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CHARACTERISATION OF EDIBLE LIPID-CHITOSAN FILM

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Abstract: *Purpose*: The main objective of this study was to develop an edible lipid-chitosan film in order to maintain food quality and extend the shelf life of fruits.
Methodology: Incorporation of palm stearin (PS) and palm kernel olein (PKOo) as the lipid component was used to improve the moisture barrier properties of chitosan (CH) film. The film was characterised in terms of thickness, opacity, glossiness, water vapour transmission (WVT) and mechanical properties such as tensile strength, elongation and Young's modulus.
Findings: The results obtained showed that the incorporation of PS and PKOo significantly decreased ($P \leq 0.05$) the WVT of film from 3.2x10-4g/h.m^2 for chitosan film to 1.1x10-4g/h.m^2 for film containing 4% lipid component indicating improved moisture barrier properties. Overall, the addition of PS and PKOo into chitosan film significantly increased ($P \leq 0.05$) the opacity but decreased the glossiness of the film.
Value: There was no significant difference in mechanical properties in terms of tensile strength and film elongation but there was significant difference ($P \leq 0.05$) in Young's modulus among films.

Keywords: *Edible Film; Chitosan; Palm Stearin; Palm Kernel Olein; Water Vapour Transmissions*

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INTRODUCTION

Increasing demand for fresh fruits and vegetables forces the food industry to develop new and better methods for maintaining food quality and extending shelf life. Great losses (from 20% to 80%) in the quality of fresh fruits occur from harvesting to final consumption and the short shelf life of fruits is an important drawback concerning distribution chains (Cerqueira *et al.*, 2009). Therefore, interest in maintaining food quality while reducing packaging waste has encouraged the exploration of the new materials for edible films and coatings.

An edible coating or film has been defined as a thin, continuous layer of edible material formed or placed on or between foods or food components (Barbara et al., 2006; Ghasemzadeh et al., 2008). Edible, biodegradable films and coatings can act as barriers to control the transfer of moisture, oxygen, carbon dioxide, lipids, and flavor components and thus maintain the quality and increase the shelf life of food products (Fabra et al., 2008; Garcia et al., 2004 and Zahedi et al., 2010).

Materials that can be used to make edible films include polysaccharides (Zahedi *et al.*, 2010), proteins (Gennadios *et al.*, 1994) and lipids (Hernandez, 1994), or a combination of these (Barbara *et al.*, 2006). In general, mechanical and barrier properties of biological films are highly associated with the polarity of film constituents (Debeaufort *et al.*, 1993). Most single hydrophilic films (polysaccharide or protein based films) have good mechanical properties and are excellent gas, aroma and lipid barriers but poor moisture barriers. On the other hand, most single hydrophobic (lipid-based) films have rather poor mechanical properties but high moisture resistance.

Edible coatings based on chitosan have proved to be effective to control decay of cold-stored strawberries (Han *et al.*, 2005). Chitosan has potential to be used as an alternative resource for active food packaging (Vargas *et al.*, 2006). Chitosan has also been successfully used as a food wrap because of its film forming and excellent gas barrier properties (Chien *et al.* 2007). Application of semi permeable coatings with modified atmosphere of carbon dioxide and oxygen under small storage environment conditions has been shown to improve the storability of perishable crops (Lee *et al.*, 2003). Films can be placed on fruit and vegetables surfaces through different ways like dipping, spraying and fluidized bed system (Ghasemzadeh *et al.*, 2008).

In this study, a combination of chitosan and palm stearin or palm kernel olein, is used as the coating material. Chitosan is a seafood by-product obtained by deacetylation of chitin. Chitosan films are tough, long lasting, flexible and very difficult to tear. Palm stearin and palm kernel olein are local by-products of palm oil which can be used in a coating formulation to improve its water barrier properties. Palm stearin is a byproduct of palm oil fractionation and is not used directly into food applications due to its physical characteristics. It is less valuable and a is cheap source of fat fraction. Palm kernel olein is a liquid phase and contains high proportion of saturated fatty acids and thus has limited application due to the presence of short chain fatty acids.

