Effects of Reaction Time on Degree of Substitution, Yield and Morphology of Carboxymethyl Cellulose from Banana Peel

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Abstract. Carboxymethyl cellulose(CMC) was extracted from cultivated banana peel (BP) agricultural waste. Cellulose was first extracted from BP through delignification, bleaching and hydrolysis processes. Then, CMC was prepared by the carboxymethylation reaction using monochloroacetic acid as a modifying agent. A mixture of 30% sodium hydroxide solution and isopropanol was used as the solvent medium for etherification with reaction time of 1-5 hours. The effects of reaction time on physical appearance, chemical structure, degree of substitution (DS), percent yield (%yield) and morphology of CMC were studied. Results indicated that banana peel cellulose (BPC) powder could be extracted from BP with yield of 14.81%±7.20. CMC was successfully prepared from BPC powder and confirmed by FT-IR technique. DS and %yield of CMC increased when reaction time increased from 1 to 4 hours but decreased when reaction time reached 5 hours. Reaction time of 4 hours gave optimal DS and %yield at 0.61±0.05 and 152.65±17.93, respectively. BPC presented bulk particle shape with a dense and smooth surface. After etherification, morphology of BPC was changed to a mixture of small particles with fibrous shape and a porous rough surface.

Keyword: Carboxymethyl cellulose, Cultivated banana peel, Carboxymethylation, Agricultural waste,
1. Introduction

Thailand is a world leader in agricultural products with abundant biomass residual resources such as stems, trunks, stalks, leaves and fruit peel produced each year. The government has encouraged utilization of these agricultural residues in various fields including fuels, animal feed and compost [1,2]. Cultivated banana is ubiquitous in Thailand and grown in every province. In Nonthaburi Province, cultivated banana products such as sun-dried banana and rolled dried banana are processed by Klong Phra Udom Community. Banana peel waste after food processing can cause environmental pollution. Agricultural wastes from different plant parts consist of cellulose that can be transformed into useful and valuable products such as lignocellulose, pulp, micro or nanocrystalline cellulose and cellulose derivatives. Cellulose is a polysaccharide composed of anhydroglucose ring units joined by β-1,4 glycosidic linkages. Cellulose and cellulose derivatives can be prepared from fruit peel such as orange [3], papaya [4] and banana [5]. Many research studies have investigated the extraction of cellulose from fruit peel wastes. For example, Singanusong et al. [5] studied the extraction of cellulose from banana peel. Results showed that after elimination of fat and protein, banana peel cellulose had higher moisture, fat, protein, ash content and water activity but lower fiber and cellulose contents than commercial products at 33.57% and 75.90%, respectively. Hydroxyl groups in the cellulose structure can be modified by various reactions to produce cellulose derivatives such as cellulose acetate, cellulose ester and cellulose ether.

Carboxymethyl cellulose (CMC) is a cellulose derivative that has received increased research attention because it can be used as a viscosity modifier, thickener and emulsifier in many diverse industry sectors including food and beverage, cosmetics, pharmaceutics, personal care and health care products, paints, paper processing and packaging [6]. Moreover, global consumption of CMC has recently increased through its use in food, beverage, personal care and health care products [7]. CMC is classified as a cellulose ether and called carboxymethyl cellulose. CMC is synthesized from the reaction of monochloroacetic acid and alkaline cellulose. Properties of CMC including solubility, thermal stability and morphology depend on its degree of substitution (DS) [8]. Studies of CMC synthesis from different plant parts such as trunk and stalk are abundant but details of preparation of CMC from peel waste are limited. Thus, this work is focused on the preparation and characterization of CMC from cultivated banana peel waste. In this study, cellulose was first extracted from banana peel by processes of delignification, bleaching and hydrolysis. Then, CMC was prepared by the carboxymethylation reaction of cellulose using chloroacetic acid as a modifying agent and a mixture of sodium hydroxide and isopropanol as the solvent. Reaction time was varied from 1-5 hours. The effects of reaction time on physical appearance, degree of substitution (DS), yield and morphology of carboxymethyl cellulose were assessed.

2. Materials and methods

2.1 Materials

Cultivated banana peel waste was collected from the Klong Phra Udom Community, Nonthaburi Province, Thailand. Chemicals used during the study were sodium hydroxide (AR grade, Fisher Scientific, UK), hydrogen peroxide (AR grade, QRëC® Company, New Zealand), hydrochloric acid (37%, RCI Labscan, Thailand), isopropanol (LOBA Chemical, India), monochloroacetic acid (MCA) (LOBA Chemical, India), methanol (RCI Labscan, Thailand) and 1% phenolphthalein solution (QRëC® Company, New Zealand).

