Effect of Coating Materials on the Properties of Chitosan-Starch-Based Edible Coatings

Noorsuhana Mohd Yusof¹, Junaidah Jai¹, Fazlena Hamzah¹

¹Faculty of Chemical Engineering, Universiti Teknologi MARA, Malaysia, 40450 Shah Alam, Selangor, Malaysia

Abstract. Edible coating is a thin layer on the surface that is used to extend shelf life of the fruit. The characteristics of the materials used and the properties of each substance in the coating solution will affect the quality of the edible coating. In this study, the use of chitosan at different concentrations has been assessed to produce an effective edible coating. Chitosan-starch edible coating with 1.5% (w/v) chitosan contents were chosen to give the best surface tension and wettability to coat fruit. Their structural and functional properties were also characterized through FTIR. Outcome from this study found that the shifting of peaks and the changes in the spectra were resulted due to the hydrogen bonding between OH and NH3+ of chitosan and OH group of starch. These shifts shown that the addition of glycerol promoted the hydrogen bonding interactions and plasticization effect of glycerol due to the hydrophilic nature. Additional of turmeric essential oil in the edible coating could enhance more its function to protect fruit and serves as antimicrobial agent due to the presence of phenolic group in its structure.

1. Introduction

Foodborne outbreaks, precocious decaying and economic losses are common problems related to fresh fruit retention. These problems have led to the advance of novel technologies and systems for food protection such as edible coating based on natural source materials. There are various methods of preservation that can be applied to extend shelf life of fruit. Currently, the used of edible coating in maintaining the fruits organoleptic properties are getting wide attention. These are due to its properties that able to control the moisture transfer, respiration process and oxidation process [1]. Furthermore, the used of edible coating are safe to be consume by consumer as it is made up from natural based [2].

Commonly, edible coating were made up of three types of hydrocolloids which are polysaccharides, proteins and lipids as its main bases [3]. In spite of using a type of hydrocolloid, the mixture of those three types hydrocolloids also can be used in producing the edible coating and this edible coating is known as composite edible coating [4]. Edible coating had the ability to be used with the presence of food preservatives such as antimicrobial agent, antioxidation agent, and chelating agents [5]. In this research study, turmeric oil was used as the antimicrobial agent. Turmeric oil consists of secondary metabolites that can act as antimicrobial agent such as turmerone, Ar-turmerone, curlone, cumene and many others [6]. The addition of turmeric essential oil in the edible coating film could enhance more its function as to protect fruit from deteriorate that causes by microbial and fungus.

Composite edible coating was used as the edible coating based which are the mixture of starch and chitosan. Starch is made up of amylase and amylopectin that are connected by hydrogen bond and formed the semi-crystalline granules naturally. Presence of water and heat could swelling and hydrating the granules which leads in increasing the viscosity of the solution [7]. Starch has poor mechanical properties which it has brittle and fragile characteristic. Thus, the presence of chitosan
could improve the edible coating of cassava starch based film due to its structural compatibility [8]. Chitosan is one of the biomaterials developed particularly for food and packaging applications. It is a linear polysaccharide consisting of β-(1→4)-linked 2-amino-2-deoxy-D-glucose residues, originating from deacetylated derivative of chitin, which is the second most abundant polysaccharide in nature after cellulose. It could effectively control food decay as it has strong antimicrobial and antifungal activities. Chitosan coating can reduce the respiration rate of food by controlling its gas permeability [9]. Chitosan could modify the starch granule size six times larger compared to the original size. Besides that, the hydroxyl group that present in starch will interact with the amino groups that present in chitosan. Furthermore, this interaction could reduce the starch degradation [10]. The mechanical properties of this composite edible coating are improved more by adding plasticizer such as glycerol and sorbitol.

2. Materials and methods

2.1. Materials
Local commercial brand starch (Brand Kapal ABC. Co) was used as the biopolymer for edible coating formulation. Food grade chitosan with 97% deacetylation (Nacalai Tesque, Japan) was used as composite coating. Acetic acid (Friendemann Schmidt, Australia) was added to dissolve the chitosan while glycerol (Merck, Germany) was added as plasticizer for coating formulation. Tween 80 (Systerm, Lab Sciences Engineering Sdn. Bhd., Malaysia) were used as emulsifier and turmeric was bought from the local market in Selangor.

