EXTRACTION OF CMC FROM CORNCOB AND ITS APPLICATION AS COATING AGENT ON MANGO FRUIT

Sujitra Ruengdechawiwat*, Pornwipa Sanawong and Sutjaritpan Boonmee

Abstract

This study aimed to synthesize carboxymethyl cellulose (CMC) from corncobs for use as coating agent on mango. Cellulose is converted by etherification under suitable conditions and then finally purified. Then, the extracted CMC was used as a film for coating the mango fruit. Under the optimized reaction conditions, the extracted CMC had a degree of substitution (DS) of 0.12. The results showed that the FTIR spectra of the obtained CMCs exhibited strong absorption bands in the range of 1600-1700 cm-1, which was related to the carbonyl group (C=O) vibration stretching absorption. The absorption in the 1400–1450 cm-1 region is due to symmetrical deformations of CH2 groups. The strong absorption bands in the range of 1200–1000 cm-1 are due to the stretching vibration of the ether (-O-). The FT-IR results confirmed CMC modification. Thermal analysis found that CMC had a melting temperature in the range of 163.2-181.4 oC. In degradation, CMC can be completely decomposed within 72 hrs using the soil embedding method. The results of the water vapor permeability (WVP) test showed that CMC and glycerol affected the film properties. Increasing CMC content, water vapor permeability (WVP) decreased. In contrast, with increasing glycerol, increased WVP. We conclude that fruits coated with the obtained CMC from corncob could maintain the quality of Nam Dok Mai Mango (Mangifera Indica Linn.).

Keywords: Carboxymethyl cellulose, Corncob, Coating agent

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Introduction

Corn is one of the most widely-planted crops in Thailand. According to the office of agricultural economics, in 2022, Thailand has approximately 7 million rai of maize cultivation area, yielding 5 million tons per year (Agriculture and Cooperatives office, 2022). Corncobs are a waste product from corn farming. The content contained in corncob is cellulose as much as 40-60%, hemicellulose as much as 20-30% and lignin a much as 25-30%. The starch content in corncob is 27.1%. Functionalized cellulose is strategic in the developments and applications of new biomaterials. The cellulose derivatives are useful, for example, cellulose could be converted by etherification (Kirk & Othmer, 1967). Carboxymethyl cellulose (CMC) is a derivative of cellulose and is a cellulose ether compound that exhibits a wide range of potential uses in various applications in many industries such as food, pharmaceutical, detergent, textile, cosmetic product and a suspending aid in agriculture. CMC is clear, odorless and non-toxic to the environment (Nuttawadee et al., 2012) and has high water solubility as well as outstanding light and thermal stability (Shuiet al., 2017; Sumitra, 1980). It is environmentally friendly and adds value to agricultural waste (Sothornvit & Krochta, 2001). Many have applied CMC for prolong shelf-life of fresh products such as avocado (Maftoonazad & Ramaswamy, 2005), peach and pear (Toğrul & Arslan, 2004) and cucumber (Adetunji et al., 2013).

Commercial CMC is produced from virgin cellulosic plants such as cotton linter and wood pulp. These sources are very costly agricultural products and also their use increases the deforestation and environmental problem (Hailu, 2016). The increasing environmental concerns have forced the researchers to obtain useful industrial materials from plant biomass. In order to decrease this problem, the production of CMC from various waste raw materials has been examined. The purpose of this research was to synthesize and investigate the quality of carboxymethyl cellulose (CMC) from corncob and as a coating reagent on Nam Dok Mai Mango (Mangifera Indica Linn.). Because Nam Dok Mai Mango (Mangifera Indica Linn.) is among major fruit crops grown in Thailand. However, the postharvest handling problem contributes to huge postharvest loss of fruits. This experiment was conducted to study the effect of coating with the obtained CMC from corncob on quality of mango fruit.

Materials and methods

Materials

Corncops and Nam Dok Mai Mango (Mangifera Indica Linn.) were collected from corn farming in Phitsanulok province, Thailand. The chemicals used during the study were AR-grade: sodium hydroxide (NaOH) (RCI Labscan), Chloroacetic acid (LOBO Chemie), Hydrochloric (HCl) (RCI Labscan), Acetic acid (QReC), Isopropanol (RCI Labscan), Nitric acid (HNO_3) (RCI Labscan), Methanol (MERCK), Ethanol (RCI Labscan), and Glycerol (KEMAUS).