2.2 Cellulose powder extraction and carboxymethyl cellulose preparation

The banana peel was cut into small pieces and dried in an oven for 24 hours. Then, 100 g of dried banana peel was soaked in 0.5 M NaOH solution for 24 hours before heating at 100 °C for 4 hours with occasional stirring to remove the lignin. The delignified banana peel was bleached twice with 6% hydrogen peroxide solution at 90-100 °C for 1 hour to obtain cellulose pulp and then hydrolyzed with 2.5 M hydrochloric acid at 60-70 °C for 1 hour. The hydrolyzed pulp was washed with distilled water.
until the pH was neutral, dried in an oven at 60 °C for 24 hours and then ground and sifted through a No.40 mesh sieve.

The synthesis condition of CMC followed the method of Yuliasmi et al.[8]. Two grams of dried cellulose were dissolved with co-solvents of 30 ml isopropanol and 10 ml 30% NaOH solution at 80 °C for 2 hours using a hotplate stirrer. After the cellulose swelled, 3 g of sodium monochloroacetic acid were added and stirred for 1, 2, 3, 4 and 5 hours at 80 °C until the carboxymethylation process was completed. The mixture was coagulated in methanol and then filtrated. The residue was dried in an oven at 60 °C for 24 hours to obtain CMC powder that was kept in a desiccator until required for use.

2.3 Characterization
The percent yield of synthesized CMC was calculated based on the dry weight of CMC and cellulose, following the equation (1)

$$\text{CMC yield\%} = \frac{\text{weight of obtained CMC}}{\text{weight of dried cellulose powder}} \times 100$$ (1)

The degree of substitution (DS) of CMC was evaluated by back titration method according to a standard ASTM method (D1439-94) and Bono et al.[9]. The degree of substitution (DS) of CMC is the average number of the substituted hydroxyl group in cellulose structure which is substituted by carboxymethyl and sodium carboxymethyl group. The DS of the CMC sample was calculated as follows equation (2) and (3).

$$A = \frac{(BC-DE)}{F}$$ (2)

$$\text{Degree of Substitution} = \frac{(0.162)xA}{1-(0.058xA)}$$ (3)

where A is the Mili-equivalents of consumed acid per gram of specimen, B is the Millimeters of added sodium hydroxide, C is the Normal sodium hydroxide, D is the Millimeters of consumed hydrochloric acid, E is the Normal hydrochloric acid and F is the dried weight of sample used. While, 162 is molecular weight of anhydro glucose unit and 58 is net increment in the anhydroglucose unit.

Functional groups of the obtained CMC were studied using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrophotometer (TensorII, Bruker, Switzerland). Powder samples of cellulose were performed in ATR mode at ambient temperature in the region of 500-4000 cm⁻¹ by an average of 32 scans with a resolution of 4 cm⁻¹. Morphology of the obtained CMC was characterized using a Scanning Electron Microscope and Energy Dispersive X-ray (IT-500HR, JEOL, Tokyo). Samples were mounted on a carbon-coated copper grid and coated with gold for conductivity. The SEM micrograph was collected at the accelerating voltage of 15 kV.

3. Results and Discussion

3.1 Physical appearance of banana peel cellulose(BPC) powder and banana peel carboxymethyl cellulose (BP CMC)
BPC powder showed a mixture of particle and flake shapes with a brown-yellow color. As observed by naked eye, BPC powder grains were larger than CMC powder because of a tendency for agglomeration, while BP CMC was a finer powder and lighter yellow than BPC powder. Some agglomeration was recorded in the CMC sample that was prepared from long reaction time of etherification (4-5 hours). Furthermore, the color of CMC turned brownish when reaction time reached 5 hours, possibly due to degradation of CMC at long reaction time (Figure 1).
3.2 Functional group analysis

The spectrum of BP raw material presented an absorption band in the range 3400 to 3200 cm\(^{-1}\) showing the stretching frequency of the -OH group due to intramolecular and intermolecular hydrogen bonds in cellulose molecules. The broad bands at wavenumbers 2900-2800 cm\(^{-1}\) and 1200-1000 cm\(^{-1}\) were attributed to stretching of C-H and -O- in the cellulose structure [10,11]. The absorption peak in the region 1600-1300 cm\(^{-1}\) resulted from lignin. Peaks at 1373, 1446 and 1616 were characteristic of C=C aromatic ring vibration in lignin structure [11-13]. The small peak around 1700 cm\(^{-1}\) was assigned to C=O vibration of acetyl and uronic ester groups of hemicelluloses or to the ester linkage of carboxylic groups of ferulic and p-coumaric acids of lignin [12,13]. After bleaching and acid hydrolysis, FTIR spectra of BPC and BP were similar. Nevertheless, absorbance of the band around 1600-1300 cm\(^{-1}\) decreased owing to diminished lignin content [11] (Figure 2).

