Agro-Industry*
**ISSN 1906-3040**
Available online at www.ajofai.info

*Research Article*

# Properties of biodegradable films from hydroxypropyl sago starches

**Febby J. Polnaya[1,*], Josefina Talahatu[1], Haryadi[2] and Djagal W. Marseno[2]**

[1]Faculty of Agriculture, Pattimura University, Jl. Ir. M. Putuhena, Kampus Poka- Ambon 97233, Indonesia.

[2]Faculty of Agricultural Technology, Gadjah Mada University, Jl. Flora, No. 1, Bulaksumur, Yogyakarta 55281, Indonesia.

*Email: febbypolnaya@yahoo.com

This paper was originally presented at the 10th International Sago Symposium, Bogor, Indonesia, October 29-30, 2011.

## Abstract

One of each of *tuni*, *molat* and *ihur* sago starch was hydroxypropylated with propylene oxide. The resulting hydroxypropyl sago starches (HPSS) with a molar substitution (MS) of 0.03 and 0.08 were used for biodegradable film preparation. Biodegradable films were prepared from the solutions containing different amounts of starch (3, 4 and 5%, w/v) by heating at 70°C for 30 min and glycerol (0.5%, w/v) was used as plasticizer. The films were characterized for film tensile strength, elongation, solubility, water vapour transmission rate (WVTR) and oxygen permeability (OP). The increase in the starch concentration resulted in an increase in film tensile strength, but the elongation, solubility, WVTR and OP decreased. The films made from HPSS showed higher elongation, solubility, OP and lower WVTR compared to that from the native starches. The films made from HPSS with a MS of 0.08 showed lower thickness, tensile strength, WVTR, but HPSS with a MS of 0.03 showed lower solubility and OP.
**Keywords:** HPSS, *Metroxylon* sp., thickness, tensile strength, water vapour transmission rate, oxygen permeability, Indonesia.

## Introduction

Development of alternative edible and/or biodegradable packaging material to partially or totally replace petroleum based synthetic polymers may offer opportunities that would benefit both manufacturers and consumers. Various natural biodegradable polymers can potentially serve as coating materials for environmental friendly packaging. According to Demšar et al. [1], polymer degradation is an irreversible chemical reaction which leads to cleavage of chemical bonds, decomposition of polymer matter, reduction of molecular mass, change in functional groups of polymer and originating of low molecular decomposition products. Biodegradable films or coatings have been proved their functional properties as barrier to solute and gas and prolong food quality and shelf life.

Biodegradable polymers based on natural polysaccharides, particularly starch, are used to develop biodegradable films because they have the capability of forming a continuous matrix and they are a renewable and abundant resource [1]. As polysaccharides themselves do not have plasticity, they are often used after chemical modification and/or as a blend with a biodegradable synthetic polymer [2, 3]. There are some studies in the literature showing native starches like cassava starch [4, 5], yam starch [6, 7] and sago starch [8] can be used for obtaining biodegradable films.

Sago palm, the common name of *Metroxylon* sp., is one of the most important economic plants, mainly because it has the highest yielding starch in terms of its calorific yield per hectare. It is grown in several humid tropical countries, such as Indonesia, Malaysia and Thailand [9]. Sago starch, unlike the other starches, is derived from the pith of numerous kinds of palm trees. Sago palms has been classified into three different types, i.e. *M. rumphii* Mart. (Indonesian name: *Tuni*), *M. sylvestre* Mart. (Indonesian name: *Ihur*) and *M. sagu* Rottb. (Indonesian name: *Molat*) [10]. Tropical Asia is home to most of the 2,500,000 ha of sago palm cultivatedworld-wide and it is an important source of dietary fibre and the main carbohydrate source [11]. The rapidly increasing awareness of the importance of sago palm has brought about a considerable amount of research on sago starch and comprehensive reviews on sago starch have been written [12]. However, sago starch is an interesting alternative substrate for biodegradable film production. The sago starch has a low cost of production and high yield, when compared to other kinds of starch.

