CMC- Banana Flour Edible Film: Production & Characterization

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A study has been conducted to produce edible film from banana flour and carboxylmethyl cellulose (CMC) with glycerol as plasticizer. The CMC- banana films were synthesized by casting method with different CMC concentration (0, 5, 10 and 15% w/w). The characterization of the film is made based on mechanical strength, solubility, FTIR, water vapor permeability (WVP) and color. The thicknesses of the films range between 0.133±0.05 to 0.165±0.09 mm. As CMC is added into banana film from 0 to 10%w/w, the increase in tensile (TS) were found with the range of 1.86±0.08MPa to 1.99±0.26MPa and reduced upon addition of 15%CMC with similar trend of elongation at break (EAB). The CMC-banana films have the solubility range from 41.39±0.19 to 50.55±6.16% and this study found that the solubility reduced upon addition of CMC between 5 to 15% and increase in solubility as the temperature increase (25, 39, 90°C). WVP in the CMC-banana film is reduced in 5%CMC addition (3.7± 0.16 x10^{-9} g.mm/h.cm^{2}.Pa) and keep increasing as CMC increase. The film form brownish color due to its natural content banana flour. All the parameters of films were compared with other natural sources of edible film and it is believed that CMC-banana flour film applicable to certain type of food packaging application.

Keywords— Banana flour, Carboxylmetyl cellulose (CMC), Edible film

I. INTRODUCTION

The demand of good quality and longer shelf life foods and increasing awareness to reduce disposal packaging materials and dependence of petroleum packaging sources [1] have driven the extensive research of edible film [2],[3]. Edible film is the thin layer made up of any edible material used widely in primary food packaging [4],[5]. The composite edible film is said to have better properties than single component film as it minimizing the disadvantage of single component film at the same time utilize each component's strengths [6]. The application of natural blends from agricultural sources has unique properties and appears to be new sources of film [7]. Romero-Bastida *et al.*, (2005) in their study revealed that one of the interesting renewable source of edible film production is banana fruit [7]

As starch has been identified to have many application since it is renewable source, easy to handle, inexpensive and widely available [2], the exploration of alternative starches has been widely conducted to obtain better functional and physicochemical characteristics. Due to this fact, the application of non-conventional starch made from banana has been made. Recent study has been conducted by Romero- Bastida et al.,(2005) which isolated starch from banana, okenia and mango for edible film and concluded that banana film has highest tensile strength (TS) compared to okenia and mango. In other work, the effect of different plasticizer in banana film has been investigated [8]. The permeability of oxygen and mechanical properties of banana films were evaluated by Sothornvit & Pitak.,(2007)[9]. Jirukkakul., (2016) on the other hand studied the edible film production from unriped banana flour and riped banana puree [10]. Meanwhile, the optimization of process conditions for plantain banana film [1] and the comparative study of film from plantain banana flour and starch [11] were both conducted by F.M Pelissari *et al.*,(2012). The findings of work agree that banana starch has big potential in edible film..

Carboxylmethyl cellulose (CMC) in the other hand is the polysaccharides derive from cellulose and currently has important role in polymer industry with the wide range application in food, drug reduction, textiles, detergents, papers and flocculation. In film production, this modified form of cellulose is able to dissolved in water, firm by it thus improve the film strength[12]. Thus, many studies were found to use CMC as the component in edible film such as CMC-pullulun film[3], CMC-sago starch film[12], CMC-cassava starch film[13], CMC-corn starch film[14] and CMC-sorghum starch [15] and found that addition of CMC is able to produce good film properties.

Because there is no study conducted from the combination of banana and CMC in edible film yet, the objective of the present study are to produce, analyze the characterization and compare the properties with natural biodegradable film.

II. MATERIAL & METHODOLOGY

A. *Materials*

The banana flour was purchased from Secret Barn Sdn Bhd (Kedah, Malaysia) as major component in the film. The flour used *Musa x paradisiaca* or also known as *Pisang Nangka* and was treated with sodium metabisulfite (NaMS) during the manufacturing to prevent the browning reaction. Food-grade carboxylmethyl cellulose (CMC) and glycerol were obtained from Food Technology Laboratory Faculty of Chemical Engineering UiTM Shah Alam.