Methods

Extracting cellulose and modifying to carboxymethyl cellulose (CMC)

Corncobs were washed, dried and cut manually into small pieces about 1.5-2.0 cm prior extraction with alkaline solution using 8% (w/v) NaOH at 100°C for 3 hrs (Tikhamporn et al., 2019). The cellulose residue was separated by filtration, washed thoroughly with water to neutral, dried and with a bleaching agent (5 % (v/v) H_2O_2) at 60 °C for 24 hrs (Pongnoree & Kongbangkerd, 2006). Five grams of prepared cellulose was mixed with 90 ml of isopropanol, and 50 ml of 20%, 25%, 30% (w/v) NaOH solution in a beaker for 1 hr. Then, chloroacetic acid was added to the mixture and stirred at 60 °C for 24 hrs. The obtained solid was neutralized with 90 % acetic acid, filtered, washed with 70% (v/v) ethanol. The final product was obtained after drying at 60°C for 12 hrs or until reaching a constant weight (Tikhamporn et al., 2019).

Characteristic carboxymethyl cellulose

FTIR spectroscopy

Infrared spectrum (IR) spectrum was used to investigate the functional group of carboxymethyl cellulose from corncob (CMC) with carboxymethylcellulose from commercial (CMC). Infrared spectra of CMC were recorded in the middle region 400-4000 cm^{-1}.

Thermal analysis

Thermal analysis be used as information to preserve the quality of CMC. In this research.

Degree of substitution (DS)

Degree of substitution (DS) of CMC was determined by according to ASTM D 1439–03. The obtained CMC from corncob 1 g was mixed 20 ml of ethanol solution with magnetic stirring, 25 min later then, HNO_3 was added 1 ml and stirred for 15 min, filtered, washed with 70 % (v/v) ethanol and methanol solution. The residue dried at 100 °C for

3 hrs. The obtained CMC 0.1 g in 20 ml water, 0.3 M NaOH was added 5 ml and stirred for 15 min add phenolphthalein 2-3 drops later then, titration with 0.3 M HCl (Tikhamporn et al., 2019). Degree of substitution (DS) determined followed equation of (Elomaa et al., 2004) according to equation 1 and 2. Solution of NaOH, which is an etherifying agent, will help the cellulose to swell. The carboxymethyl group then replaces the hydroxyl group in the cellulose structure finally as CMC (Rachtanapun et al., 2012).

$$A = (BC - DE) / F \tag{1}$$

$$G = 0.162 / (1 - 0.058A) \tag{2}$$

When A = Equivalent amount of acid consumed per 1 g of sample

B = Volume of NaOH solution used (ml)

C = Concentration of NaOH solution

D = Amount of titrated HCl acid (mL)

E = Concentration of HCl solution

F = Weight of CMC (CMC) (grams)

G = Degree of substitution

Biodegradation of CMC films

Film-forming solutions were prepared as previously described (Gouhua et al., 2006). Film forming dispersions were obtained by the dispersion and solubilization of CMC in water at 80 °C. Then pour into the petri dish glass for 24 hours. Biodegradation determined with soil embedding methods. CMC film sample, size 1 x 1 cm (shown in Figure 1 and 2), pieces were placed in each container and buried in the prepared soil at a depth of 10 cm. The degradation period was 0, 12, 24, 36, 48, 60 and 72 hrs (Rudnik & Briassoulis, 2011).

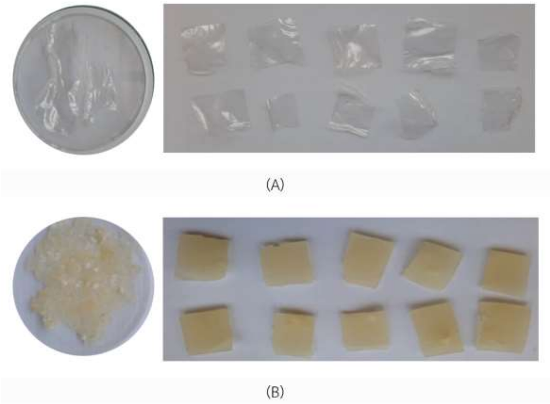

Figure 1 The specimens from (A) commercial CMC and (B) CMC extracted from corncob

Water vapor permeability

WVP of films was determined gravimetrically under ambient temperature by according to ASTM E96-00e1 procedure as described elsewhere (Aytunga & Ferhunde, 2017). CMC was prepared under optimum conditions at concentrations of 1, 2 and 3 % (w/v) in distilled water mixed 0.25, 0.5, 1.0 % (v/v) glycerol solution into the petri dish glass and dried at 50 ^{o}C.