There is a good correlation between amylose content and film forming ability of starch solutions. Starches with high amylose content (approximately 30% amylose) have excellent film forming properties compared to starches with low amylose content [7, 13]. Based on this, sago starch can be used as a raw material in the manufacture of biodegradable films, because the concentration of sago starch amylose is high enough. According to Polnaya *et al*. [14, 15], amylose content of sago starch was 27% and 35%, respectively, which is assumed to be used as the basis for good biodegradable films.

Starch and starch derivative films have been widely studied due to the film forming properties, high oxygen barrier and good mechanical strength [6, 16] but have a low solubility [17] and the resulting film is brittle [7, 17]. Modified starch was used to improve the properties of film, for example, a blend of gelatin/hydroxypropyl starch/plasticizer [18] and acetylated cassava starch [5].

The objective of this study was to manufacture native sago starch (NSS) and hydroxypropyl sago starch (HPSS) based biodegradable films and to investigate the effect of polymer concentration and MS rate on the film properties.

## Materials and Methods

### *Materials*

NSS (approximately 35% amylose) and HPSS (MS 0.03 and 0.08) were obtained from previous studies [15]. Glycerol was used as plasticizer and HCl were purchased from Merck, $O_2$ and $N_2$ were purchased from local distributors, and all chemicals used were analytical grade.

### *Biodegradable film preparation*

Biodegradable films were prepared from NSS and HPSS using a method described by Parra *et al*. [4]. The film solutions were prepared from sago starch (3, 4 and 5% starch, w/v) with the addition of glycerol (0.5%, w/v). The solutions were prepared by addition of starch in a beaker with distilled

water (80 ml) at ambient temperature and stirred for 5 minutes. After that, the solutions were kept at 70°C for 15 min in a controlled temperature water bath. Then glycerol was added and the solutions were made up to 100 ml and the heating step repeated. Then the sample was cast onto polyacrylic plates (22 × 17 cm). The cast films were dried at 40°C for 24 h in an oven. The dry films obtained were peeled off and stored in desiccator at 25°C for futher analysis.

***Mechanical test***

The film thickness was measured with a hand-held micrometer (Coolant Proof Micrometer IP-65 MITUTOYO Corp., JP) having a sensitivity of 0.001 mm. The thickness was measured at various locations (at least five) of the film and then an average value was calculated.

Tensile strength and elongation of each film were measured according to ASTM-D D412-98a [19] using a Mechanical Universal Testing Machine Swick Z0.5, a velocity of 1.0 mm $s^{-1}$, with the distance between clamps was 50 mm. Test samples were cut in dumb-bell Die I dimensions (Dumb Bell Ltd. Saitana, Japan) according to the ASTM standard method. The results are the average of five samples.

***Water vapour transmition rate***

Three film specimens were tested for each type of film. WVTR ($g/m^2$ h) was determined gravimetrically using a modification of ASTM Method E 96-95 [20] described by Gennadios *et al*. [21]. Film specimens were mounted on polymethylmethacrylate cups contaning 20 ml of silica gel. The cups were placed in an environmental chamber at 25°C and 75% RH (40% NaCl, w/v). The weights of the cups were recorded every hour for a total of 8 h. Linear regression was used to estimate the slope of this line in g/h. Water vapour transmission rate is determined by the equation:

WVTR = Slope of the mass of the test cup vs. time (g/h) / Film surface area ($m^2$).