Absorption bands of all CMC were similar to BP and BPC, indicating that BP, CMC, BPC and BP had similar functional groups. However, BPC presented peaks around 1300 cm\(^{-1}\) and 1000-1100 cm\(^{-1}\) that were assigned to -OH bending and ether group (-O-) vibration, respectively [11], while strong absorbance peaks around 1590 and 1400 cm\(^{-1}\) were attributed to antisymmetric and symmetric stretching of the COO- group. These results confirmed substitution of carboxymethyl group on the cellulose structure [11-14], concurring with Suriyatem et al. [11] and Alizadesh et al. [14] who reported that peaks around 1600-1590 cm\(^{-1}\) and 1420-1400 cm\(^{-1}\) were contributed to carboxyl and groups of carboxymethyl cellulose. Results proved that the hydroxyl group of banana peel cellulose structure was substituted by carboxyl and carboxymethyl groups to become carboxymethyl cellulose (CMC).

3.3 Effects of reaction time on degree of substitution (DS) and yield percentage of CMC

BPC powder was extracted from cultivated banana peel waste (maturity stage 2-4) using delignification, bleaching and hydrolysis processes. Yield percentage of extracted cellulose powder (% dry basis) was 14.81% ± 7.20. The degree of substitution (DS) is the average number of hydroxyl groups in the cellulose structure substituted by carboxymethyl or sodium carboxymethyl groups at carbon 2, 3 and 6. Figure 3 (a) and (b) presents the degree of substitution (DS) and yield of CMC at various reaction times (1, 2, 3, 4 and 5 hours). Results showed that DS and yield of obtained CMC ranged 0.40-0.61 and 97.98-152.65, respectively. DS and yield increased when reaction time increased from 1 to 4 hours due to substitution of carboxymethyl groups on the cellulose structure. The reaction time of carboxymethylation at 4 hours gave the highest DS and yield of BP CMC as 0.61±0.05 and 152.65±17.93, respectively, when compared to other reaction times. DS and yield of CMC decreased at reaction time of 5 hours because the side reaction dominated, causing the formation of sodium glycolate as a by-product and the degradation of CMC at long reaction time. These results concurred with Rachatanapun et al. [15] and others [11-14] who reported two competitive reactions that arise in the carboxymethylation process. The first involved carboxymethylation between the hydroxyl group of cellulose and sodium monochloacetic acid (NaMCA) to produce CMC, while the second was a side reaction between NaOH and NaMCA that formed sodium glycolate. At strong alkaline concentration, the side reaction took precedence over the carboxymethylation of cellulose hydroxyl, resulting in decline of DS, while a high level of NaOH concentration led to degradation of CMC. Moreover, Pushpamalar
et al. [16] explained that increased reaction time induced contact between the etherifying agent and cellulose. A suitable reaction time contributed to optimal DS value due to better diffusion and absorption of reactant, with the ultimate effect of inducing better contact between the etherifying agent and cellulose, leading to increased DS and yield, while prolonged reaction time was possible to degradation of CMC.

![Figure 2 FT-IR spectrum of banana peel(BP), banana peel cellulose(BPC) powder and banana peel carboxymethylcellulose(BP CMC) at various reaction time](image)

Figure 2 FT-IR spectrum of banana peel(BP), banana peel cellulose(BPC) powder and banana peel carboxymethylcellulose(BP CMC) at various reaction time

![Figure 3. (a) Degree of substitution (DS) and (b) yield of BP CMC at various reaction time.](image)

Figure 3. (a) Degree of substitution (DS) and (b) yield of BP CMC at various reaction time.