Results from a study by Abd Rashid *et al.*, (2009) on the application of water-based stearin wax coating showed that the maximum ethylene production in uncoated seedless guava shifted from the third day to the ninth day of storage at room temperature indicating a delay in the ripening process of seedless guava. However, there is no research data on the study of functional properties of chitosan based dispersion incorporated with palm stearin and palm kernel olein, as such dispersion can act both as moisture and gas barriers in the resulting coating formulation.

The aim of this work was to formulate and develop edible film from chitosan, palm stearin and/or palm kernel olein and to determine the effect of incorporation of lipids on the moisture barrier, mechanical and optical properties of chitosan film. Results obtained from this study can be used to assess the potential of lipid-chitosan film on improving the quality and extending the postharvest life of fruits, besides diversifying the use of palm stearin and palm kernel olein.

Materials and methods

The raw materials used included chitosan, palm kernel olein and palm stearin RBD medium-hard palm stearin (IV: 33, SMP: 54) and palm kernel olein (IV: 24, SMP: 25) were obtained from Cargill Specialty Fats (M) Sdn.Bhd, Port Klang, Malaysia. High molecular weight chitosan, with a deacetylation degree of 85%, glacial acetic acid (99.5%), glycerol and Tween 80 were used to prepare the film forming dispersion (FFD).

Preparation of film-forming dispersions (FFD)

Three g of chitosan was dispersed in an aqueous solution of glacial acetic acid (0.75% v/v), at 40°C. Tween 80 at 0.1% (v/v) and 0.5% of glycerol were added and the FFD was shaken by using an orbital shaker at 350 rpm, 65°C. After 8 hours, palm stearin and palm kernel olein were added at 0%, 2% and 4% (v/v) to the chitosan solution based on the formulations. These mixtures were then emulsified at room temperature using a high speed homogenizer at 13500 rpm for 4 minutes (Vargas *et al.*, 2009).

Preparation of films

The film was prepared by pouring 20.0 ml of the FFD into a glass plate (area=56cm^2) and casted at 40°C. Dry films were peeled off from the casting surface and preconditioned in a humidity chamber 25°C at 58% relative humidity (RH) prior to testing.

Water vapour permeability of film

Water vapour permeability (WVP) of the film was determined gravimetrically at 25±2°C using ASTM standard method E96-00 (ASTM E96-00, 2000). Two specimens, 4 cm diameter discs were cut from each film. Each specimen was sealed with the smooth and shiny side facing up, by a rubber O-ring to the test cup (Plexiglass) containing anhydrous calcium chloride in small lumps and placed in a humidity chamber at 32°C which was maintained within ±1°C. The relative humidity was maintained at 58±2%. Both temperature and relative humidity were measured and recorded continuously. The steady state of weight loss was reached after 5 hours (Yang and Paulson, 2000).

Mechanical properties of film

The mechanical properties of films were measured by using a universal testing machine (Testometric Micro 500, Type SM-500N, Maywood Instruments, Basingstoke Hants, England). Films were cut into 20 mm wide and 80 mm long strips, according to the ASTM standard method D882-02 (ASTM D882, 2002). Grip separation was set at 50 mm, with a cross-head speed of 12 mm/min. Tensile strength (TS), elongation (E) at break, and Young's modulus (YM) were evaluated in five samples from each type of film.

Film gloss

Glossiness was measured at the incidence angle 10° using a gloss meter (Multi-Gloss 268, Minolta, Langenhagen, Germany). Prior to gloss measurements, films were conditioned in a humidity chamber at 25°C and 58% relative humidity. Film gloss was reported in gloss units (GU). Measurements were made in triplicates (Villalobos *et al.*, 2005).

Film opacity

Opacity of films was determined using a UV-VIS spectrophotometer. Three film specimens (1×4 cm strips) were taken from each film and placed on the inner side of a transparent plastic cuvette. The absorption spectrum of the sample was obtained at 400 nm. Film opacity was defined as the area under the recorded curve which was obtained through an integration procedure, and was expressed as Absorbance unit's × wavelength product (A × nm) (Yang and Paulson, 2000).

Film thickness

A hand-held micrometer was used to measure the thickness of the conditioned films.Five random measurements for each film were taken and averaged.

Statistical analysis

SPSS for Windows Evaluation (version 15.0) was used for all statistical analyses. Analysis of variance and Duncan multiple comparisons were performed to detect significant differences in film properties at 5% confidence level.