***Film solubility***

The film solubility was determined according to Gontard *et al*. [22]. Solubility was tested as follows: the sample was cut into strips of 2 × 2 cm. Sample with filter paper is dried at a temperature of 105°C for 24 h. The filter paper and samples were weighed to determine the weight of the sample as the initial weight ($W_1$). Insert the sample into a 50 ml of 0.02% sodium azide solution. Addition of sodium azide is intended to prevent the growth of microorganisms. Soaking was conducted over 24 h, slowly stirring periodically. An insoluble film with filter paper of each sample was dried in an oven at 105°C to constant weight ($W_2$).

$$\% \text{ Solubility} = ((W_1 - W_2) / W_1) \times 100\%$$

***Oxygen permeability***

Oxygen permeability (OP) was determined according to Ayranci and Tunc [23]. The film was sealed between two specially designed glass cups, each having a diameter of 4 cm and a depth of 5 cm. Both cups have two channels. Oxygen enters to the cup on one side of the film from one channel and leaves from the other with a controlled flow rate to keep the oxygen pressure constant in that compartment. The cup on the other side of the film was purged by a stream of nitrogen entering from one channel and leaving from the other. This nitrogen acted as a carrier for oxygen permeated from the other side of the film to the wet analysis system. Up to the wet analysis system, the design was mainly based on the ASTM standard [19]. A modification was made to the $O_2$ analysis and a classical wet analysis, based on the well-known method of iodimetry was applied for

the determination of the amount of permeated $O_2$. The stoichiometry indicated that 1 mol of dissolved oxygen required 4 mol of thiosulphate. The OP of the film was then calculated by equation:

$$OP = (m \times d) / (A \times t \times \Delta P)$$

where $m$ is the mass of $O_2$ permeated through the film with a thickness of $d$ and an area of $A$ over the measured time interval $t$. $\Delta P$ is the difference in $O_2$ pressure between the two sides of the film. The OP of the films was determined according to the method described above at 25 ± 1°C. Both $O_2$ and $N_2$ gases were dried by passing through a gas drying column containing anhydrous calcium chloride before entering the system.

***Statistical analyses***

The data obtained from the study were analyzed using analysis of variance at a 95% confidence level and comparisons significant for all treatments used Tukey test. SAS 9.0 software (SAS Inc.) was used to analyze the data.

## Results and Discussion

***Mechanical properties***

The tensile strength (0.09-21.34 MPa) and elongation (0.07-1.32%) of sago starch films are given in Figures 1 and 2, respectively.

At concentration starch 5%, NSS-*ihur* film showed the highest tensile strength but lowest elongation. The increased starch concentration in the film forming solution caused an increase of tensile strength but a decrease of elongation. This may be because the increase of the amylose concentration in the solutions causes an increase in the number of hydrogen bonds so that it forms rigid film. The number of hydroxyl groups increased with increasing starch ratio in the film-forming solution [24] and eventually can produce a rigid film.

The tensile strength and elongation of HPSS film were significantly lower and higher, respectively, than that of NSS film due to substitution of the hydroxypropyl group. The same results are also shown by Polnaya *et al*. [8] for hydroxypropyl-acetyl sago starches. NSS with strong gel strength will form a rigid biodegradable film than that film produced by modified sago starch which is more flexible. Wattanachant *et al*. [25] suggest that sago starch exhibits long cohesive gels with very high gel strengths; however this undesirable property could be counteracted by hydroxypropylation. HPSS film with MS 0.03 is significantly lower than that of HPPS film with MS 0.08.

