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Effect of chitosan-palm stearin edible coating on the post harvest life of star fruits (*Averrhoa carambola* L.) stored at room temperature

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Abstract

This study was conducted to develop an edible coating containing combined hydrophilic (chitosan) and hydrophobic (palm stearin) components which demonstrated gas barrier and moisture barrier properties, respectively, to prolong the post harvest life of star fruits (*Averrhoa carambola* L.). The emulsions of chitosan (C) and palm stearin (S) were prepared by using different ratios of C:S which were 1:0, 1:1, 1;2, 1:3, 2:1, 3:1 and 0:1. Viscosity of emulsions was studied. The physicochemical properties of coated star fruits were also evaluated in terms of weight loss, firmness, visual appearance, oxygen concentration, carbon dioxide concentration and ethylene concentration during storage at room temperature (26-28˚C) for 18 days. The results obtained showed that coating reduced weight loss, maintained firmness and appearance, slowed down the production of respiratory gases and reduced ethylene production. The most recommended coating for star fruits was C:S of 1:1 ratio as it showed good water barrier and gas barrier properties and could extend the post harvest life of star fruits up to 20 days as compared to the control samples which had a post harvest life of 12 days.

Introduction

Malaysia is the largest exporter of star fruits in the world since 1989 and has been exporting star fruits to Europe, one of the world major destinations for the commodity. Over the years, significant export growth has been recorded with export figures of 8745 and 9182 MT for years 2000 and 2001, respectively. This was more than 60% increase from the export in 1991, which was 2723 MT and in 2002, star fruits ranked third in terms of fruit export value (Abdullah *et al*., 2007).

However, these fruits ripen rapidly during transit and storage, thus often requiring rapid shipment. Respiration rate of fruits can be slowed down by decreasing the storage temperature but tropical fruits present a special problem in that they are chilling sensitive. Therefore, low temperature cannot be used effectively to extend their storage life.

Star fruits are also very susceptible to mould growth. According to Burg (2004), within a few weeks, carambolas stored in normal atmosphere storage were totally engulfed by moulds and were completely spoiled. In Malaysian context of Selangor Fruit Valley (2009), 5% annual losses of star fruits during shipment to Amsterdam were reported. Therefore, a lot of strategies have been developed in order to improve the yield and quality of the star fruits.

The extension of fruit shelf life is an important goal to be attained. Many storage techniques have been developed to extend the marketing distances and holding periods for commodities after harvest. Different preservation methodologies have been studied. One method of extending post harvest shelf life is the use of edible coatings (Falcao-Rodrigues *et al*., 2007).

Proteins, lipids, and polysaccharides are the main constituents of edible coatings. Due to their hydrophobicity, lipid compounds have been used as edible coatings to prevent moisture exchanges between food product and the surrounding medium, or between adjacent components within heterogeneous foods. Many studies focussed on lipid coating permeability have reported that the moisture barrier properties of some fatty food grade coatings are comparable with synthetic films such as low-density polyethylene or polyvinyl chloride (Phan *et al*., 2009).

In addition, the moisture barrier efficiency of lipid coatings depends closely on their physical

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state. Lipids having a high solid fat content are usually more efficient than liquid lipids (Morillon *et al*., 2002). However, the performance of lipid films against mass transfer resides also on their structural integrity. Solid lipids are generally brittle and cannot form cohesive layers. Therefore in edible films and coatings, they usually need a support structure matrix such as polysaccharides or proteins to attain better mechanical properties.

Proteins and polysaccharides generally form film with good mechanical properties. They are also better gas barriers since hydrocolloids exhibit moderately low permeability to gases and are useful to delay ripening of climacteric fruits. However, they are poor moisture barriers because of their hydrophilicity. Improved film performances can be obtained when hydrocolloids (proteins or polysaccharides) form a continuous network and the hydrophobic substances (lipids) provide the moisture barrier properties. However, constituent compatibility is an important issue dealing with mixtures of biopolymers, and this might drastically alter the performance of composite films (Diab *et al*., 2001). Hence the exact ratios for combination of both substances as moisture barriers and gas barriers are very important to improve film performances.

Currently, there is an increasing interest in the use of chitosan as edible fruit coating because of its potential to inhibit fungal growth and extend the shelf life of fruits (Han *et al*., 2004; Jiang *et al*., 2005; Ribeiro *et al*., 2007). However, little research had been done using chitosan which is incorporated with lipid constituents such as palm stearin which is a cheap palm oil fraction, making it a cost effective ingredient in the application of edible fruit coating.