### 3.4 Effect of reaction time on morphology of BP CMC

The morphologies of BPC powder and BP CMC at 300 magnification are shown in Figure 4. BPC powder presented bulk particle shape with a dense and smooth surface, while BP CMC had a larger particle size than BP CMC. Average particle size of BPC powder was approximately 300 μm which was estimated by imageJ software. After etherification, the microstructure of CMC changed when compared to BPC. Morphology of CMC after 1 hour of carboxymethylation was particles like BPC but a low level of distortion and small pores occurred on the surface. After carboxymethylation for 2-5 hours, CMC altered shape from bulk particles with a dense and smooth surface to a mixture of small particles with fibrous shape and a porous rough surface. The transformation of morphology and distortion of CMC resulted from a chemical modification, similar to carboxymethyl bagasse [11] and carboxymethyl sago wastes [16].
Figure 4. SEM micrograph of (a)BPC and extracted BP CMC after reaction time of (b)1, (c)2, (d)3, (e)4, and (f)5 hours.

4. Conclusion
Banana peel cellulose (BPC) powder was extracted from cultivated banana peel (BP) waste. Yield of extracted cellulose powder (% dry basis) was 14%. The cellulose powder was used as raw material in the synthesis of carboxymethyl cellulose (CMC) by etherification between cellulose and chloroacetic acid under alkaline conditions. FT-IR results showed that CMC was successfully prepared from BPC powder. DS and percent yield of CMC increased when reaction time increased from 1 to 4 hours but at 5 hours DS and percent yield of CMC decreased due to side reactions and degradation of CMC. Reaction time of 4 hours gave optimal DS and percent yield at 0.61 and 152%, respectively. Carboxymethylation led to transformation and distorted shape of CMC. After modification, BPC altered its microstructural shape from bulk particles with a dense and smooth surface to a mixture of small particles with fibrous shape and a porous rough surface.

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References
[1] Jutidamrongphan W 2018 Sustainable Waste Management and Waste to Energy Recovery in Thailand (Advances in Biofuels and Bioenergy) (IntechOpen Limited, UK) chapter 11 pp 217-238
[2] Visvanathan C Chiemchaisri C 2019 Management of agricultural wastes and residues in thailand: wastes to energy approach http://faculty.ait.ac.th/visu/wp-content/uploads/sites/7/2019/01/Agri-waste2energy-Thai.pdf
[3] Yaşar F Toğrul H Arslan N 2007 J. Food Eng 81 pp 187-199
[4] Rachtanapun P 2009 Kasetsart J. (Nat. Sci.) 43 pp 259 – 266
[5] Singanusong R Tochampa W Kongbangkerd T Sodchit C 2014 Suranaree J. Sci. Technol. 21(3) pp 201-213
[6] Haleem N Arshad M Shahid M Muhammad A T 2014 Carbohydr. Polym. 13 pp 249-255
[7] Global Carboxymethyl Cellulose Market Research Report https://www.marketresearchfuture.com/reports/carboxymethyl-cellulose-market-6235
[8] Yuliasmi S Ginting N Wahyuni HS Sigalingging RT Sibarani T 2019 Maced J Med Sci 7(22) pp 3874-3877
[9] Bono A Ying P H Yan F Y Muei C L Sarbatly R Krishnaiah D 2009 Advances in Natural and Applied Sciences 3(1) pp 5-11
[10] Klunklin W Jantanasakulwong K Phimolsiripol Y Leksawasdi N Seesuriyachan P Chaiyaso T Insomphun C Phongthai S Jantrawut P Sommano R Punyodom W Reungsang A Ngo T M P Rachtanapun P 2021 Polymers 13(1) pp 81.
[11] Suriyatem R Noikang N Kankam T Jantanasakulwong K Leksawasdi N Phimolsiripol Y Insomphun C Seesuriyachan P Chaiyaso T Jantanawut P Sommano R Chaiyaso T Insomphun C Seesuriyachan P Chaiyaso T Jantanawut P Sommano R. and Rachtanapun P 2020 Polymers 12(7) pp 1505
[12] Kamsonlian S Sundaramurthy S Balomajumder C Chand S 2011 Int. j. sci. technol. manag. res. 2 pp 1-7
[13] Tibolla H Pelissari F M Menegalli F C 2004 LWT - Food Sci Technol 59(2)(2) pp 1311-1318
[14] Asl S A Mousavi M and Labbaf M 2017 J Food Process Technol 8 pp1-8
[15] Rachtanapun P Rattanapanone N 2011 J. Appl. Polym. Sci. 122(5) pp3218-3226
[16] Pushpamalar V Langford S J Ahma M d Lim Y Y 2006 Carbohydr. Polym 64 pp 213-218