The Effects of CMC on the Mechanical Properties of Starch Protein Edible Film

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Abstract—**The purpose of this research is to investigate the effects of carboxymethyl cellulose (CMC) on the mechanical properties of starch protein edible film. Characterization such as tensile properties, water vapor permeability (WVP) and solubility in water were the focus of the investigation. It was found that CMC had significant effects on the tensile properties of the starch protein film. The addition of CMC to the starch protein films significantly increased elongation at break from 8.027 to 52.707% and tensile strength from 10.323 to 72.733 MPa. The incorporation of CMC in the films decreased the WVP significantly with 3.1939 x 10^{-12}, 2.7025 x 10^{-12} and 2.2930 x 10^{-12} g.Pa^{-1}h^{-1}m^{-1} for films containing 0, 5, and 10% CMC respectively. However, when the CMC content of the films reached to 15%, the WVP increased significantly to 3.1529 x 10^{-12} g.Pa^{-1}h^{-1}m^{-1}. The results of solubility in water showed that with the increase of CMC content in the starch protein film, the water solubility of films increased. The %TSM calculated were 45.23, 50, 62.96 and 71.01% for 0, 5, 10, 15% CMC, respectively. It was observed from this work that the content of CMC at 10% in the starch protein polymer matrix may be the best selection for desirable properties of edible film.**

Keywords— CMC, starch protein film

I. Introduction

The starch or protein based films are biodegradable. However, the mechanical properties of these films are still less than commercial petroleum-based plastics. Several research attempts have been done to improve the properties of the films. Due to its cheap, durable and easy to manufacture properties, plastic has become the top choice of food packaging in the industry. More than 40 million tonnes of petroleum-based plastic material were used worldwide in the packaging industry in 2000 (Ban *et al*., 2005). According Aytunga Arik Kibar & Us (2012), current global consumption of plastics has an annual grow of approximately 5%, which signifies the largest field of application for crude oil. The current global consumption of plastics highlights how dependent the plastic industry is on oil and consequently the increment of crude oil and natural gas price have an economic impact on the plastic market.

Plastic is made of major toxic pollutants that are known to cause illness. It is meant for durability therefore it is not biodegradable. Waste, originate mostly from plastic food packaging is sent to a landfill for disposal. The problem with dumping plastics in the landfill is that when they interact with water, they form hazardous chemicals. When these chemicals seep undergound, they degrade the water quality, which is utilized in our daily lives for internal and external purposes. In some countries, this waste disposal issue is becoming a huge and worrying problem that requires comprehensive solutions to curb the issue. Therefore, researchers have come up with an innovative use of edible film idea in order to replace these harmful plastic wraps.

Edible film, made of food-derived ingredients, is a thin layer that is produced for the purpose of placing it on or between food components (McHugh, 2000). The immense potential use of edible film has been and still being widely explored by researchers to replace non-degradable polymers such as plastic that are currently being used as food packaging. For the past decades, the production and functional properties of the film have been broadly investigated. The idea of producing this film is to potentially reduce or completely replace the plastic packaging material that is being used widespread globally. In contemplation of doing so, the film must behave like standard packaging and deliver the same functions such as protection, preservation, convenience and also good value for money.

Preparation of the film involves the use of a polysaccharide, a protein, a solvent, and a plasticizer. Polysaccharides create films with good mechanical properties. Eventhough they are effective barriers against low polarity compounds, however, polysaccharide-based films have a low barrier against humidity (Azeredo *et al*., 2000). Proteins create films with better barriers than polysaccarides and they are usually water resistant and impermeable to oxygen (Azeredo *et al*., 2000). Although polysaccharide and protein films show admirable mechanical and structural properties, they have a poor barrier capacity against moisture transfer (Morillon *et al*., 2002). Meanwhile, solvent, another component used in the preparation of the film is used to maintain edibility of film and are restricted to water and ethanol only (Peyron, 1991). Plasticizer is a major component of edible film. The purpose of adding plasticizer in the formulation of the film is to control film brittleness that is caused by high intermolecular forces. Plasticizer works by reducing these forces and increase the mobility of polymer chains. The effects of these actions are improved flexibility and adaptibility of the film. However, adding plasticizers can notably change the properties of the film, that includes decreasing tensile strength, increasing film permeability to water and increasing the capacity of the films to adsorb water (Fakhoury *et al*., 2012).