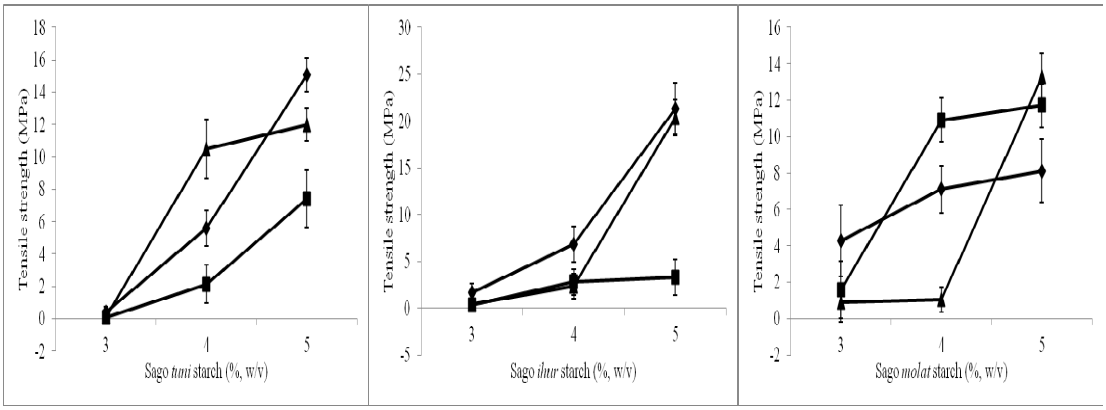


**Figure 1**. **Tensile strength of sago starch biodegradable films by weight of starch (3, 4 and 5%, w/v) and types of sago starch.**

native (♦), hydroxyproyl MS = 0.03 (■) and hydroxyproyl MS = 0.08 (▲).
Error bars indicate standard deviation (r = 3).

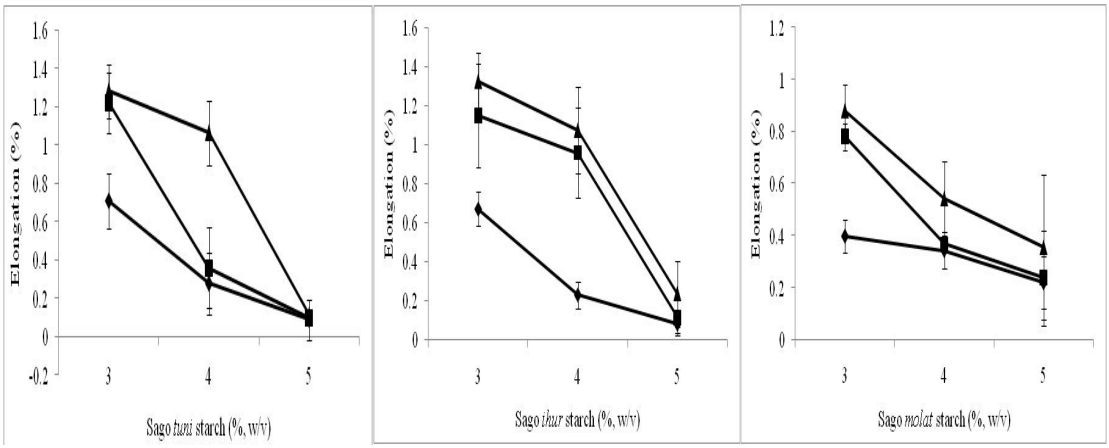


**Figure 2**. **Elongation of sago starch biodegradable films by weight of starch (3, 4 and 5%, w/v) and types of sago starch.**

native (♦), hydroxyproyl MS = 0.03 (■) and hydroxyproyl MS = 0.08 (▲).
Error bars indicate standard deviation (r = 3).

***Water vapour transmission rate***

The WVTR of sago starch films (0.07-1.32 g $H_2O/m^2$ h) are given in Figure 3. At concentration starch level 5%, HPSS-*tuni* film showed the lowest WVTR. At the same starch concentration (3%), the WVTR of HPSS-*tuni* film (MS 0.08) was significantly lower than that of NSS film while the other treatments were not significantly different. The substitution of hydroxypropyl groups produces tissue structure that can withstand moisture diffusion through the film. As a consequence, it decreases the WVTR. Xu *et al.* [24] reported that an increase in the chitosan-starch ratio caused a significant decrease in WVTR.