B. *Methods*

1) *Film preparation*

The films were prepared by casting method and followed F.M Pelissari et al, (2013) method with some modifications. 100 ml of distilled water was heated at temperature 70 to 95°C[1]. Banana flour were mixed with different concentration of CMC (0, 5, 10 and 15% w/w)[13]and added slowly in the mixture in high shear to obtain homogenization. Glycerol (40% w/w) was added at temperature 70°C to give plasticizer effect [1] and the mixture was heated until gelatinization is achieved. 15 ml of mixtures were casted on 8cm petri dish and dried in oven at 40°C for 24 hours.

2) *Film thickness*

The thickness of the film was measured by using Mitutoyo Coolant Proof Digital Micrometer with accuracy of 0.001mm. The average thickness is taken at three random points on the samples.

3) Mechanical strength

The mechanical strength were measured according to the standard testing method ASTM D882-10 using Instron Universal Testing Machine model 55669 with 50kN load cell. The samples were cut into rectangular centre with 70mm length and 25mm width to be mounted on the tensile grips. The initial gauge length and the crosshead speed were set to 50 mm and 50mm/min [13]. The elongation at break is calculated as below

$$\varepsilon = \frac{\Delta l}{l} = \frac{l - l_o}{l_o} x100\%$$

Where l is the displacement (mm) and l_o is the gauge length (mm)

4) Solubility

The solubility test was performed using a method produced by Perez-Gago & Krotcha, (2001) with some modifications[16]. The films were cut into 2cmx2cm size and soaked in 50 ml distilled water at different temperatures (25, 37 and 90°C) for 5 minutes. The soaked sample then were dried in oven at 40°C for 24 hours. The solubility percentage was calculated by the formula

$$Solubility\ (\%) = \frac{W_i - W_f}{W_i} x\ 100\%$$

Where W_i is the initial dry weight and W_f is the final dry weight of the samples.

5) FTIR

The films were prepared for all infrared spectra by using Perkin Elmer Spectrum One FTIR Spectrophotometer. The scanning frequencies ranged from 4000 to 551cm^{-1} with spectra resolution of 4cm^{-1}. The test was conducted to determine the functional groups present and analyze the effect of interaction between banana flour and CMC in the films. All measurements were held in room temperature laboratory.

6) Water vapor permeability

The water vapor permeability test was conducted by (Jahit et al.,2016) method with some modifications [17]. Modified polystyrene cups (diameter 5.5cm) containing 10g blue of silica gels were individually sealed by each films and place in desiccator. A cup of distilled water was placed at the same distance from all the tested cups. The test cups were weight for every one hour for seven hours. The water vapor permeability was calculated based on formula below

$$WVP(\frac{g.mm}{h.cm^2.Pa}) = \frac{\Delta W\ (g)x\ Film\ thickness\ (mm)}{Time\ (h)x\ Test\ Area\ (cm^2)x\Delta P(Pa)}$$

Where ΔW is the weight difference and ΔP is the partial pressure.

7) Color

The colors of films were analyzed at three different points by Konica Minolta Chroma Meter model CR-400 in the transmittance mode, with the classification of the CIELAB and illuminant D65 (daylight). The L* (lightness), a*(redness-greeness) and b*(yellowness-blueness) were reported for each samples[18]

III. RESULTS AND DISCUSSION

A. Film formation

The films produced were brownish in color, scattered with black spots of banana seeds and have favorable banana smell. The films were easily detached from the petri dish without tearing thus possessed good handling characteristics. The films were not sticky and too brittle thus make it applicable to use as primary packaging. The addition of glycerol as plasticizer produced more flexible film while the addition of CMC produced more transparent film.

B. Film thickness

The film thickness is measured to analyze further characteristics of film. The thicknesses of films were determined at three different points. From the measurement, the additions of CMC increase the film's thickness. This might be due to increase in volume and reduced of film density similar to the addition of CMC in sago starch[12]. Table 1 shows the thickness of the samples.