The intention of this research is to prolong the shelf life of star fruits (*Averrhoa carambola* L) stored at room temperature. Results from a recent study on the application of water-based stearin wax coating showed that the maximum ethylene production in uncoated seedless guava shifted from the third day of storage to the ninth day of storage indicating a delay in the ripening process of seedless guava (Abd. Rashid *et al*., 2009). The main objectives of this study were to formulate and develop an edible coating from chitosan incorporated with palm stearin using different ratios and to study the effect of chitosan-palm stearin coating on the physicochemical characteristics of star fruits.

Materials and Methods

Materials

The raw materials included star fruits and palm stearin. RBD palm stearin (SMP 54˚C, IV 33) was obtained from Cargill Specialty Fats (M) Sdn. Bhd, Pelabuhan Klang, Malaysia. Star fruits of uniform size and free from external defects of maturity index 2 were obtained from Selangor Fruit Valley, Batang Berjuntai, Selangor, Malaysia. Chitosan (food grade) was purchased from Chito-Chem (M) Sdn. Bhd, Parit Buntar, Perak, Malaysia, with deacetylation degree of 85%. 99% glacial acetic acid (food grade) and Tween 80 were used to obtain coating solutions.

Preparation of the coating emulsions

Chitosan (1% w/v) was dispersed in an aqueous solution of glacial acetic acid (1%, v/v), at 40˚C. After the chitosan was completely dissolved, the previously melted palm stearin (60 ºC) was mixed with chitosan according to the ratio of C:S 1:0, 1:1, 1:2,1:3,2:1,3:1 and 0:1. Tween 80 was added at 0.1% concentration. These mixtures were emulsified at 13 500 rpm for 4 min (Vargas *et al*., 2006).

Viscosity of coating emulsions

Viscosity of the emulsions were determined by using a viscometer (Brookfield Viscometer, USA) with temperature of emulsions maintained at 26˚C. Viscosity readings were expressed in centipoises (mPas.s).

Coating application

The selected fruits were washed using distilled water containing 200 ppm of sodium hypochlorite solution and then drained (Martínez-Romero *et al*., 2006). The fruits were dipped in the coating solutions for 15 s except for fruits coated with C:S (3:1). The C:S (3:1) coating was applied on fruits by using a clean and soft brush. Control samples followed the same treatment of washing and dipping technique but samples were dipped in distilled water. Samples were allowed to dry at ambient temperature. The samples were then stored at room temperature (26-28ºC) until analysis was carried out (Vargas *et al*., 2006).

Physicochemical properties determination

Physicochemical determinations of samples were performed at 1, 3, 6, 9, 12, 15 and 18 days of storage at room temperature. Each analysis was carried out with three replicate samples.

Weight loss

Weight loss was determined by weighing the samples on a laboratory digital balance (A & D HF-300, Japan) at the beginning of the experiment just after coating and air-drying, and thereafter at 1, 3, 6, 9, 12, 15 and 18 days of storage period at room temperature. The results were then expressed as percentage loss of moisture based on the original mass (Maftoonazad and Ramaswamy, 2005).

Gas concentrations

Carbon dioxide and ethylene concentrations were measured by placing a fruit in a 0.5L plastic jar, hermetically sealed with a rubber stopper for one hour. One millilitre of the atmosphere in the plastic jar was withdrawn into a gas tight syringe. Carbon dioxide and ethylene concentrations were quantified using a Gas Chromatography (Agilent 78990A) equipped with Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID) respectively. The column and detector temperatures were 60˚C and 180˚C, respectively. Results from the means of triplicate determinations for each one of the replicates used were expressed as ppm (Martínez-Romero *et al*., 2006).

For oxygen concentration, a portable oxygen and carbon dioxide analyser (Mocon Pac-Check Model 325, US) was used. The result was expressed in percentage.

Firmness retention

For each fruit, texture was determined using a TA-XT2i Texture Analyzer (Stable Microsystems, Surrey, UK) equipped with a compression cell of 5 kg and a cylindrical and flat acrylic probe of 1 cm in diameter, using 1 mm/s crosshead speed, a 1 N force and a 75% strain to penetrate the fruit. The results were expressed as percentage of firmness retention (compression force during storage time was compared to force on day 1) (Tanadu-Palmu and Grosso, 2005).

