Value added of mulberry paper waste by carboxymethylation for preparation a packaging film

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Abstract. Cellulose from mulberry paper waste was converted to carboxymethyl cellulose (CMCm) by etherification using chloroacetic acid and various sodium hydroxide (NaOH) concentrations (30-60 g/100 mL). The degree of substitution of the various CMCm materials produced ranged between 0.33-0.45. The chemical structure of cellulose and the synthesized CMCm materials was characterized using Fourier transform infrared spectroscopy. CMCm films were cast and tested. The tensile strength (TS) and percent elongation at break (EB) of the films were investigated. The highest TS (32.58 MPa) and EB (2.39%) were found using the 50g /100 mL NaOH-synthesized CMCm film. The effect of glycerol as a plasticizer on TS and EB of this CMCm film was also evaluated. Increasing the glycerol content decreased TS and increased EB of the CMCm films.

1. Introduction
Mulberry paper, or saa paper as it is known in Thailand, is widely used to make lanterns, book covers, decorative products, greeting cards, office equipment, packaging and a variety of other items [1]. Mulberry paper is made from the bark of the mulberry tree, a plentiful fibrous resource [2]. Mulberry trees are extensively grown in many countries of Asia, including Thailand, China, India, Laos and Myanmar. In northern Thailand, many industries produce mulberry paper and mulberry paper products for both domestic consumption and export. The waste from the paper production is discarded. This waste is both natural and a superlative cellulose source [3].

Cellulose normally appears in the cell walls of plants. It consists of a linear chain of glucose units joined together by β-glycosidic bonds between the C-4 of one sugar unit and the anomeric C-1 of the second sugar. Cellulose can be utilized in many forms, including as its original unmodified fibers or with derivatives as carboxymethyl cellulose (CMC) [4, 5]. CMC is a copolymer of two units: β-D-glucose and β-D-glucopyranose 2-O-(carboxymethyl)-monosodium salt that are connected via β-1, 4-glycosidic bonds. Due to its simple and inexpensive production, CMC is used extensively in food and non-food industrial applications [6]. CMC is obtained via carboxymethylation between cellulose and
chloroacetic acid (an etherifying agent) in an alkaline condition. The first step is an alkalization procedure as in equation (1), where NaOH reacts with the hydroxyl groups of the cellulose.

\[
\text{Cellulose-OH} + \text{NaOH} \rightarrow \text{Cellulose-ONa} + \text{H}_2\text{O} \quad (1)
\]

In the second step, etherification occurs as in equation (2) to obtain CMC and a side reaction as in equation (3), which results in sodium glycolate [4].

\[
\text{Cellulose-ONa} + \text{Cl-CH}_2\text{-CO-ONa} \rightarrow \text{Cellulose-O-CH}_2\text{-COONa} \rightarrow \text{NaCl} \quad (2)
\]

\[
\text{NaOH} + \text{Cl-CH}_2\text{-CO-ONa} \rightarrow \text{HO-CH}_2\text{-CO-ONa} + \text{NaCl} \quad (3)
\]

According to published reports, CMC has been produced from a variety of agricultural waste cellulose sources, including cotton linters [7], sugar beet pulp [8], cashew tree gum [9], cavendish banana pseudo stem [10], papaya peel [12], Mimisa pigra peel [6], durian rind [4] and cotton gin waste [13]. However, the production and characterization of CMC film from mulberry paper waste (CMCm) has not previously been reported.

This study evaluated the influence of varying NaOH concentrations for CMC synthesis from mulberry paper waste on the degree of substitution and chemical structure of CMCm. The study also investigated the effects of NaOH concentrations on the mechanical properties, including tensile strength (TS) and percent elongation at break (EB), of the synthesized CMCm films. In addition, the effect of the amount of plasticizer on the CMCm films, including on TS and EB, was determined.

2. Methodology

2.1. Materials

Mulberry paper waste was purchased from Bankradassa (Chiang Mai, Thailand). All chemicals used in the preparation and analysis of carboxymethyl cellulose (CMC) were AR grade or the equivalent. Isopropanol, methanol, ethanol, glycerol, distilled water and commercial grade carboxymethyl cellulose (CMCc) were purchased from Northern Chemical Co., Ltd. (Chiang Mai, Thailand). Monochloroacetic acid was purchased from Sigma-Aldrich (Steinheim, Germany). Sodium hydroxide and glacial acetic acid were purchased from RCI Lab-scan Co., Ltd. (Bangkok, Thailand).