Table 1: The thickness of the sample

Sample	Thickness (mm)
0%CMC-Banana film	0.133±0.07
5%CMC-Banana film	0.137±0.01
10%CMC-Banana film	0.159±0.00
15%CMC-Banana film	0.165±0.01

*The values show with standard error

C. Mechanical strength

Edible film for food packaging require good tensile strength (TS) and higher elongation for the end-use handling properties[3], transportation and sale[10]. The TS and elongation at break (EAB) of films are shown in the Figure 1 and Figure 2 respectively. From Figure 1, the tensile strength of CMC-banana flour film is slightly increase from 1.86±0.08MPa to 1.99±0.26MPa until 10%CMC addition and this might be due to the cross linkage between the CMC and starch that produced more compact molecule structure [19] and due to the chemical similarity between structures of polysaccharides[12] such as in CMC-cassava starch[13], CMC-sago starch[12] and CMC-corn starch[14].However, the TS of the film reduced to 1.53±0.06MPa in 15%CMC-banana film. Tong et al., (2008) also found the similar result as there is no significant changes in TS with the addition of CMC in pullulun[3].

Tongdeesoontorn *et al.*,(2011) reported that the tensile strength were inversely related to elongation at break in CMC-cassava starch [13]. However, EAB of the CMC-banana films increase from 20.67±3.02% to 47.27±1.16% in addition of CMC up until 10% but reduced to 38.53±1.12% in 15%CMC. This is similar to CMC-sago starch film as there is significantly decrease of elongation from 17.70 to 15.40% with increasing CMC concentration from 0 to5%of CMC-nanoparticles. As comparison, the CMC-banana flour film has better TS and EAB compared to the apple-puree film with 0.7MPa and 11.8%EAB [9] and banana flour film treated with KMS with ratio of 3:2 of flour to glycerol which only has 0.73MPa and 14.5%EAB [10].

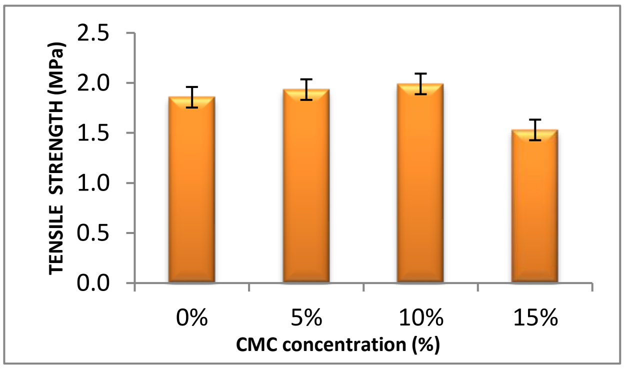

Figure 1: The effect of CMC concentration in tensile strength on banana-based film. Error bar shows standard error

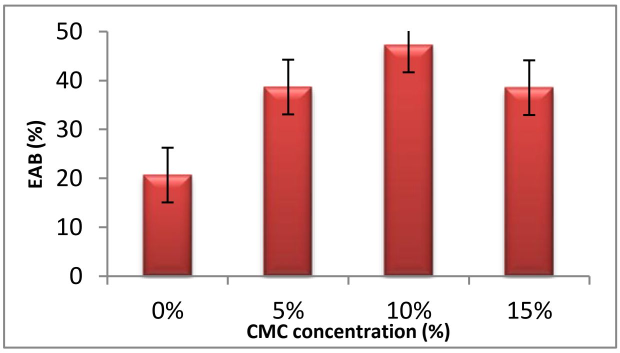

Figure 2: The effect of CMC concentration in elongation at break (EAB) on banana based film. Error bar shows standard error

D. Solubility test

Solubility is an important parameter in edible film and it differs based on the applications[10]. Certain applications of film may require good insolubility properties especially to prevent deterioration of product but some application need good soluble film especially for encapsulation of additives and ingredients[13][16].