Visual appearance

Fruits were observed for signs of decay. Star fruits that showed any sign of fungal development were considered decayed.

Statistical analysis

Results were expressed as means ± SE. Statistical comparison was made by one-way analysis of variance (ANOVA) followed by Duncan's Multiple Range Test and was analysed by SPSS, version 12.0 software. .

Results and Discussion

The C:S ratios of 1:0, 1:1, 1:2, 1:3, 2:1, 3:1 and 0:1 were chosen based on the results of a preliminary study. These coating emulsions were selected because they gave better stability of emulsions without any separation of oil or water layers. Particle size and microstructure analysis had also been carried out for all the selected emulsions and the results showed that the emulsions were stable up to 60 days of storage at room temperature.

Table 1. Viscosity of chitosan-stearin coating emulsions

Chitosan : Stearin	Viscosity, x10^3 mPa.s
1:0	0.54 ±0.01^d
1:1	0.62±0.01^d
1:2	1.51± 0.01^c
1:3	1.47 ±0.01^c
2:1	6.00 ±0.01^b
3:1	37.17±0.29^a
0:1	0.56 ±0.01^d

Data followed by different lower case superscript letters are significantly different (P<0.05).

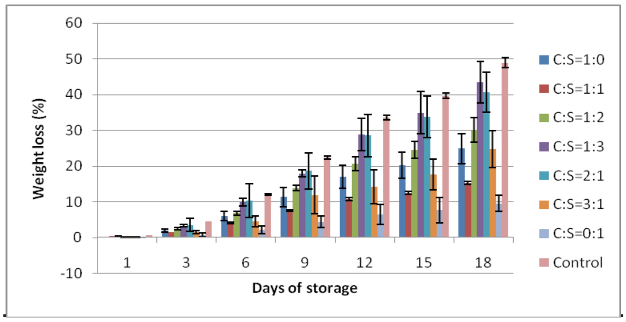

Figure 1. Effect of different concentrations of chitosan- stearin coatings (C:S=1:0, C:S=1:1, C:S=1:2, C:S=1:3, C:S=2:1, C:S=3:1, C:S=0:1, and control) on the weight loss of star fruits stored at room temperature. Each value is the mean of three replicates. The vertical bars represent the standard error of the means.

Viscosity of emulsions

Viscosity of the coatings increased with the increase in the concentration of chitosan (Table 1). The viscosity of coatings also increased when the ratio of palm stearin was increased. However, when chitosan to stearin ratio were 1:3 and 0:1, the viscosity of coating decreased. This result contradicted the result obtained by Zorba (2006) who studied the effect of the amount of emulsified oil on the viscosity of myofibrillar proteins (hydrophilic component) where the emulsion viscosity of myofibrillar proteins increased when the oil ratio increased. According to Tipvarakarnkoon *et al*. (2010), the factors that influence emulsion viscosity included emulsion particle size and particle size distribution. These factors could be the reasons why the viscosity of chitosan-stearin ratio decreased when the ratio was 1:3.

Viscosity of an emulsion can determine the method of application of coating on fruits. According to Mishra *et al*. (2010), the spreadibility of the coating was improved with the increase in viscosity. For this reason, dipping was used for coating the star fruits in this study for all chitosan-stearin ratios except for chitosan-stearin of ratio 3:1 which was too viscous hence brushing was used for this coating application.

Weight loss

Figure 1 showed the percentage of weight loss of star fruits from different formulations of chitosan and stearin. Based on the figure, stearin coating (C:S=0:1) showed the lowest percentage of weight loss as compared to other formulations. This can be explained by its hydrophobicity. Stearin has low affinity for water, which explains why it has low moisture permeability.

The results also showed that coating of chitosan and stearin with the same ratio (C:S=1:1) had significantly ($p<0.05$) lowered the percent of weight loss during storage; but when the ratio of chitosan increased (C:S=2:1 and C:S=3:1), increase in weight loss was observed. This was due to the hydrophilicity of chitosan and the decrease in the quantity of stearin.

However, the increase of stearin ratio also showed an increase in percentage of weight loss which showed the ineffectiveness of the coating. These results contradicted the results obtained by Vargas *et al*. (2006) and Han *et al*. (2004) who reported that the moisture barrier properties of strawberries were significantly improved during storage when the concentrations of oleic acid and vitamin E were increased in the chitosan emulsion. This could be explained by the size and the distribution of lipid globules of stearin as compared to oleic acid and vitamin E. As the stearin used in this study is solid at room temperature, it could reduce the evenness of the coating applied on the surface of the fruits, thus affecting moisture losses.