Starch is the most widely used polysaccharide in the making of edible film to date (Nur Hanani, Roos & Kerry, 2014) and it is an important polymer due to its capability to form a continuous matrix. Starch is also a naturally occurring compound and has been extensively used in fermenting aside from other chemical manufacturing industries. Abundant in nature and low cost makes starch an excellent pick in commercial applications. In the last several decades, numerous works have been made to produce starch-based films that show improved film properties. However, naturally low moduli of elasticity and high hydrophilicity that can lead to enhanced biodegradability properties of starch have limited their use (Ban W., et al., 2005). Corn, wheat and potato are top three source of starch which take the world leading position with highest pecentage of availability are compared in a research done by Basiak, Lenart and Debeaufort (2016). Corn starch has the highest amylose percentage content compared to wheat and potato with 27, 25 and 20 respectively. Result of mechanical test done on the films shows that corn starch film has the highest percentage of elongation at break with 19.13% compared to wheat starch film (15.21%) and potato starch film (5.67%).

Various types of proteins have been used in producing edible film such as soy protein, sodium caseinate, wheat gluten and gelatin. Between these proteins, gelatin-based film is reported to have high potential as food packaging film due to their associated and unique characteristics. Furthermore, gelatin-based film possesses greatest level of flexibility in a results study to compare resistance to solvents demonstrated by Wang *et al*. (2007). Gelatin is gaining significant attention as an edible film because of its copiousness, comparative low cost, biodegradability and admirable functional properties owing to its excellent film forming capability (Arvanitoyannis *et al.,* 1997). Nonetheless, they are very sensitive to moisture and have low melting and dissolving temperatures, which makes their properties very unstable in time (Podshivalov *et al.*, 2016). A study done by Gómez-Guillén *et al*. (2011) confirmed that gelatin films have poor water resistance properties because high hygroscopic property and decreased mechanical properties when contacted with high moisture content surface.

The use of plasticizers has a significant effect in the properties of the films. Mechanical properties of starch films are also affected by the types and contents of plasticizers used. Glycerol and Sorbitol are two types of plasticizers that are most commonly used to form starch-based film due to their established excellence in their ability to prevent film cracking during handling and storage; the close similarity between their chemical arrangements and the arrangement of starch polymer is the possible reason of its effectiveness (Mali *et al*, 2005). Glycerol displayed a greater plasticization effect compared to Sorbitol at equal weight content. However, Cuq *et al*., (1997) argued that the effect was mainly caused by the higher molecular content of glycerol. Glycerol is possibly the most frequently tested plasticizer for edible films because of its high plasticization efficiency. A research on several plasticizers done by Jangchud and Chinnan (1999) found that glycerol was the best plasticizer for water-soluble polymers. The mechanical strength of films infused with glycerol was dependant on the relative crystallinity for amylopectin films and on the network microstructure for amylose films.

According to Siqueira *et al*. (2014), the most widely used cellulose derivative is Carboxymethyl cellulose (CMC). Constructed from cellulose macromolecules by the reaction between cellulose and monochloroacetate, CMC yields a partial substitution of the hydroxyl groups at the 2, 3 and/or 6 positions in the cellulose arrangement by carboxymethyl groups. CMC displays thermal gelation and casts excellent films due its polymeric structure and high molecular weight chains. In food processing, CMC is largely used for its viscosity, water binding properties as well as its soluble transparency. Furthermore, it is broadly available, easily processed, economical, and have admirable film-making properties. The chemical similarity of starch and CMC provides a good compatibility between them. Therefore, the addition of CMC to the starch gelatin film is expected to improve the mechanical and barrier properties of the film. However, films prepared using CMC continue to be especially vulnerable to moisture (Biswal and Singh, 2004). Thus, the objectives of this study are to produce starch-based edible film, study the effects of CMC on the mechanical properties of starch protein edible film and characterized the produced film.