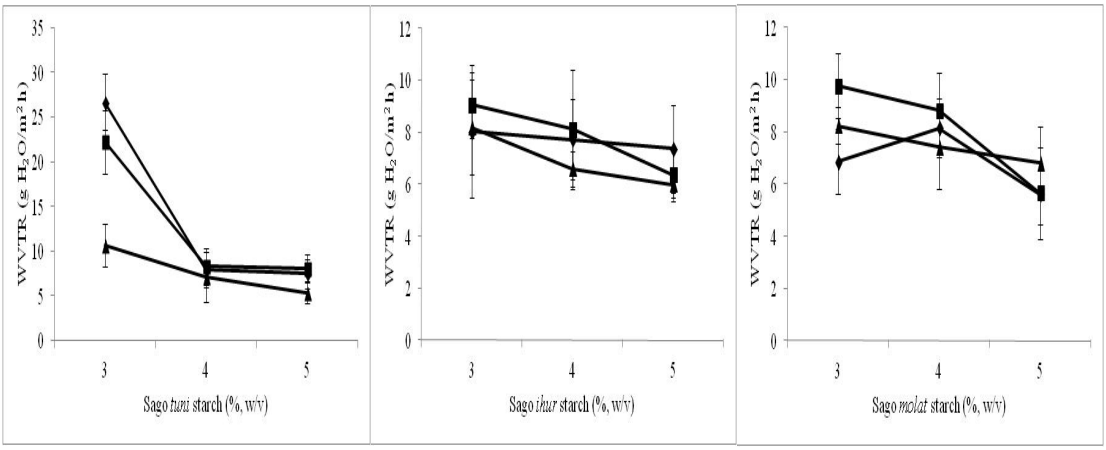


**Figure 3. WVTR of sago starch biodegradable film by weight of starch (3, 4 and 5%, w/v) and type of sago starch.**

native (♦), hydroxyproyl sago starch MS = 0.03 (■) and hydroxyproyl sago starch MS = 0.08 (▲).
Error bars indicate standard deviation (r = 3).

The WVTR of biodegradable film gets lower along with the increase of the film concentration, either on NSS or HPSS. The decrease WVTR of biodegradable film is caused by the increase of dissolved solids in the film solution and the increase of amylose molecule concentration which form stonger hydrogen bonds, so that it produces compact structure. This can be seen from the NSS with a concentration of 5%, which has approximately lower WVTR values, compared to all the other treatments. HPPS film with MS 0.08 had lower WVTR than that of HPPS film with MS 0.03. HPPS film from *molat* sago starch had lower WVTR than that prepared from *tuni* and *ihur* sago starches.

***Solubility***

The solubility of sago starch films are shown in Figure 4. The solubility of HPSS biodegradable films (32.39-92.55%) was higher than that of NSS (20.18-68.97%). This is related to the characteristics of HPSS (MS 0.058) which has higher solubility compared to those of the other treatments [15], so that the use of modified sago starch as the basic material of biodegradable film will produce films with higher solubility than the NSS film. According to Kester and Fennema [26], etherification of starch with propylene oxide increases solubility in water, since the films that result from hydroxypropyl starches are not water vapour resistant.

NSS-*ihur* shows higher solubility than that of NSS-*molat* to *tuni* for three levels of starch concentration. Increase in the sago starch concentration decreases the film solubility. The similar result was also suggested by Polnaya *et al*. [8]. This was because of the consequence of the increase of hydrogen bond along with the decrease of amylose concentration in the solution. HPSS film (MS 0.08) had higher solubility than those resulting from any other starches used in this experiment. HPSS film from *ihur* sago starch had higher solubility than that of *tuni* and *molat* sago starches.