Gas concentration

Determination of ethylene production during storage is very important since it gives the trend of ripening of fruits. Based on the Figure 2, the uncoated star fruits showed the highest concentration of ethylene released during storage time and the highest peak was on day nine, while all the coated fruits showed lower ethylene concentration. However, ethylene concentrations in coated samples were higher than those in uncoated fruits at day 15 and 18. These results were due to the ripening of coated fruits which increased the level of ethylene. On the other hand, the uncoated fruits showed mould growth and low production of ethylene due to senescence. Among the coated fruits, the production of ethylene decreased when the ratio of stearin increased.

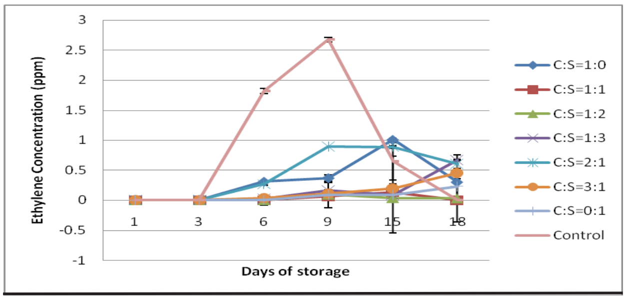

Figure 2. Effect of different concentrations of chitosan- stearin coatings (C:S=1:0, C:S=1:1, C:S=1:2, C:S=1:3, C:S=2:1, C:S=3:1, C:S=0:1, and control) on the ethylene concentrations of star fruits stored at room temperature. Each value is the mean of three replicates. The vertical bars represent the standard error of the means

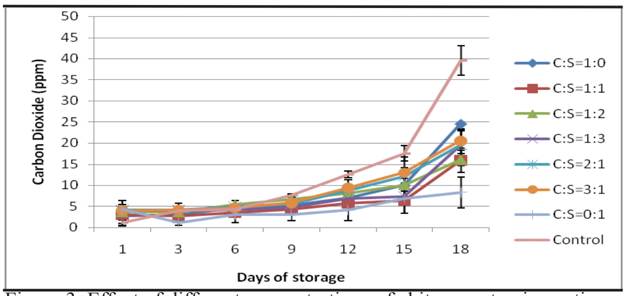

Figure 3. Effect of different concentrations of chitosan- stearin coatings (C:S=1:0, C:S=1:1, C:S=1:2, C:S=1:3, C:S=2:1, C:S=3:1, C:S=0:1, and control) on the carbon dioxide levels of star fruits stored at room temperature. Each value is the mean of three replicates. The vertical bars represent the standard error of the means

Besides ethylene, carbon dioxide released from fruits is also important to be measured because during respiration, carbon dioxide is released by fruits. It is important to decrease the amount of carbon dioxide escape from internal tissue of fruits to control their ripening. Figure 3 shows the highest concentration of carbon dioxide released from uncoated star fruits from day six until day eighteen. Coating had slowed down the rise of carbon dioxide throughout the storage time of star fruits.

Ali *et al*. (2011) analysed the internal gases of carbon dioxide of papaya by withdrawing internal gas from the papaya central cavity while the fruit was immersed under water. Their results showed that coating had increased the level of carbon dioxide concentration while decreasing the level of oxygen concentration, suggesting that coating exerted a barrier to carbon dioxide and oxygen exchange. The results of oxygen concentration in this study (Figure 4) showed that coating had prevented the decline of oxygen concentration surrounding the coated star fruits indicating the delay in fruits ripening. Other studies also reported similar results for coated fruits when atmospheric gases of the fruits were analysed (Jeong *et al*., 2003; Qiuping and Wenshui, 2007; Sánchez-González *et al*., 2011).