2.2. Preparation of turmeric essential oil
Hydrodistillation extraction was used to extract turmeric essential oil. Fresh turmeric rhizomes of 500 g were washed to remove any dirt and dried using a paper towel. They were then being grated and placed in a 5 L round bottom flask with 1250 mL of distilled water for the extraction process [11]. After 4 hours of boiling, the oil was collected, protected from light and stored at 4°C.

2.3. Edible coating preparation
The edible coatings were prepared as described by [13]. Chitosan solution (100 ml) was prepared by dissolving chitosan 1.5% (w/v) in a 0.5% (w/v) acetic acid. To ensure that the chitosan is completely dissolved, the solution was stirred for 24 hours at 350 rpm until all the chitosan flakes disappear. A starch solution (100 ml) was then prepared by dispersed starch in a 0.5% (w/v) glycerol water solution to obtain (w/v) suspensions, which were heated on a hotplate at 75°C to a complete starch gelatinization [14]. The solution was stirred for 30 minutes at 350 rpm to overcome the starch from being coagulated. The blend coatings were obtained by the addition of chitosan-acetic acid solution to gelatinized starch-glycerol solutions. Tween 80 with concentration of 0.1% (w/v) was added as a surfactant to increase wettability [15]. After that, turmeric essential oil was added to the mixture.

2.4. Surface tension and wettability
In order to determine the adhesion properties of the coating to the surface, it can be done by measuring the contact angle of a standard liquid on the surface [16]. In this study, analysis of surface tension for all the samples has been done using Contact Angle Goniometer (AST Products, INC.) using sessile drop method to measure the contact angle. It was done by dropping the coating solution on the surface of the samples and recorded by Contact Angle Goniometer. Surface tension was calculated using the surface energy software (SE2500) while wettability was determined using the equation as reported by [17]. The spreading coefficient (Ws) may be defined by equation:

\[ W_s = W_a - W_c \]  

where, \( W_a \) and \( W_c \) are the work of adhesion and cohesion, as defined by equations (2) and (3), respectively, while \( \Theta \) is the contact angle and \( \gamma \) is the surface tension.

\[ W_a = \gamma L (1 + \cos(\Theta)) \]  

\[ W_c = \gamma L \]
\[ W_c = 2 \gamma L \]  

2.5. Fourier Transform Infrared (FTIR)

The spectra obtained were used to determine possible interactions of functional groups of chitosan on the starch-based coating by using Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer, USA) at wave number ranging from 400 to 4000 cm\(^{-1}\). The sample port was cleaned by using acetone to remove any variation caused by contamination on the scanning. The spectrum yields from the sample scanning were collected and studied.

3. Results and discussion

3.1. Surface tension and wettability analysis

Surface tension analysis involves the interaction between a solid-liquid surface. Chitosan-starch coating solution with different amount chitosan at 0.5, 1.0, 1.5 and 2.0% (w/v) were used. Figure 1 shows surface tension, \( W_a \), \( W_c \) and \( W_s \) for the designed coating formulations determined above. The increased amount of chitosan will affect the surface tension to reduced gradually. As reported by Cothran [18], suitable surface tension for fresh fruit coating solution was in the range of 28 to 38 dynes/cm. It can be seen that 1.5 and 2.0% (w/v) were in the acceptable range. The higher the amount of chitosan in the formulation, the lower the surface tension, reduced the hydrophilicity, water spreading and absorption [19]. The wettability (\( W_a \), \( W_c \)) of the solution on the surface were decreased while for \( W_s \) the trend was rising up. As mention by Cerquira et. al., better spreading of solution on the surface and the \( W_s \) value should be near to zero and in negative formed [20]. Since the surface tension was in the range with \( W_s \) value nearest to zero among all, 1.5% (w/v) of chitosan was selected as a coating material in coating solution.

![Figure 1. Effect of chitosan concentration (% w/v) on surface tension and wettability \( W_a \), \( W_c \) and \( W_s \) (dyne/cm).](image)

3.2. Fourier Transform Infrared (FTIR) analysis

The infrared spectra of raw materials are presented in figure 2. Infrared spectra of chitosan figure 2(a) at 3286.1 cm\(^{-1}\) was the OH stretching, which overlaps the NH stretching in the same region. The peak at 2872.68 cm\(^{-1}\) is typical C-H stretch. A small peak at 1641.53 cm\(^{-1}\) was due to the C=O stretching (amide I), and the peak at 1554.91 cm\(^{-1}\) and 1377.37 cm\(^{-1}\) have been reported as amide II and III peaks respectively. The sharp peaks at 1411.23 cm\(^{-1}\) correspond to the CH\(_3\) symmetrical deformation mode. The peak at 1151.63 cm\(^{-1}\) indicates the saccharide structure and the band at 1062.74 cm\(^{-1}\) was due to the C-O stretching vibration in chitosan vibrations [7].

