Sago Starch-based Edible Film with Ascorbic Acid for active Food Packaging

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Abstract
This study aimed to analyse and evaluate the effect of the addictive of ascorbic acid(AA) on the properties of the produced sago starch-based edible film. Tests were run on the films with and without ascorbic acid to determine the mechanical strength, thickness, solubility of films, antioxidant activity and color. The higher concentration of AA in sago starch film shows the higher solubility compared to film without AA. It was also shown the decreasing in tensile strength and increasing in elongation on film. The water vapor permeability of films with the AA concentration was lowest. Besides, the concentration of AA in films affect antioxidant activity as it has higher percentage of radical scavenging activity (98.5%) meanwhile the colour of the film with AA is yellowish as the degradation of AA presence in film.

Keywords— Edible film, antioxidant, Vitamin C, solubility

I. INTRODUCTION

Production of plastic materials has demonstrated a continuous growth for more than 50 years in the world. It is estimated that the production of these materials will rise to 300 million tons[1]. Plastic is one of the major material used for food packaging and its usage leads to waste disposal problems as the traditional petroleum-derived materials are not readily biodegradable [2]. Food packaging is used to separated food from the surrounding environment, reducing exposure to spoilage factors such as microbial spoilage, oxygen, water vapour, and off-flavors, and avoiding losses of desirable compounds such as flavor volatiles, hence extends the food shelf-life [3].Thus, in this recent years, edible films have receive considerable attention because of their advantages as edible packaging materials [4]. Edible film are made from naturally renewable, biodegradable and edible polymers also used to improve the stability and quality of low moisture foods or pharmaceutical solid as they may act as a barrier layer between the material and surroundings[5].

Among natural polymers, starch is one of the most considered as one of the materials used for food packaging as its low price, and abundance[1]. There have been many studies reported on starch-based film from various type of high amylose such as corn, potato and cassava but there not much study on sago starch film[6]. Sago starch obtained from Sago Palm (*Metroxylon sagu Rottb.*) is an increasingly important socioeconomic crop in Southeast Asia. Sago starch has its own unique characteristics but some of its physiochemical properties are quite similar to common starch such as cassava and potato[6].

However, starch alone as packaging material has many limitations due to its hydrophilic nature and poor mechanical properties in term of brittleness. So, starch often modified chemically, physically, mechanically and/or combined with polymeric additives or plasticizer[7]. The functional additives like antioxidant or antimicrobial agent are usually used to obtain an active food packaging which could extend the shelf life of the food as well not only to the food but the film itself, resulting improve its safety and good quality properties of film[1].

Ascorbic acid or vitamin C is a powerful antioxidant found in fresh fruit and vegetables. Ascorbic acid acts as an oxygen scavenger and chelator of prooxidative metal ions [8]. Ascorbic acid is act as reducing agent and water-soluble antioxidant for food packaging [9]. Thus, ascorbic acid (AA) is used in this research as antioxidant agent for making active food packaging. The effect of different concentration of ascorbic acid incorporated with the sago starch-based films is analysed based on the properties sago starch film thickness, solubility, the antioxidant activity, tensile strength and color of the films.

II. MATERIAL AND METHOD

A. Raw material

Sago starch powder was purchased at Bintulu Farmer's Market, Sarawak, Malaysia, and 250g of ascorbic acid obtain from Kharoreny Enterprise, Chemor Perak.

B. Film preparation

This method was adopted from [10] with minor modification, the 2ml amount of glycerol was dissolved in distilled water at a temperature of 50°C. Meanwhile, sago starch (6, 7, and 8% w/v) was dispersed in distilled water at room temperature then added into the aqueous glycerol dispersion. To obtain active film, (0%,10% and 20% w/w starch) ascorbic acid were added. After heating from 50 to 75°C the aqueous solution was continuously stirred for 45 min to complete homogeneity and gelatinization in solution. This mixture was cooled to 40-45◦C. Suspension then prepared on petri dish and then the film was dry in the oven at 40◦C for 48h and peel off after drying.

C. Film solubility in water

Film solubility is test is done according to a method used by [11] with some modification. The edible film was cut into 2 x 2 cm^2 and weighed. The film is immersed in distilled water (50ml) at different temperature (25◦C, 40◦C and 90◦C) for 5 minutes. The film then filtered and dried in oven at temperature of 40◦C for 24h. The sample were collected and weighed. The percentage of solubility was calculated using the equation below.