2.2. Synthesis of carboxymethyl cellulose and characterization

Carboxymethyl cellulose (CMCm) from mulberry paper waste was synthesized according to the procedure described by Rachtanapun and Rattanapanone [6], with slight modification. Cellulose from mulberry paper waste (15 g), 750 mL of isopropanol and 150 mL of various concentrations (30, 40, 50 and 60 g/100 mL) of NaOH were mixed in a beaker for 90 min. Monochloroacetic acid (MCA, 22.5 g) was introduced and the mixture was continuously stirred for 90 min. The beaker was covered with aluminum foil and placed in a hot air oven at 55°C for 3.5 h, where the mixture separated into a liquid and solid phase. The liquid phase was removed by filtration. Then, the solid phase was isolated by precipitation into 100 mL of methanol (70% v/v) and neutralized with glacial acetic acid. The neutralized product was filtered and washed 5 times by soaking in 300 mL of ethanol (70% v/v) for 10 min and filtering. The product (CMCm) was then washed again with 300 mL of absolute methanol, filtered and dried at 55°C for 12 h. The CMCm was stored in a PE bag in a dry place.

The DS was determined using the USP XXXII method described for Crosscarmellose sodium in two steps – titration and collection of residue on ignition – as previously described by Rachtanapun and Rattanapanone [6] and Rachtanapun et al. [4]

2.3. Infrared spectroscopy (IR)

The functional groups of the cellulose and CMCm samples were determined using an infrared spectrophotometer (Bruker, Tensor 27, Germany). Pellets were made from cellulose and the CMCm samples (~2 mg) and KBr. Transmission levels measured for wavelengths of 4000-400 cm⁻¹.
2.4. Film preparation
CMC (3 g) was dissolved in 100 mL of distilled water and constantly stirred at 80°C for 10 min. The resulting solution was cooled to around 20-25°C and cast on Mylar® film using a tape casting machine (DP 150, Japan) at 20 rpm set to produce a film thickness of 30 μm. The casted solution was left to dry at room temperature for 20 h, producing the CMC film. The film was peeled and kept in a dry place.

2.5. Mechanical properties
The TS and EB of the film were determined using an Instron Universal Testing Machine Model 1000 (H1K-S, England) with the procedure according to ASTM D882-80a. The film specimen was cut into 15 x 140 mm rectangles. The initial grip separation and crosshead speed was set at 100 mm and 20 mm/min, respectively. Before testing, each film was pre-conditioned at 65±2% relative humidity for 24 h at 27±2°C. Ten specimens were measured.

2.6. Film preparation with glycerol as plasticizer
From the mechanical property tests, we selected the most promising film to further test with plasticizer. Various amounts (0.1, 0.2, 0.3 and 0.4 mL) of glycerol were introduced in the film solution to overcome film brittleness. The method of film preparation presented above and subjected to the mechanical property tests as described earlier.

3. Results and discussion
3.1. Characterization of CMCm materials
CMCm materials were synthesized via carboxymethylation between alkalized cellulose from mulberry paper waste and an etherifying agent. Various alkali concentrations (30, 40, 50 and 60 g/100 mL) during synthesis yielded four different CMCm as CMCm30, CMCm40, CMCm50 and CMCm60, respectively.

DS measurements indicate the water solubility of CMC, with increasing DS values indicating increasing hydrophillicity. CMC is completely soluble at DS values above ~0.4. Below ~0.4, CMC is swellable, but insoluble [8]. The DS values of the CMCm produced here ranged from 0.33–0.45 (table 1). The DS value increased when the NaOH concentration increased from 30 to 40 g/100 mL, reaching its maximum DS of 0.45 from CMCm40. Beyond 40 g/100 mL NaOH, the DS decreased. This result can be explained by the reactions of CMC synthesis, as described in Rachanapun and Rattanapanone [6] and Rachtanapun et al. [4] The process of carboxymethylation in the experiment yielded two main products. The first product is a desired CMC obtained from the reaction of cellulose hydroxyl and NaMCA. The secound product is a sodium glycolate as a by-product formed from the conversion of NaMCA and NaOH [14]. The results of this study imply that if the alkaline level is higher than 40 g/100 mL, the latter reaction is favored, therefore reducing the DS value of the obtained CMC. Previous studies of CMC from sugar beet pulp [8], sago waste [11], banana pseudo stem [10], Mimosa pigra peel [6] and durian rind [4] reported similar DS results.