II. METHODOLOGY

A. Materials

Corn starch manufactured by Spectrum Laboratory Products, Inc (California, United States)., kosher gelatine powder purchased from Merck Sdn. Bhd (Shah Alam, Malaysia), distilled water, glycerol supplied by SYSTERM® (Shah Alam, Malaysia) and carboxymethyl cellulose (CMC) from R & M Chemicals supplied by Ever Gainful Enterprise Sdn. Bhd (Semenyih, Malaysia).

B. Preparation of film

4 g of starch is mixed with 1 g of gelatin with the ratio of 4:1 following method from Fakhoury et al., (2012). 100 mL of distilled water and (40 ml/100g of starch) glycerol are added to the mixture. The suspensions are agitated by magnetic stirrer with speed of 500 rpm for 30 min in water bath set to 90 °C. Different amount of carboxymethyl cellulose (CMC) (0, 5, 10 and 15% W/W starch) is solubilized in 75 ml of distilled water at 75 °C for 10 min. The CMC and suspensions prepared earlier are mixed together (75 ml CMC solution + 100 ml suspension) and stirred at 75 °C for 10 min. The dispersion is then cooled at 40 °C and mixed gently for 20 min to release air bubbles. Then, about 40 mL of the sample is poured into a petri dish (without lid) and then dried at 40 °C in an oven for 24 hours to cast the film (Ghanbarzadeh, 2010).

C. Film thickness

Film thickness was measured using a micrometer (Mitutoyo No. 103 – 177, Tokyo, Japan) with an accuracy of 0.01 micrometer.

D. Tensile properties

The tensile strength and elongation at break analysis is performed according to the method described by Nguyen Vu & Lumdubwong, (2016) and of the films were determined using a universal testing machine (model H50KT), using E-modulus without 100RC

Estensormeter. The films (15mm x 60mm) were cut from each samples and were placed between the grips of the machine. Crosshead speed and initial grip distance were set to 80 mm/min and 40 mm, respectively.

E. Water Vapor Permeability (WVP)

Water Vapor Permeability (WVP) was measured via method described by Alboofetilah *et al*. (2012) with some modifications. Circular cups with diameter of 6.7 cm were utilized to determine the WVP of the films. Film samples were cut out with a diameter marginally larger than the diameter of the cup. 20mL of distilled water were poured into each cup (100% RH_1; 2.337 x 10^3 Pa vapor pressure at 20℃) and the cut out film samples were individually sealed on top of the cups for each sample concentration. Each cup was then weighed and placed in a desiccator containing silica gel (1.5% RH_2; 28.044 Pa water vapor pressure), maintained at 20℃. The cup was then weighed hourly for six hours and WVP was calculated using the following equation (Ghanbarzadeh *et al.*, 2011):

$$\text{WVP } (g.Pa^{-1}h^{-1}m^{-1}) = \frac{WVTR}{P(R_1 - R_2)} x$$

Where P is the vapor pressure (Pa) at temperature tested, 20℃, R_1 is the RH in the cup, R_2 is the RH in the desiccator and X is the film thickness (m).

F. *Solubility in Water*

Film specimens were sealed in a container containing silica gel until they reached constant weight. Subsequently, 2 cm x 2 cm of each film were cut and immersed in cups containing 30 ml of distilled water at 23 °C and put into a shaker for 24 hours. After 24 hours, the films were removed from the water and dried in an oven at 100°C until they reached a constant weight to obtain the final dry weight of the film. Percentage of the dry matter of film which is solubilized after immersion in water for 24 hours is described as solubility in water (Gontard et. *al*, 1994). The percentage of the total soluble matter (%TSM) of the films were calculated using the following equation:

%TSM = [(initial dry weight − final dry weight)/initial dry wt] × 100

III. RESULTS AND DISCUSSION

A. The effects of CMC on tensile properties

The results obtained for tensile strength (TS) and elongation at break (EAB) for all films is shown in table 1. TS increases significantly from control (8.027 MPa) to 11.483, 24.443, and 52.707 MPa, respectively. The increase is consistent with the addition of CMC content percentage thus indicating a strengthening of intermolecular forces. The result correlate with the study conducted by Ghanbarzadeh et *al*. (2010), which found that an increment in TS occurred when CMC percentage were increased in the formulation of the films, which strengthens the intermolecular forces between the film components.