Figure 2 Appearance of CMC film before and after with soil embedding methods

CMC coating

The mango fruits (Mangifera indica Linn.) cv. Namdokmai Sri Tong were dipped for 5 min in solution of 0.5 % (w/v) of CMC extracted from corncob in glycerol, and 0.5 % (w/v) of commercial CMC in glycerol and non-coated as the control treatment. Treated mango fruits were placed in plastic baskets and stored under ambient temperature. The mango fruits of each group were evaluated every day.

Results

Yield of cellulose obtained from extraction condition with processes of alkalization and bleach the crude cellulose by using H_2O_2 were relatively good at 69.0±0.25. The CMC derived from cellulose of corncob was coated on Nam Dok Mai Mango (Mangifera Indica Linn.) at a concentration of 0.5%.

Degree of substitution (DS)

As is shown in Table 1, the carboxymethylation reaction was carried out in three different NaOH concentration. It is observed that the increase in the ratio of organic solvent increases the DS of the CMC produced. A maximum of 0.12 was obtained with 20% NaOH and 10 g MCA. The results were not different from the results of 25% NaOH, 8 g MCA. The result was similar to that of commercial CMC with a DS of 0.20.

Table 1 Comparison the degree of substitution (DS) of CMC extracted from corncob under various conditions

Treatments	Degree of substitution (DS)
20% NaOH, 6 gMCA	0.103± 0.001
20% NaOH, 8 gMCA	0.113± 0.001
20% NaOH, 10 gMCA	0.120± 0.001
25% NaOH, 6 gMCA	0.100± 0.003
25% NaOH, 8 gMCA	0.116± 0.002
25% NaOH, 10 gMCA	0.107± 0.002
30% NaOH, 6 gMCA	0.101± 0.001
30% NaOH, 8 gMCA	0.102± 0.001
30% NaOH, 10 gMCA	0.109± 0.001

Characterisation of CMC

The FTIR spectra of CMCs extracted from corncob have strong absorption band in the 1600-1700 cm^{-1} is related to the stretching vibration of the carbonyl group (C=O). The absorption in the 1400–1450 cm^{-1} region is due to symmetrical deformations of CH_2 groups. While the strong absorption around 1200-1000 cm^{-1} is due to the stretching vibration of the ether (-O-). The FT-IR results confirmed the successful modification of CMC (Bono et al.,2009; Singh & Singh, 2013). The obtained CMC had melting temperature in the range of 163.2-181.4^{o}C.

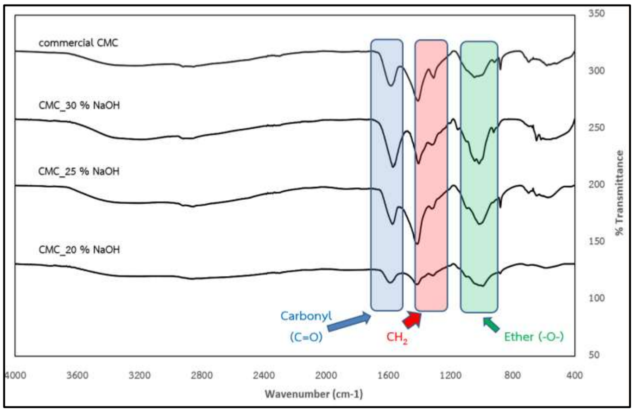

Figure 3 FT-IR spectra of the obtained CMCs from corncob by various concentration of NaOH and CMC from commercial

Biodegradation of CMC film

As is shown in Table 2, it indicated that all CMC films has the ability to degrade within 72 hrs with soil embedding methods.

Table 2 Comparison of biodegradation with soil embedding methods which compared to the percentage of weight loss

Specimens	Storage time(hr)						
	0	12	24	36	48	60	72
Commercial CMC	50	80	100	100	100	100	100
CMC from corncob	50	65	70	80	80	90	100

Water vapor permeability

When a increasing the amount of CMC will cause the structure to be closer together on water vapor permeability reduced. While increasing the amount of glycerol will increase the ability of water vapor permeability. Because glycerol has high moisture absorbing properties on penetrate into the structure of CMC resulting in water absorption and swell to increase the space between molecules (Watsamon & Satit, 2007). In addition, structure of glycerol has hydroxyl group therefore effective swelling of CMC under high relative humidity condition increased water vapor permeability (Riku et al., 2007).

