Effect of different amount chitosan, starch and glycerol in composite edible coating

N Mohd Yusof1*, J Jai1, Z I M Sharif1, F A Mustapha1 and S Pinijsuwan2

1Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
2School of Agro Industry, Mae Fah Luang University, 57100 Chiang Rai, Thailand

*noorsuhana@uitm.edu.my

Abstract. The experimental works involved the preparing of composite edible coating containing chitosan, starch, and glycerol to improve the shelf life of fruits. In this study, the number of raw materials was varied to determine the effect of each amount of raw materials towards the value of spreading, adhesion and cohesion coefficient on the fruit samples. The surface tension characteristic of the coatings is important for predicting the stability of the coatings during storage. 1.5 (% w/v) content of chitosan in coating solution was the best amount of chitosan to be used in formulating the chitosan-starch composite edible coating formulation while 2.0 (% v/v) amount of starch has got the nearest value to zero of spreading coefficient $W_s$, which make it the best formulation to be chose. Glycerol of 0.25 (% v/v) was used in formulating the starch composite edible coating formulation.

1. Introduction

From the moment a fruit or vegetable is harvested, it begins to decay because of the reactions break down cells from the inside out. Throughout the handling processes, storage and transportation, fruit products start to dry out, worsen and lose appearance within hours or days. These problems have led to the advance of methods including the application of technology by physical, chemical and biological means for food protection. Currently, the used of edible coating in maintaining the fruits organoleptic properties are getting wide attention due to its properties that able to control the moisture transfer, respiration process and oxidation process [1]. The used of edible coating is safe to be consumed as it is made up of natural-based [2].

Normally, edible coatings were made up of three types of hydrocolloids which are lipids, polysaccharides, and proteins as its main component [3]. The mixture of those three types hydrocolloids also can be used in producing the edible coating in spite of using an only a single type of hydrocolloid and this edible coating is known as a composite edible coating [4]. To improve the ability of the edible coating, it can be added with food preservatives such as antimicrobial agent, antioxidation agent, and chelating agents [5]. In this research, turmeric oil was used as the antimicrobial agent. The secondary metabolites inside turmeric oil such as turmerone, Ar-turmerone, curlone, cumene, and many others can act as an antimicrobial agent [6]. The presence of turmeric essential oil in the edible coating film could enhance its function as to protect the fruit from deteriorating that causes by microbial and fungus.

Composite edible coating from the mixture of starch and chitosan was used in this research as the edible coating based. Starch is made up of amylose and amylopectin that are connected by hydrogen
bonds and formed the semi-crystalline granules naturally. Swelling and hydrating of granules with the presence of water and heat lead in increasing the viscosity of the solution [7]. Unfortunately, the starch itself has poor mechanical properties which it has a brittle and fragile characteristic. Thus, the presence of chitosan could improve the edible coating of 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 deacetyl derivative of chitin. Chitin is the second most abundant polysaccharide in nature after cellulose where it could effectively control food decay as it has strong antimicrobial and antifungal activities. By controlling the gas permeability, chitosan coating can reduce the respiration rate of food [9]. Chitosan could modify the starch granule size six times larger compared to the original size. The hydroxyl group in starch will interact with the amino group that presents in chitosan where this interaction could reduce starch degradation [10]. By the addition of plasticizer such as glycerol and sorbitol, the mechanical properties of this composite edible coating can be improved more.

2. Materials and method

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

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

2.3. Edible coating preparation
The edible coatings were prepared as described by [12]. Chitosan solution (100 ml) was prepared by dissolving chitosan 1.5% (w/v) in a 0.5% (w/v) acetic acid. The solution was stirred for 24 hours at 350 rpm until all the chitosan flakes disappear to ensure that the chitosan is completely dissolved. 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 and were heated on a hotplate at 75 °C to a complete starch gelatinization [13]. To overcome the starch from being coagulated, the solution was stirred for 30 minutes at 350 rpm. The blend coatings were obtained by the addition of chitosan-acetic acid solution to gelatinized starch-glycerol solutions. Tween 80 with a concentration of 0.1% (w/v) was added as a surfactant to increase wettability [14].

2.4. Surface tension and wettability
The contact angle of a standard liquid on the surface has been measured to examine the adhesion properties of the coating [15]. The analysis of surface tension for all the samples has been done using Contact Angle Goniometer (AST Products, INC.) using the sessile drop method to measure the contact angle by dropping the coating solution on the surface of the samples and recorded by Contact Angle Goniometer. Surface energy software (SE2500) was used to calculate surface tension while wettability was determined using the equation as reported by [16]. The equation below has been used to determine the spreading coefficient (W):

\[
W = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}
\]
\[ W_s = W_a - W_c \] (1)

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.

\[ W_a = \gamma L \ (1 + \cos(\Theta)) \] (2)

\[ W_c = 2 \gamma L \] (3)