Solubility % = (initial dry weight of film − final dry weight of film) / (initial dry weight of film) × 100%

D. *Mechanical properties analysis*

Tensile strength(TS) and percent elongation break (EB) was tested according to [12] method with modifications. 5 specimens were prepare with size of 7 x 2 cm^2. The thickness of each of the specimen must measure with Digital Micrometer before test. The measurement will take at 5 different positions for each specimens and calculate average value. Instron Universal Testing Machine (Model 55669) with 2.5 kN load cell was used to perform tensile strength. Tensile strength and elongation at break was calculate using equation below.

$$TS(Mpa) = F_{max}/A$$
$$EB\ (\%) = (L/40) \times 100$$

Where, Fmax is the maximum load (N) to pull the testing films apart, A is the cross-sectional area (m^2) of the testing films and L is the elongation of testing films at the moment of rupture (mm).

E. *Film thickness*

Film thickness is measured by using Mitutoyo Digimatic Micrometeer with an accuracy of 0.001 mm. The mean thickness of each film was determined from an average of five random positions on the film samples.

F. *Water Vapour Permeability (WVP)*

Water vapor permeability of film is determined based on the method by [10] with some modifications. Polystyrene cups were used to determine the water vapor permeability. The cups were filled with 20g silica gel covered with film and sealed. The cups then placed to desiccator containing distilled water and kept at 25°C for 5 hours, Weight change of the cup was measured and plotted as a function of time. The slope was calculated by linear regression and the measured water vapor permeability of the film was determined as below.

$$WVP = Gx/A\Delta p$$

Where, WVP is water vapor permeability of the film, G is the slope of the straight line, x is the mean of film thickness (mm), A is the exposed film area (m^2) and Δp is the partial pressure of water vapor difference (Pa) across the two sides of the film.

G. *Colour measument*

(i) Film color

According to (Basiak,et al, 2017)method, colour of the films (3 measurement were taken) was determined using a colorimeter (Minolta, Model CR-300, Japan) using the CIE LAB colour parameters ; L, from black (00 to white (100); *a*, from green (-) to red (+); and *b*, from blue (-) to yellow (+). Colour of films was expressed as the total colour difference (ΔE) from a standard white colour ($L^*=89.6$, $a^*=0.3173$, $b^*=0.3343$) and used as the film background, based on equation below;

$$\Delta E=\sqrt{(L-L*)^2+(a-a*)^2+(b-b*)^2}$$

(ii) Fruit browning control

An apple is cut into 2cm x 2 cm was wrapped films of with 3 different AA concentrations (0%, 10% and 20% w/w starch) respectively. The sample was exposed for 1 hour to surrounding at room temperature. The colour change of the apple was observed by using a colorimeter (Minolta, Model CR-300, Japan) with the CIE LAB colour parameters ; L, from black (00 to white (100); *a*, from green (-) to red (+); and *b*, from blue (-) to yellow (+). Colour of an apple was expressed as the total colour difference (ΔE) from a standard white colour ($L^*=89.6$, $a^*=0.3173$, $b^*=0.3343$) and used as the film background, based on equation below;

$$\Delta E=\sqrt{(L-L*)^2+(a-a*)^2+(b-b*)^2}$$

G. *Antioxidant activity*

DPPH radical scavenging assay

The method used was adopted from [14] with modification, DPPH free radical scavenging activity was determined. A size of 2cm x 2cm film was extracted by soaking the film in 3 ml of methanol in water bath for 2 hours. The 3ml extract solution was mixed with methanol solution of DPPH (0.01Mm). The mixture was shaken for 10s and incubated in the dark for 30 min at room temperature. The UV absorbance of DPPH assay solution at 517 nm wavelength was measured. The DPPH radical scavenging activity was measured as equation below;

$$\text{DPPH scavenging activity (\%)} = [(A_{DPPH} - A_S)/ A_{DPPH}] \times 100\%$$

Where, A_{DPPH} is the absorbance value at 517nm of DPPH methanol solution and A_S is the absorbance value at 517nmm of the mixture DPPH methanol solution and film extraction.

III. RESULTS AND DISCUSSION

A. Film solubility

According to previous study by [10], film solubility generally increase with both the starch content and glycerol concentration. Based on Table 1, the higher concentration of AA in sago starch film shows the higher percentage of solubility which is in the range of 38.96%-95.59% compared to film without AA (50.95%-89.29%). Besides, based on Figure 1 we can observed that the higher concentration of AA in film (20% w/w starch) has better solubility in 3 difference temperature control (25°C,40°C, and 90°C). The higher content of both starch and AA in film is has higher solubility in room temperature as well as in boiling point temperature which is 90°C. The addition of the AA in the films help the solubility of the films as food packaging as the AA-catalyzed hydrolysis of starch reduces its molar mass and increasing the solubility. Besides, the AA-polymer links weakened the chain packaging which facilitated water penetration into the films. Thus, the incorporated of low molecular hydrophilic such as AA substance increased the soluble matter and giving it more sensitive to water [15].