The elongation at break (EAB) also increases significantly from control (10.323 %) to 13.723, 45.687, and 72.733 % respectively as the CMC content increases. However, increased TS generally precedes a decrease in EAB. However, results obtained in this study showed increased TS values preceding increased EAB value. The corresponding increment may be affected by the incorporation of glycerol in the formulation of the film. Glycerol enhanced the molecular ability by acting as a lubricant between the polymer chains. This plasticization effect of glycerol imparted film flexibility which in turn increases the EAB (Tong et *al.*, 2008). The increment of both EAB and TS can be seen on the curves displayed in Fig. 1 and 2 respectively.

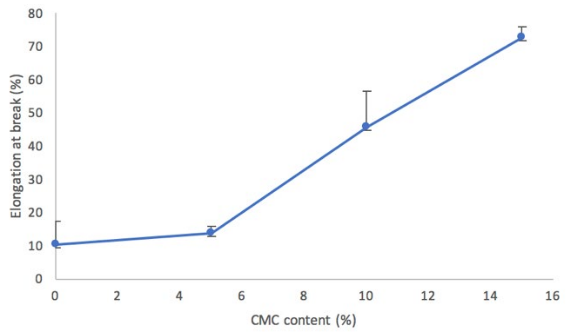

Fig. 1: The elongation at break of the films as a function of CMC content.

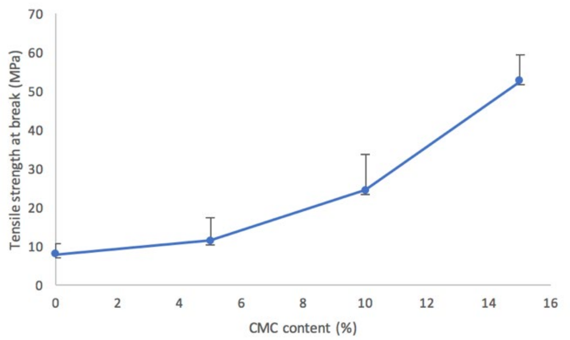

Fig. 2: The tensile strength at break of the films as a function of CMC content.

CMC Content (%)	Elongation at break (%)	Tensile strength (MPa)
0	10.323 ± 7.112	8.027 ± 2.837
5	13.723 ± 1.993	11.483 ± 5.923
10	45.687 ± 10.659	24.443 ± 9.267
15	72.733 ± 3.324	52.707 ± 6.601

Table 1: The mechanical properties of the films. Values were given as mean ± standard deviation

B. *The effects of CMC on Water Vapor Permeability (WVP)*

The WVP of the starch protein/CMC films decreased with the increase of CMC content as can be seen in Table 2. The WVP was 3.1939 x 10^{-12} $g.Pa^{-1}h^{-1}m^{-1}$ for the control sample (0% CMC) and decreased significantly to 2.7025 x 10^{-12} $g.Pa^{-1}h^{-1}m^{-1}$ and 2.2930 x 10^{-12} $g.Pa^{-1}h^{-1}m^{-1}$ for films containing 5% and 10% of CMC, respectively. The films containing 10% CMC has significantly the lowest WVP value. However, when the CMC content of the films reached to 15%, the WVP increased significantly to 3.1529 x 10^{-12} $g.Pa^{-1}h^{-1}m^{-1}$.