The solubility of banana film increased at 5%CMC addition but reduced in higher addition of CMC such as at temperature 25°C, the 5%CMC-banana film has 46±3.35% solubility compared to 41±0.19% in banana film without CMC and reduced to 44.69±1.81% in addition of 15%CMC. The reduction of solubility in the CMC addition is similar to the effect of CMC to cassava starch, corn starch and rice starch film[13]. This may be attributed due to the intermolecular interaction between starch and CMC[19] and from the reduction of starch itself [13]. The molecular interactions between carboxyl and hydroxyl group in CMC and hydroxyl group from starch enhanced the cohesiveness of the biopolymer matrix thus led to the decrease of solubility[20]

In term of temperature, the higher solubility is observed as the temperature increase. For instance, the solubility of 15%CMC is 44.69±1.81, 45.12±2.47 and 45.78±2.22% at temperature 25, 37 and 90°C respectively. M.A Bertuzzi *et al*., (2007) in their work stated that as temperature increase, the diffusivity of edible film is enhanced due to the improved motion of polymer segments and due to the increased in energy levels of permeating molecules[21].

Overall, this study reveals that CMC-banana films has average solubility of 41.39±0.19 to 50.55±6.16% which is higher compared to other natural sources of edible film such as banana flour treated with KMS with 3:2 ratio of flour to glycerol (30.89%)[10], quinoa flour in 21% glycerol (18.7%)[11] and banana flour in 19% glycerol (27.9%)[11] but lower than solubility of CMC-cassava starch(60%) [13]. The solubility percentage of CMC-banana film is shown in Figure 3.

E. FTIR analysis

FTIR has assist the different IR sampling techniques in obtaining the improve quality of infrared spectra data with minimized time. The importance of the FTIR analysis in the film is enable the identification of functional group and structure of composite blended film[17]. FTIR also able to recognize the interaction occurs between the raw materials of the film. The addition of CMC in banana films cause minimal shifting of hydroxyl (-OH) groups from 3286-3266cm^{-1} and this data shows by the increase in tensile strength as the new hydrogen bonds formed replaced the bonds between hydroxyl groups in starch molecules and hydroxyl and carboxyl group in CMC[13]. The C-H stretching vibrations were found between 2935-2933cm^{-1}. The presence of water on the other hand was identified between the ranges 1637-1635 cm^{-1}.

The bending of –CH2 in plane and C-OH bending vibrations were spotted at range 1410-1412cm^{-1} and 1325-1324 cm^{-1} respectively. The band 923 to 924cm^{-1} is obtained from the presence of glycosidic bonds of starch as in banana flour film[11]. The formation of ester bond between the hydroxyl group in amylopectin branches from banana starch and carboxylic acid groups in CMC formed a stable cross-linked structure thus affecting the solubility and mechanical properties of the film such as in CMC-cassava starch[13]. Overall, the blending of CMC in banana film resulted in similar characteristic with banana film without CMC with some minimal shifting. The FTIR spectrum of films is shown in Figure 4.

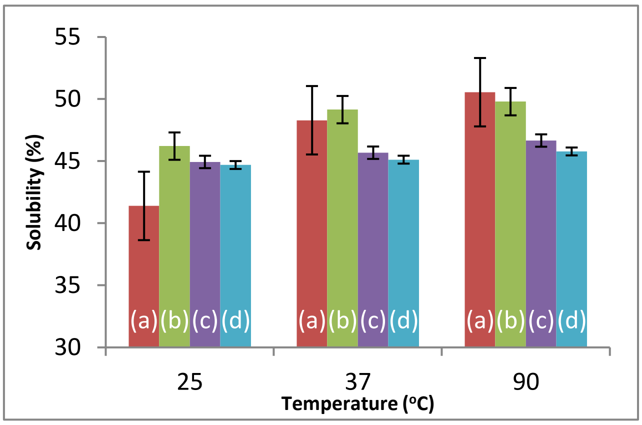

Figure 3: The effects of solubility by CMC concentration and temperature banana based film; (a)0%CMC (b)5%CMC(c)10% CMC (d)15%CMC Error bar shows standard error