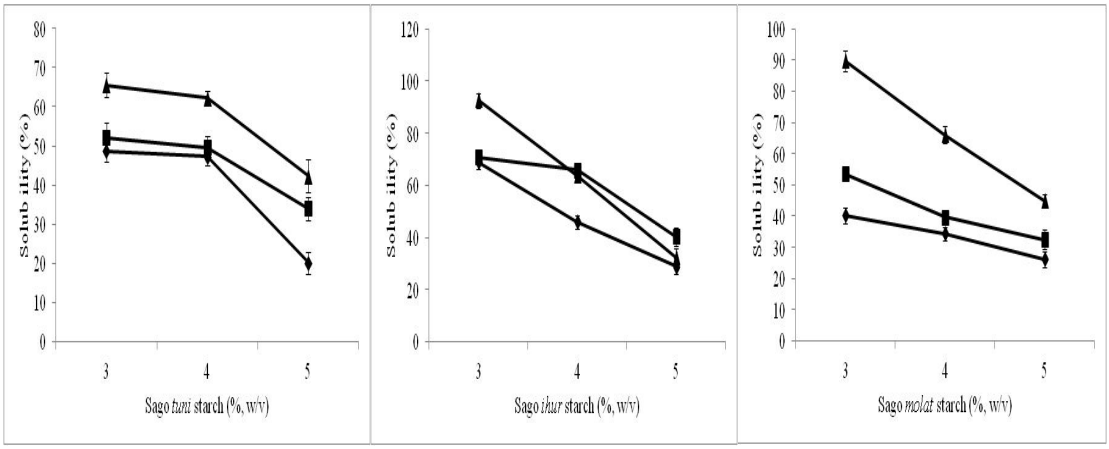


**Figure 4. Solubility of sago starch biodegradable film by weight of starch (3, 4 and 5%, w/v) and types of sago starch.**

native (♦), hydroxypropyl MS = 0.03 (■) and hydroxypropyl MS = 0.08 (▲).
Error bars indicate standard deviation (r = 3).

***Oxygen permeability***

Oxygen is one of the factors causing oxidation. It is indicated by the changes seen in most food products, such as odor, colour, flavour and lowering of nutritional value. Film with good barrier characteristics can defend the food product quality and extend shelf life. Generally, film from hydrophilic biopolymers shows good barrier properties toward oxygen [27].

The OP of sago starch films are given in Figure 5. The OP of HPSS film (0.44-1.67 × $10^9$ g/d Pa m) was significantly lower than NSS film (0.52-1.82 × $10^9$ g / d Pa m). Figure 5 shows that increasing starch concentration treatment significantly decreases OP by increasing the solid content and producing a smaller pore size. Sothornvit and Pitak [27] showed that an increase in banana flour content should tranlate in an increase in polysaccharide content (starch) which should theoretically translate in a reduction in OP.

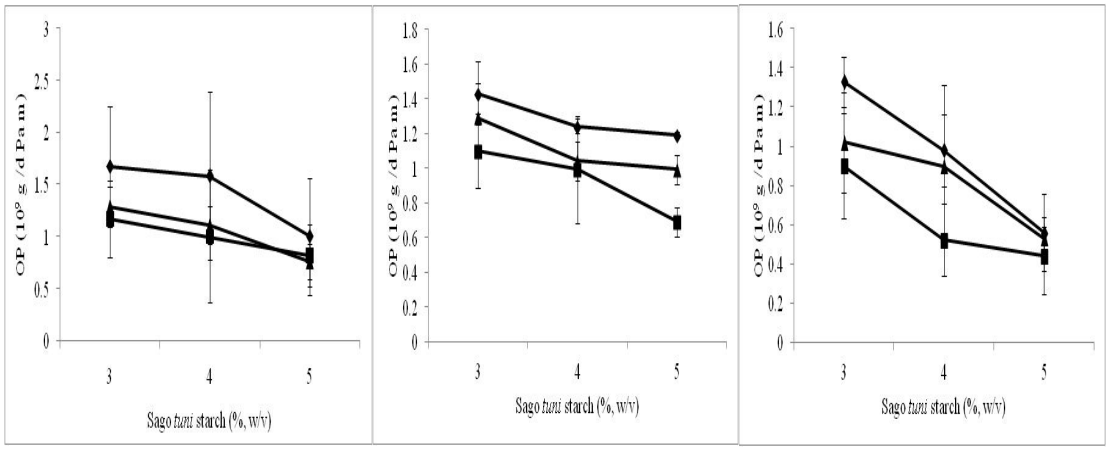


**Figure 5. Oxygen permeability of sago starch biodegradable film by weight of starch (3, 4 and 5%, w/v) and types of sago starch.**

native (♦), hydroxypropyl MS = 0.03 (■) and hydroxypropyl MS = 0.08 (▲).
Error bars indicate standard deviation (r = 2).