Reduction of the WVP with increasing CMC content shows the improvement of the functional properties of these films, considering the hydrophilic characteristics of the polymer matrix. The result could be affected by the highly crystalline and hydrophobic character of the cellulose fibers compared to starch polymer. This statement is supported by the research conducted by Ma *et al.*, (2008) which concluded that water resistance of CMC hydrocolloid film is better than starch-based film. Ghanbarzadeh *et al*. (2011) also found that CMC probably disperse well in the starch polymer matrix, blocking the water vapor transmission at low concentration.

CMC Content (%)	Water Vapor Permeability ($g.Pa^{-1}h^{-1}m^{-1}$)
0	3.1939×10^{-12}
5	2.7025×10^{-12}
10	2.2930×10^{-12}
15	3.1529×10^{-12}

Table 2: WVP of each sample calculated after 6 hours

C. *The effects of CMC on solubility in water*

The effects of CMC on the solubility of film in water are summarized in table 3. Based on the data obtained, the percentage of total soluble matter (TSM) of each film was calculated. The water solubility of films increased with the increase of CMC content in the films. The %TSM was 45.23% for the sample with 0% CMC content, which increased to 50 and 62.96% for the films containing 5 and 10% CMC, respectively. The highest CMC content which is 15% showed a significant increase in solubility with 71.01%.

When CMC is added into the composition of the films, the solubility of the films were enhanced. The rapid dissolution behaviour of the films could be influenced by the more open structure stimulated by CMC, making the films matrices more accessible to water compared to films with no CMC. Furthermore, the addition of plasticizers in the formulation of film could add to the decreased solubility of the films. The decreased soluble time is possibly due to the increased film hydrophilicity instigated by the hydroxyl groups from the glycerol. As glycerol is highly water-soluble, its extraction from the film into water can correspondingly be developed in a more open polymer matrix which enabled the diffusion of water into the film, thus enhancing the solubility of film (Tong et. *al*, 2008).

CC Content (%)	%TSM
0	45.23
5	50.00
10	62.96
15	71.01

Table 3: The solubility of films in water after 24 hours

IV. Conclusion

The objectives of the experiment which are to produce starch-based film, study the effects of CMC on the mechanical properties of starch protein edible film and characterized the produced film are achieved. The tensile properties (tensile strength, elongation at break) increased with the addition of CMC, signifying that CMC could be used prominently to improve film strength and flexibility. At 10% CMC, WVP of film was significantly decreased. The result showed that water barrier properties of starch protein film were noticeably improved by the incorporation with CMC into the film. The addition of CMC also increased the solubility of film in water. The result of percentage of total soluble matter confirmed that CMC enhanced the solubility of the films. Therefore, it can be concluded that incorporation of CMC with the starch protein film would be an attractive method to develop new edible films. It was observed from this work that the content of CMC at 10% in the starch polymer matrix may be the best selection for desirable properties of edible film.

Acknowledgment

Thank you to my supervisor Madam Fariza Hamidon and Universiti Teknologi Mara.

References

[1] Alboofetilah M., Rezaei M., Hosseini H., Abdollahi M. (2012). Effect of montmorillonite clay and biopolymer concentration on the physical and mechanical properties of alginate nanocomposite films. *Journal of Food Engineering,* 117 (2013) 26-33.

[2] Arvanitoyannis I., Psomiadou E., Nakayama A., Aiba S., Yamamoto N. (1996). Edible films made from gelatin, soluble starch polyols, Part 3. *Food Chemistry*, Vol. 60, No.4, pp. 593-604.

[3] Aytunga Arik Kibar E., Us F. (2012). Thermal, mechanical and water adsorption properties of corn starch-carboxymethylcellulose/methylcellulose biodegradable films. *Journal of Food Engineering,* 114 (2013) 123-131.

[4] Azeredo, H. M. C., Faria, J. A. F., & Azeredo, A. M. C. (2000). Embalagens ativas para alimentos. *Ciencia e Tecnologia de Alimentos*, 20(3), 337–341.

[5] Ban W., Song J., Argyropoulos D. S., Lucia L. A. (2005). Improving the Physical and Chemical of Functionality Starch-Derived Films with Biopolymers.