Results and discussion

Homogeneous, thin and flexible films were obtained and all films had slightly yellow appearance. As lipid concentration in the FFD increased, the colour of films became more whitish. The thickness of the lipid-chitosan films varied from 0.11 mm to 0.29 mm.

Water vapour transmissions (WVT)

Permeability is the main factor that influences the effectiveness of coating. The lower the water vapour transmission values the lower is water loss in the fruits. Since the main objective of edible film application is to decrease moisture transfer between the food and the surrounding atmosphere, water vapour transmissions should be as low as possible. WVT of the chitosan-lipid composite films at various lipid concentrations was evaluated at 32°C and 58% RH.

As shown in Fig. 1, incorporation of PS and PKOo significantly decreased ($P \leq 0.05$) the WVT of film from $3.2x10^{-4}$g/h.m^2 to $1.1x10^{-4}$g/h.m^2 for chitosan film and CH: 4% PS film, respectively indicating improved moisture barrier properties of

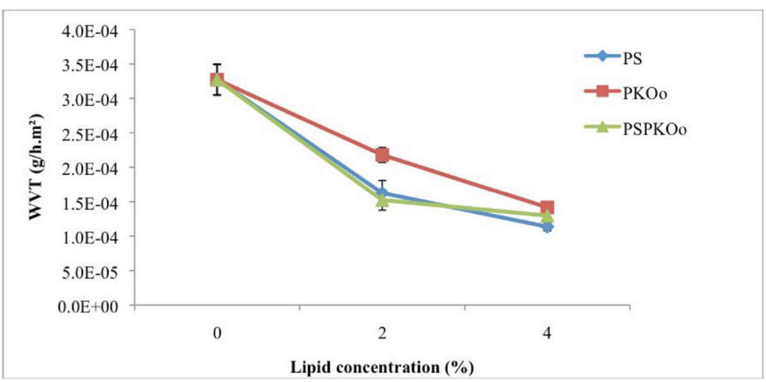

Fig. 1:
WVT of Chitosan-Lipid Edible Film as a Function of Lipid Concentration (Error Bars are Standard Error of the Mean of Three Measurements).

chitosan film. At 2% of lipid level, WVT of films with PS was significantly ($P \leq 0.05$) lower than films with PKOo but there was no significant difference among films at 4% of lipid incorporation. The results also showed that there was no significant difference ($P<0.05$) between WVT of CH: PS and CH: PSPKOo.

In this study, the 1:1 blend of PS/PKOo as well as PS and PKOo were selected to evaluate the effect of lipids on the properties of chitosan/lipid composite films because of ease of preparation andlow cost. The results revealed that although both PS and PKOo, at appropriate concentrations could effectively reduce the WVT of chitosan films, PS was found to be more effective.

According to Yang and Paulson (2000), long chain fatty acids are able to effectively improve the moisture barrier properties of hydrophilic films. WVT of film decreased with increased chain-length and degree of saturation of the lipids. Since palm stearin contains palmitic acid, oleic acid and linoleic acid while PKOo contains lauric acid and oleic acid as the major fatty acids, the presence of long chain fatty acids (palmitic acid, 16:0; oleic acid 18:1 and linoleic acid 18:2) in PS and PKOo improved the moisture barrier properties of chitosan film as shown in the WVT results. Although fatty acids are considered to be hydrophobic substances, their molecules contain highly polar carboxyl groups that may interact with water molecules and consequently facilitated moisture transfer through the film. Besides that, the difference in barrier efficiency between lipids could be attributed to their different polarity. In general, WVT of edible films comprising of biopolymers and lipids strongly depend on the type, structure and quantity of the lipids.

Mechanical properties

Tensile strength and elongation of film were determined to estimate the influence of chitosan behavior and lipid fraction on the mechanical properties of edible film. Adequate mechanical strength and extensibility are generally required for a packaging film to withstand external stress and maintain its integrity.

The effect of incorporating lipids on the mechanical properties of chitosan film is presented in Table 1. Generally, Young's modulus of edible films decreased as the concentration of lipids increased. Incorporation of hydrophobic substances into hydrocolloid network induced structural disruptions resulting from partial replacement of chitosan polymers by the lipids in the matrix film (Yang and Paulson, 2000). The negative effects could be related to the different polarity of compounds. However, in this study, incorporation of PS and PKOo up to 4% did not significantly affect the tensile strength and elongation of chitosan film.