3. Results and discussion

3.1. Effect of chitosan on surface tension

The result in Figure 1 shows that the surface tension along with the adhesion coefficient (\( W_a \)) and cohesion coefficient (\( W_c \)) decreased as the chitosan concentration increased independent of plasticizer (glycerol) concentration. It also can be seen that an increase in the concentration of chitosan in coating solution brought about a slightly increment in the spreading coefficient (\( W_s \)) values of the coatings. Starting with 0.5, 1.0, 1.5 and 2.0 (% w/v) of chitosan, the surface tension of the coating solution is 48.93, 46.79, 36.03, and 34.07 dyne/cm respectively, which can be seen decrease significantly. Based on these results, only 1.5 and 2.0 (% w/v) content of chitosan are in the acceptable range of surface tension. Meanwhile, the formulation had an increased in spreading coefficient (\( W_s \)) as the chitosan concentration increased. In this situation, the nearest value to zero is the best to choose. This is because of high energy loss when spreading on the surface of a strawberry. Even though \( W_s \) for 2.0 (% w/v) amount of chitosan was better than others in terms of spreading, they were not compatible to use in formulating edible coating emulsion due to the lower viscosity that can reduce the ability of coating. Therefore, this can be concluded that between 1.5 and 2.0 (% w/v), 1.5 (% w/v) content of chitosan in coating solution was the best amount of chitosan to be used in formulating the chitosan-starch composite edible coating formulation. The wettability of the coatings attributed to the higher hydrophobicity of the chitosan surface layer, which was the higher amount of chitosan involved, the higher tendency of the coatings to absorb moisture which was related to the role of the available hydrophobic acetyl groups present in the chain of chitosan [17].

![Figure 1. Surface tension and wettability at different amounts of chitosan.](image-url)
3.2. Effect of starch on surface tension

By referring to Figure 2, it is noticeable that the trend of surface tension is decreasing with the increasing amount of starch. The decreased of surface tension happened because of the interaction between hydroxyl groups of the chitosan and starch consumed more polar groups [18]. It is also clearly shown that surface tension of 1.0 ( % v/v) of starch concentration in coating solution with a value of 46.79 (dyne/cm) has exceeded the general range for surface tension. Thus, only 2.0 and 4.0 ( % v/v) amount of starch was considered as a suitable amount of starch to be added in the formulation. Out of these two formulations, 2.0 (% v/v) amount of starch has got the nearest value to zero of spreading coefficient W_s, which makes it the best formulation to be chosen. This was indicated to the high ability to spreading. As mentioned by Cerqueira et al. (2009), the W_s value should be in negative form and nearest to zero because the higher the value of W_s, the incomplete wetting of the surface can occur (contact angle is higher than 90°). On the other hand, the number of raw materials should used as minimum as possible so that it can reduce the cost.

![Figure 2. Surface tension and wettability at different amounts of starch.](image)

3.3. Effect of glycerol on surface tension

The stability and edibility properties of glycerol made it widely used as plasticizers [17]. The thermoplasticity of the chitosan-starch coating has been imparted by that important role of glycerol. Figure 3 shows that the surface tension of 0.25, 0.5 and 0.75 ( % v/v) of glycerol concentration in coating solution with a value of 37.74, 31.62 and 33.10 (dyne/cm) respectively are all in the range of the general range for surface tension. Thus, they were all considered as a suitable amount of glycerol to be added in the formulation. In order to choose the right amount of glycerol had the nearest value to zero of W_s was being selected which is belongs to 0.25 ( % v/v) of glycerol concentration. This indicates that the coating has more barrier properties, as absorption is not favored. The morphology of films affected by the glycerol concentration, as well as the surface properties significantly affected by the swelling properties [20]. Moreover, the higher amount of glycerol used can cause the coating solution to be soggy due to the amount of hydroxyl group content in glycerol is higher compared in the chitosan-starch and tend to bond with the hydroxyl group that presents in the moisture of surrounding. When plasticizer has been introduced into a chitosan-starch matrix, the intra-molecular affinity between the starch chains reduced by the formation of hydrogen bonds between plasticizer and chitosan-starch molecules. Thus, the best amount of glycerol of 0.25 ( % v/v) was used in producing the starch composite edible coating formulation.
Figure 3. Surface tension and wettability at different amounts of glycerol.

4. Conclusion
This work shows that chitosan-starch based can be used as coatings to coat fruits while glycerol can strongly affect the stability properties. The main remarks are as follows: high chitosan content which causes less effective as it will disturb the spreading process thus 1.5 (% w/v) is choosing; 2.0 (% v/v) amount of starch has a high ability in spreading and the contact angle is very sensitive to starch content in the mixture; coatings containing 0.25 (% v/v) glycerol contributes a lower moisture absorption capacity than coatings with a higher glycerol content. The optimization of the composition of the coating solutions can be made by considering three parameters: the surface tension, the adhesion coefficient, the cohesion coefficient, and the spreading coefficient. As a conclusion, the ratio for chitosan:starch:glycerol needed to develop a chitosan-starch based edible coating is 1.5:2.0:0.25.