[6] Basiak E., Lenart A., & Debeaufort F., (2016). Effect of starch type on the physico-chemical properties of edible films. *International Journal of Biological Macromolecules*, S0141-8130(16)31643-9.

[7] Biswal, D. R. and Singh, R. P. (2004). Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymer,* 57: 379–387.

[8] Cuq, B., Gontard, N., and Guilbert, S., (1997). Thermoplastic properties of fish myofibrillar proteins: application to biopackaging fabrication. *Polymer*, 38, 4071-4078.

[9] Fakhoury F., Martelli S., Bertan L., Yamashita F., Mei L., Queiroz F., (2012). Edible films made from blends of manioc starch and gelatin. *LWT – Food Science and Technology*, Vol 49. P 149-154.

[10] Ghanbarzadeh B., Almasi H., and Entezami A. A. (2010). Physical Properties of Edible Modified Starch/carboxymethyl Cellulose Films. *Innovative Food Science and Emerging Technologies* 1-6. Print.

[11] Ghanbarzadeh B, Almasi H, Entezami AA. 2011. Improving the barrier and mechanical properties of corn starch-based edible films: Effect of citric acid and carboxymethyl cellulose. *Ind. Crop. Prod*, 33, 229-235.

[12] Gómez-Guillén, M. C., Giménez, B., López-Caballero, M. E., & Montero, M. P. (2011). Functional and bioactive properties of collagen and gelatin from alternative sources: A review. *Food Hydrocolloids*, 25(8) 1813–1827.

[13] Gontard, N., Guilbert, S., & Cuq, J.-L. (1992). Edible wheat gluten films: Influence of the main process variables on film properties using response surface methodology. *Journal of Food Science*, 57, 190–195.

[14] Jangchud, A., Chinnan, M. S. (1999). Properties of peanut protein film: Sorption isotherm and plasticizer effect. *LTW - Food Science Technology*, Oxford, v. 32, n. 2, p. 89-94.

[15] Ma, X., Chang, P. R., & Yu, J. (2008). Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. *Carbohydrate Polymers*, 72, 369−375.

[16] Mali S., Sakanaka L.S., Yamashita F., Grossmann M.V.E. (2005). Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydrate Polymer*, 60(3):283–9.

[17] McHugh, T. H. (2000). Protein-lipid interactions in edible films and coatings. *Nahrung*, 44, 148e151.

[18] Morillon, V., Debeaufort, F., Bond, G., Capelle, M., & Volley, A. (2002). Factors affecting the moisture permeability of lipid based edible films: a Review. *Critical Reviews in Food Science and Nutrition*, 42(1), 67e89.

[19] Nur Hanani Z. A., Roos Y. H., Kerry J.P. (2014). Use and application of gelatin as potential biodegradable packaging materials for food

products. *Int. Journal of Biological Macromolecules*, 71 (2014) 94-102.

[20] Peyron, A. (1991). Coating and film-forming products: a new mode of packaging. *Meat Production Carnes*, 12, 41-46.

[21] Podshivalov, A., Zakharova M., Glazacheva E., Uspenskaya M. (2016). Gelatin/potato starch edible biocomposite films: Correlation between morphology and physical properties. *Carbohydrate Polymers*.

[22] Siqueira E. J., Brochier Salon M.-C., Mauret E. (2014). The effects of sodium chloride (NaCl) and residues of cellulosic fibres derived from sodium carboxymethylcellulose (NaCMC) synthesis on thermal and mechanical properties of CMC films. *Industrial Crops and Products*, 71 (2015) 87-96.

[23] Tong Q., Xiao L., Lim L. (2008). Preparation and properties of pullulan-alginate-carboxymethyl cellulose blend films. *Food Research International.*

[24] Wang L., Liu L., Holmes J., Kerry J.F., Kerry J.P., Int. J. (2007). Assesment of film-forming potential and properties of protein and polysaccharide-based biopolymer film. *Food Sci. Technol*, 42 1128–1138.