In the spectrum for starch in figure 2(b), the broad band of starch at 3287.69 cm\(^{-1}\) is due to the hydrogen-bonded hydroxyl groups that contribute to the complex vibrational stretches. The sharp band
at 2924.28 cm\(^{-1}\) is characteristic of C-H stretches associated with the ring methane hydrogen atoms. The bands at 1636.46 and 1359.43 cm\(^{-1}\) are assigned to the \(\delta\) (O-H) bending of water and CH\(_2\), respectively [15]. The bands from 759.44 to 1148.83 attributed to the C-O bond stretching.

The spectra of glycerol in figure 2(d) has a wide band caused by stretching of O–H bonds with either inter or intra-molecular hydrogen bonds, that could also be formed by water molecules, at 1704.74 cm\(^{-1}\). An additional O–H vibrational mode was also seen at 1211.93 cm\(^{-1}\). The peak located at 2879.52 cm\(^{-1}\) was due to the C-H stretching. It is used as an indicator of the interaction of glycerol with chitosan, starch or more glycerol molecules [22].

Tween 80 shows many sharp absorption peaks that are due to the different functional groups present as shown in figure 2(e). Methyl group (–CH\(_3\)) shows absorption band at 2922.31 cm\(^{-1}\), while the band at 2856.54 cm\(^{-1}\) is due to –CH\(_2\) stretching. The band at 1735.34 cm\(^{-1}\) can be attributed to carbonyl C=O. Hydrophilic groups in this compound are polyethers which are polymers of ethylene oxide. These polymers are amphiphilic and soluble in water to help in binding the molecules of water in the emulsion. Carneiro-da-Cunha discussed the effect of adding Tween 80 to a coating solution due to its surface-active properties, aiming at improving the wettability of the coatings/films [23].

The major bioactives in turmeric are polyphenols, including curcumin, which is well known for its strong antioxidant activity [24]. As can be seen in figure 2(f), the infrared spectra at 3456.26 cm\(^{-1}\) is due to O-H stretching vibrations, while at 2961.29 cm\(^{-1}\) and its doublet at 2928.88 cm\(^{-1}\) are due to asymmetric and symmetric stretching vibrations of the CH\(_2\) group. Infrared spectra at 1376.77 cm\(^{-1}\) was the phenol or tertiary alcohol, O–H bend in which the properties of turmeric essential oil.

The blends film can be seen in figure 3. Changes in the spectra as well as the shifting of peaks due to the hydrogen bonding between OH and NH\(^{3+}\) of chitosan and OH group of starch was observed in the starch-based incorporated with chitosan. Yin et al. [25] reported that when two or more substances are mixed, physical blends versus chemical interactions are reflected by changes in characteristic spectral peaks [12]. The carbonyl, C = O-NHR, amine, NH\(_2\) and ammonium, NH\(^{3+}\) bands were situated in the region between 1400 cm\(^{-1}\) and 1700 cm\(^{-1}\). The carbonyl, C = O-NHR band was observed at 1645 cm\(^{-1}\), and the amine NH\(_2\) band at around 1560 cm\(^{-1}\) appeared as a small shoulder in pure chitosan. The wavenumber for C-OH group and C-O-C were reduced showing that OH group of

![Figure 2. FTIR of materials in chitosan-starch edible coating incorporated with turmeric essential oil; a) chitosan b) starch c) acetic acid d) glycerol e) Tween 80 f) turmeric essential oil.](image-url)
starch took part in hydrogen bond formation [14]. Due to stability and compatibility with hydrophilic biopolymeric packaging chain, glycerol being chosen as the most popular plasticizers used in edible coating due to the presence of hydroxyl group [23]. The addition of turmeric essential oil in the edible coating could act an effective antimicrobial activity due to the presence of phenolic group in its molecular structure.