Table 3 Comparison water vapor permeability (WVP) of CMC films extracted from corncob

Proportion by weight of film		Water vapor permeability (WVP)
CMC %(w/v)	Glycerol %(w/v)	
1	0.25	1.60 ± 0.01
	0.50	2.20 ± 0.02
	1.00	3.54 ± 0.02
2	0.25	1.20 ± 0.01
	0.50	1.65 ± 0.02
	1.00	2.40 ± 0.02
3	0.25	1.08 ± 0.01
	0.50	1.22 ± 0.01
	1.00	1.80 ± 0.02

CMC coating

As shown in Figure 4, the CMC extracted from corncob and the commercial CMC can be applied as the Nam Dok Mai Mango (Mangifera Indica Linn.) coating agent in glycerol to extend the shelf life showed obviously retarded ripening and skin color development on Nam Dok Mai Mango (Mangifera Indica Linn.).

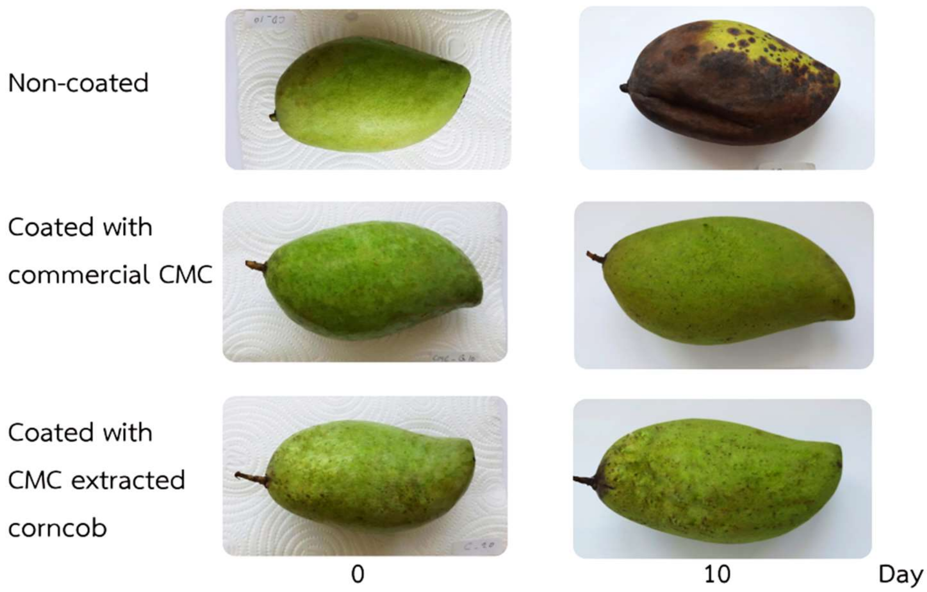

Figure 4 Appearance of Mango fruit before and after coating with CMC for 10 days

Discussions

CMC synthesis from cellulose using NaOH solution, which is the etherifying agent on swelling of cellulose later then, carboxymethyl group will instead of hydroxyl groups in the structure of cellulose finally as CMC (Rachtanapun et al., 2012). From the results, the optimum condition of CMC preparation was 10.0 g of MCA and 20.0 % NaOH. Under the optimized reaction conditions, degree of substitution (DS) of CMC is 0.12. The substitution level (DS) is lower than 0.4, the obtained CMC will swell at room temperature (Nattawadee et al., 2012) but can soluble in water above 60°C. The characteristic analysis was identified by using infrared Fourier transform spectroscopy. The results showed the function of CMC (Bono et al., 2009). A similar trend of extend the shelf life on mango has been reported in CMC coated (Sajid et al., 2022) and CMC-coated corn peel (Tikhamporn et al., 2019). The CMC coating is a modified atmosphere storage could reduce weight loss and gas exchange for reduced of deterioration rate (Rawiwan & Atchara, 2021; Kasinee et al., 2017)

Conclusions

From the results, we conclude that the CMC extracted had the same structure as the commercial CMC and could be decomposed. In addition, the CMC extracted and the commercial CMC had efficiency on coating agent in glycerol showed obviously retarded ripening and skin color development on Nam Dok Mai Mango (Mangifera Indica Linn.). A similar trend of extend the shelf life on mango has been reported in CMC coated and CMC-coated corn peel.

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References

Adetunji CO, Arowora KA, Fawole OB, Adetunji JB, Olagbaju AR. Effect of edible coating of carboxymethyl cellulose and corn starch on cucumber stored at ambient temperature. Asian Journal of Agriculture and Biology 2013;1(3):133-140.

Agriculture and Cooperatives office (Online). Available https://www.opsmoac.go.th/nakhonsawan-dwl-files-441591791095; 2022.