Table 1 Film solubility of sago starch with and without AA with varies temperature control.

Sago starch content (% w/v)	AA content (% w/w starch)	Solubility (%)		
		25℃	40℃	90℃
6	0	56.28	61.03	80.35
	10	56.51	59.29	95.60
	20	38.96	60.20	65.59
7	0	50.92	87.84	89.78
	10	62.36	59.92	69.8
	20	59.93	64.78	65.97
8	0	55.40	60.60	81.62
	10	57.70	59.48	66.31
	20	61.03	62.05	95.5

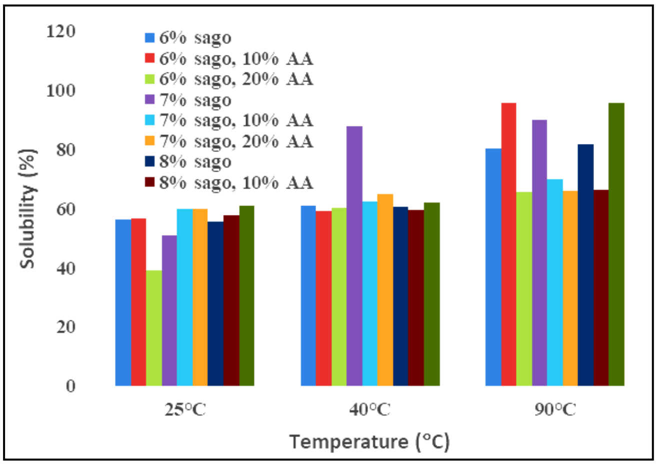

Figure 1 Film solubility of sago starch with and without AA with varies temperature control

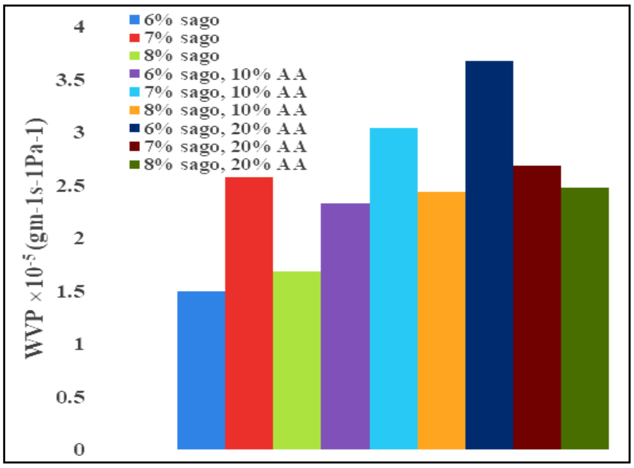

Figure 2 Effect of concentration of ascorbic acid on water vapor permeability film

B. Mechanical properties

The mechanical properties of the produced film shown in Table 2 indicate that there was a decrease of tensile strength as the AA concentrations increased from 3.64 MPa to 1.76 MPa. This can be seen in all starch concentrations. The films structure that contain starch alone has higher tensile strength which is from 3.24 MPa to 5.45 MPa. The films that contained 20% (w/w starch) of AA has the lowest tensile strength. However, on the other side, increasing concentration of AA has resulted the opposite effect on elongation as well as the film without AA.

Table 2 Comparison of barrier and mechanical properties of the films

Sago starch content (% w/v)	AA (w/w) (%)	Thickness mm	Tensile strength MPa	Elongation (%)	WVP (10^{-5}) $gm^{-1}s^{-1}Pa^{-1}$
6	0	0.0618	3.24	35.25	1.5
	10	0.0942	3.19	30.25	2.58
	20	0.0968	1.76	43.75	1.69
7	0	0.0764	5.45	38.00	2.33
	10	0.0938	3.07	39.75	3.04
	20	0.0968	2.19	59.5	2.44
8	0	0.138	4.68	46.5	3.67
	10	0.0996	3.64	67.00	2.68
	20	0.0984	2.33	29.50	2.48

As presented in Table 2, in overall, higher of AA content increased the elongation of films 30.25% to 67% (except for 20%(w/w 8g starch, which decreased strongly). Increasing of the elongation on films is led to improve the films flexibility due to the present of AA in the film. Meanwhile, the decreasing of elongation on film structure in 20% AA concentration in 8%(w/v) starch solution maybe related to the heterogeneity of the films where the film does not heterogeneous completely at the gelatinization temperature. This result is similar with several reports [15],[7].