Elongation of edible films showed significant differences among some films. Incorporation of 1:1 blend of 2% and 4% PSPKOo had better elongation compared to chitosan film because the lipid could act as plasticizer or lubricant in hydrocolloid networks, which improved the elongation of edible films.

Samples	Tensile strength (N)	Elongation (mm)	Young's modulus ($N.mm^{-2}$)
Chitosan film	20.8±7.8	12.7±4.1^{ab}	51.3±17^{bcd}
CH: 2%PS	19.3±1.3	13.0±4.1^{a}	70.0±6.2^{b}
CH: 2%PKOo	20.0±6.1	7.9±1.0^{b}	172.2±69^{a}
CH: 2%PSPKOo	20.3±3.3	13.1±2.4^{a}	39.9±4^{bcd}
CH: 4%PS	15.4±2.6	9.6±2.9^{ab}	19.6±0.8^{d}
CH: 4%PKOo	16.6±3.8	11.4±2.0^{ab}	66.0±15^{bc}
CH: 4%PSPKOo	13.8±1.5	13.4±3.6^{a}	23.5±8^{cd}

Means±standard errors for three replicates with different superscript indicated significant difference ($p \leq 0.05$).

Table 1:
Tensile Strength, Elongation and Young's Modulus of Chitosan-Lipid Films

Generally, chitosan film that incorporated with 2% and 4% of PKOo had higher Young's modulus compared to films with PS and PSPKOo.

Optical properties

Gloss and transparency were observed to influence the appearance of coated products. Transparency of the film was related to the internal structure developed during film drying (Villalobos *et al*., 2005) which is greatly affected by the initial structure of the film forming dispersion. The effect of the size of lipid aggregates on optical properties, for a determined volume fraction of the dispersed phase, is difficult to predict due to the complexity of the interactions between particle size and light scattering (Fabra *et al*., 2008).

Chitosan film without lipids was rather transparent while addition of lipid caused the film become whitish. However, incorporation of PS and PKOo resulted in a sharp increase ($P \leq 0.05$) in film opacity which increased as the concentration of the lipids increased.

The increase in film opacity probably arose from light

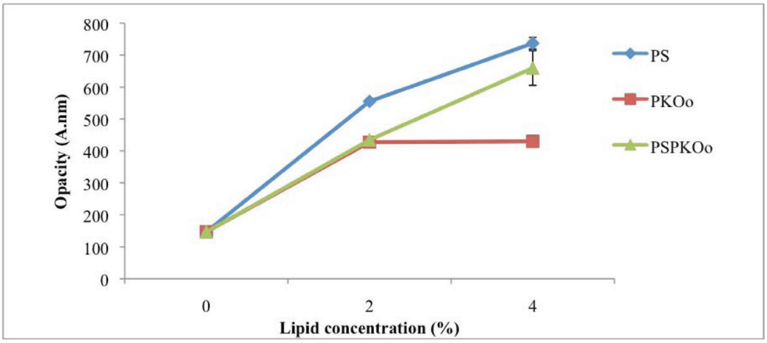

Fig. 2: Opacity of Chitosan-Lipid Edible Film as a Function of Lipid Concentration (Error Bars are Standard Error of the Mean of Three Measurements).

scattering of lipid droplets which were dispersed in the emulsion and continuously distributed throughout the polymer network after the film formed. It was also observed that the film with PS was more opaque than the film with PKOo for the same concentration. Consequently, light scattering became more accentuated as palm stearin increased. However, when PS and PKOo were blended together in the ratio 1:1, film opacity significantly decreased (P≤0.05) and this was most likely due to differences in optical properties of the two types of lipid. Optical properties of films depended on the structure or droplet size distribution of film forming dispersion.