Aytunga AK, Ferhunde U. Starch-cellulose ether films: Microstructure and water resistance. Journal of Food Process Engineering 2017;40:1-8.

Bono A, Ying PH, Yan FY, Muei CL, Sarbatly R, Krishnaiah D. Synthesis and characterization of carboxymethyl cellulose from palm kernel cake. Advances in Natural and Applied Sciences 2009;3(1):5-11.

Elomaa M, Asplund T, Soininen P, Laatikainen R, Peltonen S, Hyvarinen S. Determination of the degree of substitution of acetylated starch by hydrolysis, 1 H NMR and TGA/IR. Carbohydrate Polymers 2004;57:261-267.

Gouhua Z, Ya L, Cuilan F, Min Z, Caiqiong Z, Zongdao C. Water resistance, mechanical properties and biodegradability of methylated cornstarch/poly (vinyl alcohol) blend film. Polymer Degradation and Stability 2006;91(4):703-711.

Hailu A. Production and optimization of carboxymethyl cellulose from waste cartons. Master of Science, Department of Science, University of Addis Ababa; 2016.

Ismail N, Bono A, Valintinus A, Nilus S, Chng L. Optimization of reaction conditions for preparing carboxymethyl cellulose. Journal of Applied Sciences 2010;10:2530-2536.

Kasinee S, Rujira D, Lampan K. Effect of carboxymethyl cellulose as edible coating on postharvest quality of rambutan fruit under ambient temperature. International Journal of Agricultural Technology 2017;13(7.1):1449-1457.

Maftoonazad N, Ramaswamy HS. Postharvest shelf - life extension of avocados using methylcellulose -based coating. LWT. Food Science and Technology 2005;38:617–624.

Nuttawadee J, Jurmkwan S, Sutthira S, Suthaphat K. Properties of carboxymethyl cellulose (CMC) film from rice straw pulp. Journal of Science Agricultural 2012;43(3):616-620.

Pongnoree J, Kongbangkerd T. Preparation of cellulose from corncobs I: Study on cellulose extraction. Songklanakarin Journal of Science Technology 2006;28(1):191-199.

Rachtanapun P, Luangkamin S, Tanprasert K, Suriyatem R. Carboxymethyl cellulose film from durian rind. *LWT.* Food Science and Technology 2012;48(1):52-58.

Rawiwan P, Atchara J. Development of carboxymethyl cellulose coating combined with galanga extract on postharvest guava presevation. Proceedings of 6 th National Kamphaengphet Rajabhat University 2021; 874-881.

Rudnik E, Briassoulis D. Degradation behaviour of poly (lactic acid) films and fibers in soil under mediterranean field conditions and laboratory simulations testing. Industrial Crops and Products 2011;33(3):648-658.

Sajid A, Muhammad A, Ahmad S, Aamir N, Shaghef E, et al. Carboxymethyl cellulose coating delays ripening of harvested mango fruits by regulating softening enzymes activities. Food Chemistry 2022;380:1-11.

Shui T, Feng S, Chen G, Li A, Yuan Z, et al. Synthesis of sodium carboxymethyl cellulose using bleached cellulose fractioned from cornstalk. Biomass and Bioenergy 2017;105:51-58.

Singh R, Singh A. Optimization of reaction conditions for preparing carboxymethyl cellulose from corn cobic agricultural waste. Waste and Biomass Valorization 2013;4(1):129-137.

Sothornvit R, Krochta J. Plasticizer effect on mechanical properties of β-lactoglobulin films, Journal of food engineering 2001;50:149-155.

Sumitra P. Isolation of cellulose from some plants and synthesis of its derivatives. Master of Science, Department of Science, Chiangmai University; 1980.

Tengrang S, Xenmak P, Liapwan N, Loylert K, Sukhakasem S, Watthanawichit, W., et al. Research and development of packing degradable products from agricultural products. In Research and development package report. Bangkok Office of postharvest and product processing research and development, farmers' products, Agriculture 2015;198.

Tikhamporn C, Benjawan B, Piched A. Carboxymethyl cellulose from corn peel. Kasetsart University, Kamphaengsaen Campus; 2019.

Toğrul H, Arslan N. Extending shelf-life of peach and pear by using CMC from sugar beet pulp cellulose as a hydrophilic polymer in emulsions. Food Hydrocolloids 2004;18:215-226.

Watsamon K. and Satit C. Effect of carboxymethyl cellulose film from papaya peel/starch maize on mechanical properties and water vapor permeability. Master of Science, Department of Science, Chiangmai University; 2007.