Figure 2 represent the barrier properties of sago starch films incorporated AA in minimizing the moisture transfer between product and surrounding atmosphere. The films without AA concentration has higher WVP as the concentration of the starch increased meanwhile as the concentration of AA increased in film, the WVP of the films is decreased (except for 10% AA in 7%(w/v) starch and 20% AA in 8%(w/v) starch, which slightly increased to 3.04 x 10^{-5} $gm^{-1}s^{-1}Pa^{-1}$ and 3.67 x 10^{-5} $gm^{-1}s^{-1}Pa^{-1}$ respectively). This is likely caused by the amount of AA in the films surface area is higher. Based on the previous study by [10], the increasing water vapor permeability in edible film is common as the hydrophilic nature in starch is sensitive to the environmental humidity. Thus, the films without AA content has higher water vapor permeability as the amylose content is higher because of it hydroxyl group where in this case preferred water vapor permeability diffusion through films. Moreover, the addition of the AA in films resulting lower water vapor permeability where it absence in the film improve the film moisture and does not affect water vapor barrier propetiess of the films. Since the water vapor permeability should be lowest as possible to prevents water from leaving the content of the film as the deterioration of food packaging depends on the water content transfer throughout interior product from surrounding[16].

C. Antioxidant activity

DPPH radical scavenging activity

Antioxidant properties is important especially radical scavenging activities due to the deleterious role of free radicals in foods and in biological system. DPPH scavenging [17].Based on Table 3, the DPPH scavenging activity percentage of 3 different concentration of AA in SG-Film has been analyse. The higher the concentration of AA in the film resulted the best antioxidant activity, 98.51% compare to the film without any concentration of AA which is 82.09%. Besides, we can observed the colour of the DPPH solution with film extract where the more the concentration of AA content in film, the absorbance resulting more yellowish compared to the film without AA where the colour is still purple (same as the colour of DPPH solution). The change of the colour to clearer from DPPH solution colour shown that the presence of AA as antioxidant in the film. This is due to the ability of AA to donate electron make it an excellent reducing agent and antioxidant [17].

Table 3 Comparison of antioxidant activity for Sago starch films with and without AA

Film solution + DPPH solution	0	10	20
			
DPPH scavenging activity (%)	82.09	98.93	98.51

D. Colour Measurement

(i) ***Film colour measurement***

Color of film packaging is essential on the film's appearance influences consumer's acceptance for the packed products. Table 4 shows the colour properties of Sago starch films incorporated with AA. It can be seen that the increasing of AA concentration in sago films, the value of L* gradually decreased, while values of a*, b* and ΔE respectively decreased too. For L*=0 is black and L*=100 is white, the reduced L* value was indicated the sago starch with AA is become darker as the concentration of AA increased. This is due to the presence of AA, the colourless sago film becomes a little bit yellowish as incorporated with AA because of the browning process in the films occur due to the degradation of AA [18]

Table 4 Color measurement of film

Sago starch content (% w/v)	AA (% w/w)	Colour indices			
		*L**	*a**	*b**	*ΔE*
6	0	35.15	0.23	28.69	2664.86
	10	31.67	0.11	-2.83	2379.87
	20	31.03	-0.62	0.12	2426.62
7	0	31.67	0.11	-2.83	2379.87
	10	30.77	-0.01	-0.3	2447.64
	20	33.84	-0.35	-1.49	2201.45
8	0	34.45	-0.41	-0.41	2151.19
	10	35.13	-0.20	-1.11	2099.37
	20	32.28	-0.62	-0.66	2324.86

(ii) Fruit browning colour control

From table 5 below, the fruit colour were obtained as leave in surrounding for 60 minutes. From the table, the L* value is slightly decrease as the apple wrap with higher contain of AA concentration film. The value a*(+ value red) is decrease as well as b* (+value yellow). The apple that packed and leave for an hour with sago starch film without AA resulted the a* and b* value towards positive value which it is indicated the apple become more browning compare the other 2 sample. Thus, it clearly show that the incorporated of AA in film is one of the effective method for conveying antioxidant activity to starch-based edible films.

Table 5 Fruit colour indices after 60 minutes

AA (% w/w)	Colour indices			
	L*	a*	b*	ΔE
0	71.66	-1.21	22.16	566.06
10	76.99	-3.4 -	26.66	612.45
20	77.64	3.70	23.48	491.3

IV. CONCLUSION

The conclusion can be make based on the result obtained in this research. The incorporated of AA in sago starch-based edible film makes the stronger. This can be seen on the mechanical properties of the film where tensile strength and elongation at break obtain was both decrease and increase respectively. The water vapor permeability of films lowest except on certain ratio of film. Thus, active food packaging obtained where the AA as antioxidant agent resulting higher antioxidant activities as well as good in preventing of fruit browning. Thus, future studies will be necessary to obtain on physical properties of the films including thermal conductivity, seal strength, FTIR and SEM.

V. ACKNOWLEDGEMENT

Thank you to my supervisor, Madam Fariza binti Hamidon and Universiti Teknologi Mara.

VI. REFERENCES

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