However, according to the graphs of oxygen and carbon dioxide concentrations, the effectiveness of coating decreased when the stearin ratio was increased in the chitosan-stearin coating. This might be due to

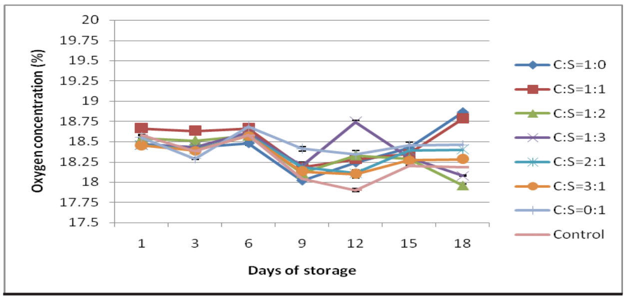

Figure 4. Effect of different concentrations of chitosan- stearin coatings (C:S=1:0, C:S=1:1, C:S=1:2, C:S=1:3, C:S=2:1, C:S=3:1, C:S=0:1, and control) on the oxygen levels of star fruits stored at room temperature. Each value is the mean of three replicates. The vertical bars represent the standard error of the means

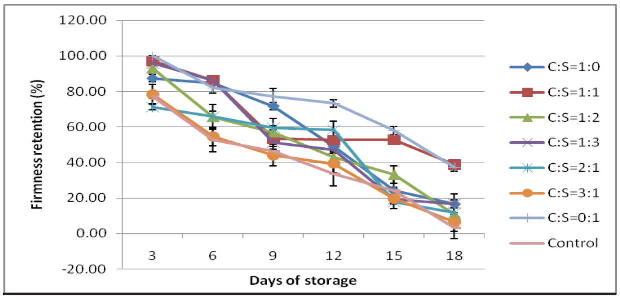

Figure 5. Effect of different concentrations of chitosan- stearin coatings (C:S=1:0, C:S=1:1, C:S=1:2, C:S=1:3, C:S=2:1, C:S=3:1, C:S=0:1, and control) on the firmness retention of star fruits stored at room temperature. Each value is the mean of tree replicates. The vertical bars represent the standard error of the means

the hydrophobicity of the stearin, but the increase of chitosan concentration did not prevent the decline of oxygen concentration hence the effectiveness of the coating could only be observed when the fruits were coated with chitosan-stearin coating ratio of 1:1.

Since star fruits are a non- climacteric fruit, they show generally low carbon dioxide and ethylene production rates during ripening as compared to those of climacteric fruits. According to O'Hare (1993), the rise of those gases tends to be related to microbial decay or tissue senescence, and occur after the fruit is considered ripe. While Pérez-Tello *et al*. (2001) reported that the respiration pattern was probably influenced by a yellow mould growth on the star fruits skin stored at 20ºC which appeared after 20 days of storage.

Firmness retention

During storage, firmness of star fruits decreased due to cell wall breakdown, as well as to water loss. Coating acts as a gas barrier which slows down the outward loss of carbon dioxide and inward movement of oxygen, while still allowing for respiration. Low oxygen and high carbon dioxide concentrations reduce the activity of enzymes and allows retention of the firmness of fruits during storage (Yaman and Bayoundurh, 2002).

According to Figure 5, coated fruits with the same ratio of chitosan-stearin (1:1) could maintain the firmness up to 40 percent at day eighteen of storage. This is because this coating reduced weight loss and reduced the gases concentration which led to ripening hence maintaining the firmness of star fruits. As expected, other formulations of chitosan-stearin improved the firmness retention as compared to the control but they were not as effective as chitosan-stearin with ratio of 1:1.

Visual appearance

According to Maftoonazad and Ramaswamy (2005), coating slowed down the respiration rate, reduced the colour changes of skin and flesh and increased the shelf life of fruits. In this study, the skin colour of star fruits started to change on day six of storage. After 12 days of storage, uncoated star fruits showed the presence of mould growth. This was due to the drastic increase in carbon dioxide concentration and the decrease in the ethylene production as a sign of senescence.

On the other hand, coating had lengthened the post harvest life of star fruits up to day 18. The presence of mould could be observed on star fruits which were coated with chitosan alone during this time of storage (day 18) while for other formulations, no mould was observed. However, after 18 days of storage, almost all star fruits were totally engulfed by mould except for star fruits coated with C:S=1:1. This was accompanied by the decrease in ethylene production and the decrease in firmness from day 15 of storage.

Conclusion

Application of chitosan-stearin edible coatings was able to improve the quality and shelf-life of star fruits during storage time at room temperature by reducing weight loss, maintaining appearance, and slowing down respiratory CO_2 and ethylene productions while preventing the decline of oxygen concentration. Overall chitosan-stearin (C:S=1:1) was the best coating formulation as it showed good moisture barrier and gas barrier properties.

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