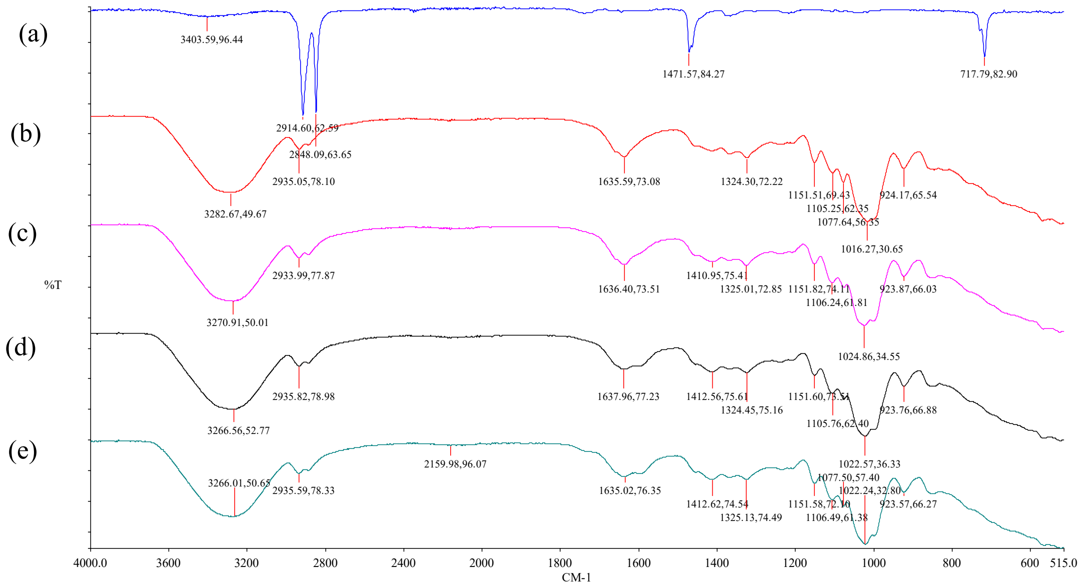

Figure 4: The FTIR-spectra of CMC- banana film; (a) commercial biodegradable plastic,(b) 0%CMC-banana film, (c) 5%CMC-banana film, (d) 10%CMC-banana film,(e) 15%CMC-banana film

F. Water vapor permeability

Water vapor permeability in film is the film ability in migration of water that caused the deterioration of food[2]. This result may be useful to acknowledge the possible mass transfer mechanism and solute-polymer interactions in any films. The permeability was discovered to vary based on number of parameters such as film thickness, plasticizer content and temperature[21]. All WVP data is presented in Figure 5.

The WVP of the CMC-banana film range from 3.99±0.02 x10^{-9} to 5.24±0.08 x10^{-9} g.mm/h.cm^2.Pa. Ghanbarzadeh *et al*.,(2011) in their study deduce that addition of CMC diminished in the WVP of film due to the improvement of hydrophilic properties of the matrix but at certain limit, WVP is constant[14].

However, in this study only addition of 5%CMC in banana film produced slightly lower WVP and the WVP increase as the CMC is added in higher quantity (10-15%w/w). This may be due at low content of CMC, CMC probably disperse well in the starch matrix and blocks the water vapor transmission but in additional amount, CMC might congregate thus decrease the effective content of CMC and eventually assist the water vapor permeation through the film matrix[3],[14]. Tong et al.,(2008) in their study also reported that the increase in WVP in CMC-pullulun film is due to the interaction of bulkier anionic side groups that lead to increase of free-volume in composite matrix[3]. Another reason to support the increase in WVP of the composite film is further added by Tongdeesoontorn *et al*.,(2009) which stated that the plasticizer effect of water instead of glycerol have enhanced the polymer mobility and reducing the intermolecular forces within the film structure such as the CMC addition in cassava starch had no significant effect in WVP. This is because of the content of high amylose in the starch would form strong and compact film thus inhibit the permeability [22].

