Optimization of Starch Composite Edible Coating Formulation on Fresh-Cut “Fuji” Apple through Surface Tension, Wettability and FTIR Spectroscopy

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Abstract. Fresh-cut “Fuji” apples are easily oxidised and deteriorated. Therefore, starch composite edible coating formulation were formulated to extend its life span. In this study, the effect of different amount of carboxymethyl cellulose (CMC) (1, 2, 3 and 4% (w/v)), glycerol (1, 2, 3 and 4% (v/v)) and turmeric oil (TO) (50, 175 and 300ppm) were evaluated through surface tension and wettability analysis. Furthermore, the molecular interaction between raw materials of the edible coating film were analysed through FTIR analysis. The results showed that formulation using 2% (w/v) CMC and 2% (v/v) glycerol were the best amount to formulate composite edible coating. Meanwhile, the range of turmeric oil were 50, 175 and 300ppm suitable to be used for further analysis on fresh-cut “Fuji” apples as it does not exceed the general rule of surface tension. The findings for intermolecular reaction of raw materials revealed that there were interactions occurred when citric acid (CA), glycerol and CMC were added; further enhanced functionality of the starch. Besides that, FTIR showed that the functional group in turmeric oil that acts as an active compound to inhibit the oxidation process and microbial activities were present in the edible coating film.

1. Introduction
Maintaining fresh-cut “Fuji” apples quality and organoleptic properties is difficult due to elimination of the apple skin and the cutting process [1]. This could lead to oxidation process and growth of microbial, thus, decrease the life spans of the fresh-cut “Fuji” apples. Edible coating is one of the preservation method that able to preserve the quality of the fresh-cut “Fuji” apples by controlling the water permeability, exchange of gases, oxidation process, microbial growth etc. Edible coating is made from hydrocolloid (polysaccharide, protein and lipid). Composite edible coating are formed when two or more types of hydrocolloid are used as the base material that provide benefits to each other along with reducing their drawbacks [2]. According to Cothran et. al. [3], the surface tension value should be in the range of 28 to 38 dyne/cm to formulate coating for fruits with uniform surface. Meanwhile, the great wettability should be high in work of adhesion (Wₐ), low in work of cohesion (Wₖ) and negative value that near to zero for spreading coefficient (Wₛ) [4]. The edible coating properties could be enhanced with addition of preservatives such as turmeric oil due to the presence of active compounds which are phenolic compound, curcumin, sesquiterpenes etc. [5]. Therefore, the aims of this research are to i) optimize the best amount of raw materials in forming the starch composite edible coating formulation through surface tension and wettability, and ii) determine the molecular interaction that occurred during formation of starch composite edible coating film.
2. Material and methodology

2.1. Materials
Fresh ‘Fuji’ apples were acquired from local market in Shah Alam, Selangor. Cassava flour (Cap Kapal ABC Co., Malaysia) and CMC (Novelecell, Malaysia) were used as base materials for composite coating formulation. CA (Merck, United State) served as the cross-linking agent. Glycerol (Merck, United State) was used as plasticizer and turmeric oil (Soul, Malaysia) was used as antioxidation agents. Below figure 1 shows the flowchart of the research process.

![Figure 1. The flowchart of research process](image)

2.2. Preparation of edible coating formulation
The 6% (w/v) cassava starch was diluted in 100 mL of distilled water (DW) for 40 minutes at temperature 80°C. Then, 0.5% (w/v) CA was added in the formulation as the cross-linking agent. Glycerol (1, 2, 3 and 4% (v/v) glycerol) was added in the formulation as plasticizer. The CMC (1, 2, 3 and 4% (w/v) CMC) was solubilized in 100 mL of distilled water for 30 minutes at 75°C. pH of the formulation was titrated with standard alkaline solution to pH 5.6 [6]. The formulation was cooled down at 40°C and stirred slowly for 20 minutes to release the air bubbles. Lastly, TO (50, 175 and 300ppm) was added into the formulation.

2.3. Surface tension
Surface tension analysis was used in order to determine the number of energy needed to raise the surface per unit area [7]. Sessile drop method was used to analyse the contact angle by using Contact Angle Goniometer (AST Products, INC.). The formulation was dropped on the surface of fresh-cut “Fuji” apples and the process were recorded by Contact Angle Goniometer video. Surface tension was calculated using the surface energy software (SE2500). This process was replicated for four times for each of the formulation.