5. Acknowledgment
The authors would like to thank Institute of Research Management & Innovation (IRMI), UiTM Shah Alam for providing financial support under UiTM Internal Research Grant LESTARI, grant no.: 600-IRMI/MYRA 5/3/LESTAR I (021/2017) to carry out this research.

References

[1] Sharif Z I M Mustapha F A Jai J Yusof N M and Zaki N A M 2017 Review on methods for preservation and natural preservatives for extending the food longevity Chem. Eng. Res. Bull. 19, p. 145–153.
[2] Phani Tej R N 2012 Effect of composite edible coatings and abiotic stress on post harvest quality of fruits New York: Mc. Graw-Hill.
[3] Bourtoom T 2008 Review Article Edible films and coatings : characteristics and properties Int. Food Res. J. 15, p. 237–248.
[4] Baraiya N S Rao T V R and Thakkar V R 2016 Composite coating as a carrier of antioxidants improves the postharvest shelf life and quality of table grapes (Vitis vinifera L. var. Thompson Seedless) J. Agric. Sci. Technol. 18, p. 93–107.
[5] Sabharwal P K Garg M Sadhu S D Khas H and Delhi N 2016 Advancement in conventional packaging – edible World J. Pharm. Life Sci. 2, p. 160–170.
[6] Awasthi P K and Dixit S C 2005 Chemical Composition of Curcuma Longa Leaves and Rhizome Oil from the Plains of Northern India Pharmacognosy 1, p. 312–16.
[7] Azeredo H 2012 Edible Coatings in Advances in Fruit Processing Technologies Rodrigues S and Fabiano F CRC Press p. 345–362.
[8] García M A Pinotti A Martino M N and Zaritzky N E 2009 Characterization of Starch and Composite Edible Films and Coatings Edible Films and Coatings for Food Applications eds Huber K Embuscado M p. 169-209.
[9] Davis S P 2011 Chitosan: Manufacture, Properties, and Usage (Biotechnology in Agriculture, Industry and Medicine) UK.
[10] Yongjia D Xu S Wenting S Zhongkai Z Zhiwei W and Paiyun Z 2017 Effect of interactions between starch and chitosan on waxy maize starch physicochemical and digestion properties J. Food 15, p. 327–335.
[11] Avanço G B Ferreira F D Abreu Filho B A D Mikcha J M G Machinski Jr M 2017 Curcuma longa L. essential oil composition, antioxidant effect, and effect on Fusarium verticillioides and fumonisin production Food Control 73, p. 806–813.
[12] Azevedo A N Buarque P R Oliveira C E M Blank A F Alves P B Nunes M L Anquino Santana L C L 2014 Response surface methodology for optimisation of edible chitosan coating formulations incorporating essential oil against several foodborne pathogenic bacteria Food Control 43, p. 1–9.
[13] Vásconez M B Flores S K Campos C A Alvarado J and Gerschenson L N 2009 Antimicrobial activity and physical properties of chitosan-tapioca starch based edible films and coatings Food Res. Int. 42, p. 762–769.
[14] Santos N S Athayde Aguiar A J Oliveira C E Veríssimo Sales C Melo Silva S Sousa Silva R Stamford T C Souza E L 2012 Efficacy of the application of a coating composed of chitosan and Origanum vulgare L. essential oil to control Rhizopus stolonifer and Aspergillus niger in grapes (Vitis labrusca L.) Food Microb. 32, p. 345–353.
[15] Moncayo D and Buitrago G 2015 The surface properties of biopolymer-coated fruit : A review Ingeniería e Investigación 33, p. 11–16.
[16] Moncayo D Buitrago G and Algecira N 2013 The surface properties of biopolymer-coated fruit : A review Ingeniería e Investigación 33, p. 11–16.
[17] Bangyekan C Aht-ong D and Srikulkit K 2006 Preparation and properties evaluation of chitosan-coated cassava starch films Carbohydrate Polymers 63, p. 61–71.
[18] Shahbazi M Rajabzadeh G and Sotoodeh S 2017 International Journal of Biological Macromolecules Functional characteristics, wettability properties and cytotoxic effect of starch film incorporated with multi-walled and hydroxylated multi-walled carbon nanotubes Int. J. Biol. Macromol. 104, p. 597–605.
[19] Cerqueira M A Lima A M Teixeira J A Moreira R A and Vicente A A 2009 Suitability of novel galactomannans as edible coatings for tropical fruits J. Food Eng. 94, p. 372–378.
[20] Laohakunjit N and Noomhorm A 2004 Effect of Plasticizers on Mechanical and Barrier Properties of Rice Starch Film Starch 56, p. 348–56.