![Figure 3. FTIR of blend film consists of chitosan, starch, acetic acid, glycerol, Tween 80 and turmeric essential oil.](image)

4. Conclusion
Coating material greatly affects the surface tension and together with the wettability of the coating solution on fruits. Chitosan shows a decreasing pattern of surface tension when different masses of it being added in 100 mL of the coating solution. Since this edible coating formulation for hydrophobic surfaces such as surfaces of fruits with natural protection layer, it is good to observe the reduction of the surface tension of the coating solution. Edible coating formed by blending of two polymers result in modified physical properties compared to edible coating made of the individual components. Chitosan-starch edible coating showed certain shift of peak patterns in FTIR. It resulted to exhibit good coating property due to the existence of their own functional groups which contribute to the characteristics in coating properties.

Acknowledgement
The authors would like to acknowledge Universiti Teknologi MARA for the financial support to carry out this research through 600-IRMI/MYRA 5/3/LESTARI (021/2017). Authors also thankful to the staff of Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam for their help in performing laboratory work.

References
[1] Sharif Z I M, Mustapha F A, Jai J, Yusof N M and Zaki N A M 2017 Chem. Eng. Res. Bull. 19(Special Issue on Conference) 145–53.
[2] Phani Tej R N 2012 Effect of composite edible coatings and abiotic stress on post harvest quality of fruits, McGill University.
[3] Bourtoom T 2008 Int. Food Res. J. 15(3) 237–48.
[4] Baraiya N S, Rao T V R, and Thakkar V R 2016 J. Agric. Sci. Technol., 18 93–107.
[5] Sabharwal P K, Garg M, Sadhu S D, Khas H, and Delhi N, World J. Pharm. Life Sci. WJPLS, 2(3) 160–70.
[6] Awasthi P K and Dixit S C 2005 Pharmacognosy 1(4) 312–6.
[7] Azeredo H 2012 “Edible Coatings,” in Advances in Fruit Processing Technologies, S. Rodrigues and F. Fabiano Andre Narciso, Eds. CRC Press, 345–62.
[8] Garcia M A, Pinotti A, Martino M N, and Zaritzky N E 2009 Characterization of Starch and Composite Edible Films and Coatings, 1900.
[9] Davis S P 2011 Chitosan: Manufacture, Properties, and Usage (Biotechnology in Agriculture, Industry and Medicine), UK. United Kingdom.

[10] Yongjia D, Xu S, Wenting S, Zhongkai Z, Zhiwei W, and Paiyun Z 2017 J. Food, 15(3) 327–35.

[11] Avanço G B et al. 2017 Food Control 73 806–13.

[12] Samadi M, Abidin Z Z, Yunus R, Awang Biak D R, Yoshida H and Lok E H 2017 Chinese J. Chem. Eng. 25(2) 216–22.

[13] Azevedo A N et al., 2014 Food Control, 43 1–9.

[14] Vásconez M B, Flores S K, Campos C A, Alvarado J, and Gerschenson L N 2009 Food Res. Int. 42(7) 762–9.

[15] Santos N S et al. 2012 Food Microb. (32) 345–53.

[16] Moncayo D and Buitrago G 2015 The surface properties of biopolymer-coated fruit: A review The surface properties of biopolymer-coated fruit: A review Propiedades de superficie en frutas recubiertas con biopolímeros no. April.

[17] Moncayo D, Buitrago G and Algecira N 2013 The surface properties of biopolymer-coated fruit, A review Propiedades de superficie en frutas recubiertas con biopolímeros 33(3) 11–6.

[18] Aug P and Cothran C D W 1945 KiET.

[19] Glycerol H and Films E 2018 How Glycerol and Water Contents Affect the Structural and Functional Properties of Starch-Based.

[20] Cerqueira M A, Lima Â M, Teixeira J A, Moreira R A and Vicente A A 2009 J. Food Eng. 94(3–4) 372–8.

[21] Liu P et al. 2011 Carbohydr. Polym., 85(1) 180–7.

[22] Liu H, Adhikari R, Guo Q and Adhikari B 2013 J. Food Eng. 116(2) 588–97.

[23] Cervera M F et al., 2004 Eur. J. Pharm. Biopharm. 58(1) 69–76.

[24] Miquel J, Bernd A, Sempere J M, Díaz-Alperi J and Ramírez A 2002 Arch. Gerontol. Geriatr. 34(1) 37–46.

[25] Vinet L and Zhedanov A 2010 Polym. Int. 433(November 1998) 429–32.