2.4. Wettability
Wettability is to ascertain the emulsion ability in spreading, its adhesion on solid surface and also their cohesion work. Wettability analysis was calculated in order to determine the value of spreading coefficient (Ws). The closest Ws value towards zero indicates the best in spreading activity and its adhesion between emulsion and surface fresh-cut ‘Fuji’ apple. This analysis was done based on J. Viera method. Ws was calculated according to below equation. Where Ws is work of adhesion, Wc is work of cohesion, Wa is spreading coefficient and γL is surface tension.

\[
W_s = W_a - W_c \\
W_a = \gamma_L (1+\cos(\Theta)) \\
W_c = 2 \gamma_L
\]

2.5. Fourier transform infrared (FTIR) spectroscopy
FT-IR spectroscopy was used to determine the molecular interaction between raw materials during formation of edible coating [9]. The changes of the wavelength and transmittance were resulted from the molecular interaction between the raw materials in forming the edible coating film.
3. Results and discussion

3.1. Surface tension and wettability analysis

3.1.1. Different amount of carboxymethyl cellulose (CMC). CMC was used as filler in starch composite edible coating formulation and was represented as C. Analysis from table 1 shows that the surface tension value decreased with increased amount of CMC added which were 37.49 dyne/cm, 37.92 dyne/cm, 30.18 dyne/cm and 28.34 dyne/cm, respectively. Therefore, it can be considered that CMC has surface active properties due to increase in formulation viscosity and tends to have high water vapour permeability. It can be analysed that C2 formulation had $W_s$ value near to zero (-25.04 ± 25.72 dyne/cm) and had the highest $W_a$ (40.66 ± 30.68 dyne/cm) compared to others. This was due to its high energy loss when spreading on the surface of fresh cut ‘Fuji’ apples flesh. This finding was in agreement with Choi et al. [10] studies that reported that high value work of adhesion attributed to huge loss of energy during spreading process. Table 1 also shows the $W_s$ value for C3 formulation was low due to high CMC content which was less effective as it would flock and disturb the spreading process. Tongdeesoontorn et al. [11] also reported similar findings which the use of higher CMC content could lead to congregate. Meanwhile, the $W_c$ value decreased as the amount of CMC increased. Even though $W_c$ for C3 and C4 were better than C2, they were not compatible to be used in the formulation of edible coating emulsion due to the high amount of CMC and low $W_a$ and $W_s$. Therefore, it can be concluded that C2 was the best amount of CMC to be used in formulating the starch composite edible coating.

3.1.2. Different amount of glycerol. Table 1 also shows the surface tension and wettability for formulation that consists different amount of glycerol (G1 – G4). The result shows that the surface tension of G4 has exceeded the general range for surface tension. Thus, only G1, G2 and G3 were considered as the suitable amount of glycerol to be added in formulation. Furthermore, G2 had the highest value of $W_s$ and $W_a$ compared to others. This finding was observed due to the high ability in adhesion and spreading. The similar findings were found from Casariego et al. [12] which reported that concentration of glycerol influence the surface properties of coating. Increased in glycerol concentration will lead to decrease of $W_a$ and $W_s$. $W_c$ was decreasing with increasing amount of glycerol. According to Garcia et al. [13], the maximum amount of glycerol that is suitable to be used with starch edible coating formulation is 20 g/L. Therefore, volume of glycerol in formulation of G3 was not compatible to be used. Higher amount of plasticizer used will lead to the formation of soggy coating film due to the higher amount of glycerol in the hydroxyl group compared to the one in the starch and it tends to bond with the hydroxyl group that present in moisture of surrounding [14]. Thus, the optimum amount of glycerol in G2 was used to formulate the starch composite edible coating.

3.1.3. Different amount of turmeric oil (TO). Table 1 also tabulates the analysis of surface tension and wettability for different concentrations of turmeric oil (T1 – T4). There was a slightly decrease in surface tension, $W_s$ and $W_c$ values as the concentration of turmeric oil increased by not more than 1 dyne/cm. This finding was in agreement with Yusof et al.[15] which reported that that increase in turmeric oil concentration will decrease the surface tension value. T2 has the highest $W_s$ value which is 49.53 dyne/cm compared to T3 which is 47.28 dyne/cm. This shows that formulation T2 (49.53 dyne/cm) has the best $W_s$ on the surface of fresh-cut ‘Fuji’ apples flesh followed by T3, T4 and T1. The $W_s$ value appeared to decrease with increasing concentration of turmeric oil content, which is likely due to addition of oil (lipid) in the emulsion that leads to expansion of the emulsion droplet. Therefore, it can be concluded that addition of turmeric oil was not significant to the surface tension, $W_s$, $W_c$, and $W_s$. Hence, the concentration range of turmeric in this study can be used in the formulation.
Table 1. The surface tension and wettability analysis on different amount of carboxymethyl cellulose (CMC), glycerol and turmeric oil.