HPSS film has lower OP than NSS film. The film made from HPPS with MS 0.03 had lower OP than that from HPPS film with MS 0.08. HPPS film from *molat* sago starch had lower OP than that from sago *tuni* or *ihur* starches.

## Conclusion

Biodegradable film manufactured from HPSS had different mechanical properties compared to that from NSS, in terms of the film tensile strength, elongation, solubility, WVTR and OP. Increase in the sago starch concentration increased the tensile strength, but decreased elongation, solubility, WVTR and OP. HPSS with different MS gave the different characteristics of biodegradable film. The films made from HPSS with MS 0.08 showed the lower tensile strength and WVTR but HPSS with MS 0.03 showed the lower solubility and OP. The change of the mechanical properties was particularly caused by the substitution of the hydroxyl groups with hydroxypropyl groups which affected the biodegradable film characteristics.

## Acknowledgments

The authors gratefully acknowledge the financial support for this project provided by the grant PEKERTI by The General Director for Higher Education (2008) and Faculty of Agricultural Technology, Gadjah Mada University as institutional research partners.

## References

1. Demšar, A., Žnidarčič, D. and Gregor-Svetec, D. (2011). Impact of UV radiation on the physical properties of polypropylene floating row covers. ***African Journal of Biotechnology,*** 10, 7998-8006.

2. Ghanbarzadeh, B., Almasi, H. and Entezami, A.A. (2010). Physical properties of edible modified starch/carboxymethyl cellulose films. ***Innovative Food Science and Emerging Technologies,*** 11, 697–702.

3. Okada, M. (2002). Chemical syntheses of biodegradable polymer. ***Progress in Polymer Science,*** 27, 87–133.

4. Parra, D.F., Tadini, C.C., Ponce, P. and Lugalo, A.B. (2004). Mechanical properties and water vapor transmission in some blends of cassava starch edible films. ***Carbohydrate Polymers,*** 58, 475–481.

5. Larotonda, F.D.S., Matsui, K.N., Soldi, V. and Laurindo, J.B. (2004). Biodegradable film made from raw and acetylated cassava starch. ***Brazilian Archives of Biology and Technology,*** 47, 477–484.

6. Mali, S., Grossmann, M.V.E., García, M.A., Martino, M.N. and Zaritzky, N.E. (2002). Microstructural characterization of yam starch films. ***Carbohydrate Polymers,*** 50, 379–386.

7. Mali, S., Grossmann, M.V.E., García, M.A., Martino, M.N. and Zaritzky, N.E. (2005). Mechanical and thermal properties of yam starch films. ***Food Hydrocolloids,*** 19, 157–164.

8. Polnaya, F.J., Haryadi, Marseno, D.W. (2006). Karakterisasi *edible film* pati sagu alami dan termodifikasi. ***Agritech,*** 26: 179–185 (in Indonesian).

9. Lim, E.T., Ahmad, B., Tie, Y.L., Hueh, H.S. and Jong, F.C. (1991). Utilization of tropical peats for the cultivation of sago (*Metroxylon spp*.). Paper presented at the International Symposium on Tropical Peat Land, Kuching, 12–18.

10. Flach, M. (1997). Sago Palm, *Metroxylon sagu* Rottb. Promoting the conservation and use of underutilized and neglected crops. 13. Institute of Plant Genetics and Crop Plant Research, Gatersleben/International Plant Genetic Resources Institute, Rome, Italy. pp. 8–11.