Surface gloss is related to the smoothness or absence of irregularities on the surface. Very smooth surfaces are usually high glossy and the rougher surface, the lower of glossiness (Fabra *et al.*, 2009). Fig. 3 showed that PKOo had higher glossiness compared to PS and increasing the lipid concentration reduced the glossiness of films. At 2% of lipid incorporation, glossiness of film showed no significant difference for all types of lipid used while the gloss value decreased (P≤0.05) at 4% of blended lipid (PS and PKOo). The decrease in gloss could be explained by the coalescence and creaming of the lipid droplets during drying. PS caused an increase in surface roughness

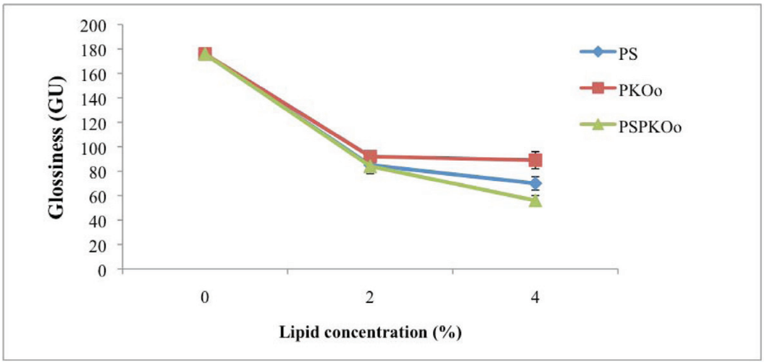

Fig. 3: Glossiness of Chito-San-Lipid Edible Film as a Function of Lipid Concentration (Error Bars are Standard Error of the Mean of Three Measurements).

since it is solid. Formation of lipid droplets and their development during film drying resulted in the interruption of the chitosan matrix, thus increasing internal heterogeneity and surface roughness of film.

CONCLUSION

In conclusion, incorporation of lipids (PS and PKOo) into chitosan film significantly decreased ($P \leq 0.05$) the WVT of film indicating improved moisture barrier properties. Overall, the addition of PS and PKOo into chitosan film significantly increased ($P \leq 0.05$) the opacity but decreased the glossiness of film. There was no significant difference in mechanical properties in terms of tensile strength and film elongation but there was a significant difference ($P \leq 0.05$) in Young's modulus among films, with chitosan film containing 2% of PKOo showing the highest value.

This study showed that lipid-chitosan edible film has better mechanical and moisture barrier properties than chitosan film. The decreased WVT of lipid-chitosan film can lead to a decrease in water loss hence its potential ability in maintaining firmness of fruits when such film is coated on fruits. The improved mechanical properties of lipid-chitosan film can help preserve the integrity of fruits during post harvest life.

BIOGRAPHY

Nurul Adilla was born on April 29, 1987 in Pahang, Malaysia. She graduated from SMK Seri Pekan, Pahang in 2004 and she continued her study in life science at Negeri Sembilan Matriculation College, Malaysia. She received her bachelor's degree in Food Science and Technology with a Minor in Islamic Food Law in 2011 from Universiti Teknologi MARA, Shah Alam, Malaysia. She initially started her graduate work as a graduate research assistant conducting research on edible fruit coating. Currently she is pursuing her M.Sc. course at Universiti Teknologi MARA, Shah Alam, Malaysia. She is married to Mohd Aziman and now lives with her husband in Shah Alam. Her husband graduated from Universiti Teknologi MARA, Shah Alam in Polymer Technology.

Halimahton Zahrah M.S. was born in December 6, 1952 in Perak, Malaysia. She obtained her B.Sc. (Hons.) in food science from Reading University, M.Sc. in food science from North Carolina State University and PhD in food science from Universiti Kebangsaan Malaysia. She joined the Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM) Shah Alam as a lecturer in 1976 and has held the posts of Head of Food Technology programme and Deputy Dean of Quality & Research, before her retirement in 1998. She has conducted research & consultation work with the food industry and government agencies on various areas, presented and published papers on edible fruit coating. Currently, she is a contract lecturer at the Faculty of Applied Sciences, UiTM.

Zaibunnisa had obtained her B.Sc from University of Nottingham,UK and MScin Food Science from UniversitiPutra Malaysia. She earned her PhD in Food Science (Flavour Chemistry) from Universiti Kebangsaan Malaysia. She has received several awards (2nd Runner up ASEAN Best Graduate Research and Excellent Service Award 2010) and had presented several papers on volatile oil extraction and stabilization technology on several conferences. She has supervised students for Master's and Doctorate degrees at UiTM.Dr. Zaibunnisa is also the author and co-author of a number of journal articles.

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