|     | CMC (%w/v) | Glycerol (%v/v) | Concentration of TO (ppm) | Surface Tension (dyne/cm) | Wettability (dyne/cm) |
|-----|-------------|-----------------|---------------------------|---------------------------|----------------------|
|     |             |                 |                           | W_a                       | W_c                  | W_s                  |
| C1  | 1           | 2               | 0                         | 37.49                     | 26.01±21.57          | 74.99±1.56           | -48.99±21.76         |
| C2  | 2           | 2               | 0                         | 37.92                     | 40.66±30.68          | 75.84±1.83           | -25.04±25.72         |
| C3  | 3           | 2               | 0                         | 30.18                     | 15.70±10.04          | 60.35±1.59           | -44.65±11.01         |
| C4  | 4           | 2               | 0                         | 28.34                     | 33.19±11.53          | 56.68±3.50           | -27.99±10.12         |
| G1  | 2           | 1               | 0                         | 34.69                     | 35.43±25.49          | 69.39±2.68           | -33.97±26.11         |
| G2  | 2           | 2               | 0                         | 37.92                     | 40.66±30.68          | 75.84±1.83           | -25.04±25.72         |
| G3  | 2           | 3               | 0                         | 28.63                     | 22.37±26.77          | 57.26±3.7           | -34.89±25.27         |
| G4  | 2           | 4               | 0                         | 27.64                     | 8.94±12.98           | 55.29±1.34           | -46.33±13.4          |
| T1  | 2           | 2               | 50                        | 37.92                     | 40.66±30.68          | 75.84±1.83           | -25.04±25.72         |
| T2  | 2           | 2               | 175                       | 37.38                     | 47.28±20.11          | 74.75±0.61           | -27.47±19.50         |
| T3  | 2           | 2               | 300                       | 37.11                     | 44.49±39.16          | 74.22±2.71           | -29.73±38.49         |
| T4  | 2           | 2               | 175                       | 37.38                     | 47.28±20.11          | 74.75±0.61           | -27.47±19.50         |

3.2. Molecular interaction analysis through FTIR

Figure 2 shows, with the additional of citric acids (CA) spectra (B), the cross-linking between CA and starch occurred. It can be seen that a new peak produced at 1716.28 cm\(^{-1}\) and the absorbance reading was reduced at 3306.20 cm\(^{-1}\) to 3291.17 cm\(^{-1}\). They were reduced due to esterification reaction occurred. Besides that, the hydrolysis reaction that occurred at the glycosidic linkage was one of the factors that caused the peak to decrease. Similar findings were found by N. Reddy [16].

When glycerol was added into the formulation in spectra (C), further decreased was occurred at the peak of –OH groups which was from 3291.17 cm\(^{-1}\) to 3271.78 cm\(^{-1}\). This is because of the esterification reaction occurred further between the -COOH group in CA with –OH groups of glycerol. The peak of 1716.28 cm\(^{-1}\) and 1591.53 cm\(^{-1}\) were disappeared due to the additional CA and glycerol together will lead to the high moisture content in the coating film as water absorption wavelength appeared at 1642.72 cm\(^{-1}\). Increase in peak occurred at 2931.93 cm\(^{-1}\) and 1412.31 cm\(^{-1}\). This indicates high content in hydrogen bond concentrations and hydrogen interaction between glycerol, starch and CA. Furthermore, it occurred due to the plasticization effect and this was also reported by Liu et al. [17].

CMC was added to the mixture to stabilize the mixture due to higher moisture permeability after the addition of citric acid and glycerol as shown in spectra in figure 2 (D). The addition of CMC caused the peak of water absorption at 1642.72 cm\(^{-1}\) to disappear. This similar finding was also found out by Tongdeesoontorn [11]. When the turmeric oil was added as shown in spectra (F), it can be observed that there was presence of phenol compounds at the peak 3271.35 cm\(^{-1}\) (O-H stretch) and 1325.45 cm\(^{-1}\) (C=C). The turmeric oil active compounds were present in the edible coating film when it was incorporated with TO. The active compounds present could postpone the oxidation process and growth of microbial.
Figure 2. Spectrum of Molecular Interaction: A) Starch, B) Starch and CA, C) Starch, CA and Glycerol, D) Starch, CA, Glycerol and CMC, E) Starch, CA, Glycerol, CMC and Sodium Hydroxide F) Starch, CA, Glycerol, CMC, Sodium Hydroxide and TO.

4. Conclusion

Results obtained from the research show that the formulation of starch composite edible coating could be formulated by using 6% (w/v) starch, 2% (w/v) CMC, 2% (v/v) glycerol and 0.5% (w/v) CA. This formulation was possibly could contributing to prolong the life span of fresh-cut “Fuji” apples. From the FTIR analysis, the molecular interaction occurred between raw materials. This can be observed due to the presence of ester bonds which represent the cross-linking process. It also can be observed that plasticization process occurred when concentration of hydrogen bond for alkene were increased and the moisture of the starch composite edible coating film was decreased when CMC was added as filler. This can be recommended that to used CMC, glycerol and CA as the raw materials to be used for edible coating for fresh-cut fruits due to their compatibility in forming the coating film.

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