The CMC-banana film is possible to be used as packaging material [9] as WVP of CMC-banana film is lower compared to other edible films such as in banana flour (7.56x10^{-8} g.mm/h.cm^2.Pa)[1], quinoa flour in 21%glycerol(2.16 x10^{-8} g.mm/h.cm^2.Pa)[11] and banana flour treated with KMS with 3:2 ratio of flour to glycerol (8 x10^{-8} g.mm/h.cm^2.Pa).

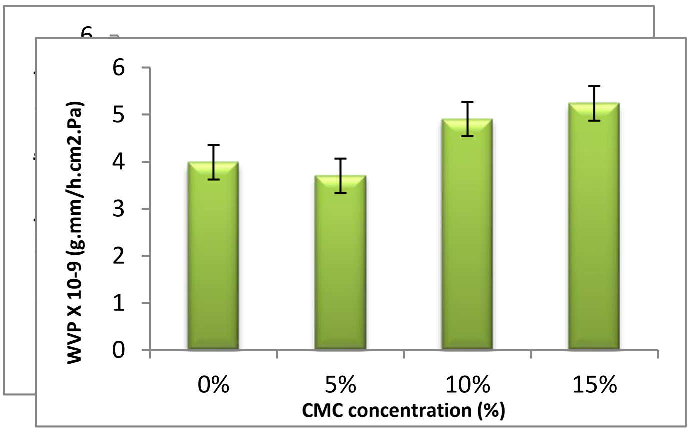

Figure 5: The effects of CMC concentration on WVP of films. Error bar shows standard error

G. Color and opacity

Color and opacity play important role in commercialization of packaging. Opacity in food packaging is made attractive as it makes the contents visible to consumer[11]. The color and opacity of the film were analyzed to identify its natural color from CMC-banana film production and all data is tabulated in Table 2. Both data of the top and bottom film were measured as they possessed different color and opacity.

CMC-banana flour films have lower L* value and b* and higher a* values compared to banana flour film by Jirukkakul *et al*.,(2016)[10] and Hanani Z.A & Abdullah. S.,(2016)[8] this can be resulted from the natural color of banana flour used in this film production. As CMC is added, the films are more transparent and it is identified based on the L value and this result is similar to the addition of glycerol in banana flour film[10] but other research reported that there is no significant color changes of glycerol addition in banana film[8]. All the CMC-banana films have small values of a* indicates the low tone of redness and negative value of b* indicates high value of yellowness color. In 0%CMC addition, the film has higher opacity due to its lower of L* value and this might be affected by presence of lipid in the banana flour[11]

Table 3: The color analysis of CMC-banana based film

TOP –PLATE FILM			
Samples	L*	a*	b*
0% CMC- Banana	34.94±0.24	1.01±0.02	-0.20±0.05
5% CMC- Banana	35.56±0.30	1.01±0.02	-0.46±0.05
10%CMC- Banana	35.50±0.15	1.03±0.07	-0.48±0.17
15% CMC-Banana	36.00±0.56	1.07±0.03	-0.56±0.27
BOTTOM –PLATE FILM			
Samples	L*	a*	b*
0% CMC- Banana	32.65±0.90	1.27±0.10	-0.48±0.09
5% CMC- Banana	33.42±0.65	1.15±0.04	-0.71±0.09
10% CMC- Banana	33.08±0.47	1.16±0.04	-0.62±0.03
15% CMC-Banana	32.80±1.50	1.45±0.07	-0.38±0.18

IV. CONCLUSION

CMC-banana film can be formed into flexible and good handling characteristics film. The increase of CMC led to increase in mechanical strength and water vapor permeability at certain ratio and at the same time reduced solubility. The uses of banana flour also produced natural brownish film thus make it attractive as packaging. However, various concentration of CMC in banana film should be investigated in order to obtain the optimum films formulation to be compared with commercial biodegradable plastic and other natural sources of edible film.

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