11. Oates, C.G. and Hicks, A. (2002). Sago starch production in Asia and the Pacific-problems and prospects. In: Proceedings of the International Symposium on Sago (Sago 2001) held on October 15–17 2001, at the Tsukuba International Congress Center Japan. Universal Academy Press Inc., Tokyo, pp. 27–36.

12. Karim, A.A., Tie, A.P.-L., Manan, D.M.A. and Zaidul, I.S.M. (2008). Starch from the sago (*Metroxylon sagu*) palm tree-properties, prospects and challenges as a new industrial source for food and other uses. ***Comprehensive Reviews in Food Science and Food Safety,*** 7, 215–228.

13. Bae, H.J., Cha, D.S., Whiteside, W.S. and Park, H.J. (2008). Film and pharmaceutical hard capsule formation properties of mungbean, waterchestnut and sweet potato starches. ***Food Chemistry,*** 106, 96–105.

14. Polnaya, F.J., Haryadi and Marseno, D.W. (2008). Characteristics of hydroxypropylated and acetylated sago starches. ***Sago Palm,*** 16, 85–94.

15. Polnaya, F.J., Talahatu, J., Haryadi and Marseno, D.W. (2009). Karakterisasi tiga jenis pati sagu (*Metroxylon* sp.) hidroksipropil. ***Agritech,*** 29, 87–95 (in Indonesian).

16. Forssell, P., Lahtinen, R., Lahelin, M. and Myllärinen, P. (2002). Oxygen permeability of amylose and amylopectin films. ***Carbohydrate Polymers,*** 47, 125–129.

17. Wu, Q.X. and Zhang, L.N. (2001). Structure and properties of casting films blended with starch and waterborne polyurethane. ***Journal of Applied Polymer Science,*** 79, 2006–2013.

18. Arvanitoyannis, I., Nakayama, A. and Aiba, S. (1998). Edible films made from hydroxypropyl starch and gelatin and plasticized by polyols and water. ***Carbohydrate Polymers,*** 36, 105–119.

19. ASTM D412-98a. (1998). Standard Test Methods for vulcanized rubber and thermoplastic elastomers-tension Annual book of ASTM standards. Designation, D412-98a. Philadelphia: ASTM pp. 43–55.

20. ASTM. (1995). Standard test methods for water vapor transmission of materials. In: Annual Book of ASTM Standards, vol. 4.06. American Society for Testing and Materials, West Conshohocken, PA, pp. 697–704.

21. Gennadios, A., Weller, C.L. and Gooding, C.H. (1994). Measurement errors in water vapor permeability of highly permeable, hydrophilic edible films. ***Journal of Food Engineering,*** 21: 395–409.

22. Gontard, N., Guilbert, S. and Cuq, J.L. (1992). Edible wheat gluten film: Influence of the main process variabels on film properties of an edible wheat gluten film. ***Journal of Food Science,*** 58, 206–211.

23. Ayranci, E. and Tunc, S. (2003). A method for the measurement of the oxygen permeability and the development of edible films to reduce the rate of oxidative reactions in fresh foods. ***Food Chemistry,*** 80, 423–431.

24. Xu, Y.X., Kim, K.M., Hanna, M.A. and Nag, D. (2005). Chitosan-starch composite film: Preparation and characterization. ***Industrial Crops and Products,*** 21, 185–192.

25. Wattanachant, S., Muhammad, S.K.S., Hashim, D.M. and Rahman R. Abd. (2003). Effect of crosslinking reagent and hydroxypropylation levels on dual-modified sago starch properties. ***Food Chemistry,*** 80, 463–471.

26. Kester, J.J. and Fennema, O.R. (1986). Edible films and coatings: A Review. ***Food Technology,*** 12, 47–59.

27. Sothornvit, R. and Pitak, N. (2007). Oxygen permeability and mechanical properties of banana film. ***Food Research International,*** 40, 365–370.