| Sample   | DS    |
|----------|-------|
| CMCm30   | 0.4473|
| CMCm40   | 0.4540|
| CMCm50   | 0.3521|
| CMCm60   | 0.3320|

The IR spectrum of CMC materials normally show the typical absorptions of the cellulose backbone, including the presence of the carboxymethyl ether group at 1605 cm⁻¹ [11]. The frequency of the absorption bands of the representative spectrum of cellulose from mulberry paper (figure 1a)
and CMCm synthesized with various NaOH concentrations (figures 1b-1e) were similar. This result indicated that cellulose and CMCm contained similar functional groups. A broad band at 3100-3700 cm\(^{-1}\) is due to O–H stretching. The band at 2900 and 1600 cm\(^{-1}\) is due to a C–H stretching and C–O stretching vibration, respectively. The bands around 1450 and 1000-1200 cm\(^{-1}\) are due to –CH\(_2\) scissoring and –O– stretching, respectively. The band at 1060 cm\(^{-1}\) is due to –CH–O–CH\(_2\) stretching [15]. The absorbent bands in each CMCm spectrum were similar, but differed from those of cellulose. The differences were noticed at 1600, 1420 and 1100 cm\(^{-1}\). This phenomenon confirmed that carboxymethylation took place on the cellulose molecules. The carboxymethyl substituent for the absorption bands were COO–, –CH\(_2\) and –O–, respectively [4, 6, 10]. Similar results have been reported previously [4, 6, 11].

![Figure 1](image-url)

**Figure 1.** IR spectra of cellulose from mulberry paper waste (a) and CMCm synthesized from various NaOH concentrations: 30 (b), 40 (c), 50 (d) and 60 (e) g/100 mL NaOH.

3.2. **CMCm films: effect of alkaline level of CMC synthesis on mechanical properties**

The effect of the various NaOH concentrations in synthesizing CMCm on the mechanical properties – strength and flexibility – of the resultant films are reported below.

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Different CMCm films were prepared. They appeared white and translucent, because of residual insoluble cellulose (figures 2a-2d). A commercial grade CMC (CMCc) film was also prepared, but was transparent (figure 2e). The CMCm60 wrinkled after drying, and as a result could not be formed into a film (figure 2d). The CMCm60 film forming solution flowed faster than the others when casted. This occurred because the hydrolysis reaction in the cellulose chain took place when a high level of alkaline was utilized, and the intermolecular hydrogen bonds decreased with the increasing basic concentration [16]. As a result, CMCm60 film could not be tested for mechanical properties.

Figure 2. The appearance of CMCm films synthesized from various NaOH concentrations: 30 (a), 40 (b), 50 (c) and 60 (d) g/100 mL NaOH; and commercial CMC (e).

Figure 3a shows the TS of the CMCm films. The TS of the films increased with increasing NaOH concentrations (30-50 g/100 mL) used in CMC synthesis. The CMCm50 showed the highest TS value of the CMCm films, and compared favorably with the commercial grade film. The increasing TS of the CMCm films may be a result of more combination between the swellable part (fibers) and soluble component (desired CMC) of the CMCm materials. The addition of fibers reinforced the tensile properties of the films, increasing their TS [17]. However, our result is contrary with previous reports for CMC films from durian rind [4] and Mimosa pigra peel [6], where the TS correlated directly with the DS value of the CMC materials. An increasing DS due to the substitution of carboxymethyl groups
increased the ionic character and intermolecular force between the polymer chains [6, 10]. Despite this, the DS of CMC materials and the TS of CMC films decreased when too high of a NaOH concentration was employed, because of sodium glycolate formation as a by-product and polymer degradation. This leads to low CMC content, which lowers the intermolecular forces [18].

The EB of the polymer is a measure of its flexibility. In this study, the EB of the CMCm films increased with increasing NaOH concentrations (figure 3b), similar to the TS results. This result agrees with the previous report of CMC films from Mimosapigrapeel [6]. In contrast, the EB of CMC films from durian rind did not change significantly with different levels of NaOH in CMC synthesis. [4] The CMCm50 showed the highest EB value, higher than that of the CMCc film (figure 3b).

![Figure 3](image.png)

**Figure 3.** Mechanical properties, (a) TS and (b) EB, of the CMCm films synthesized from various NaOH concentrations compared with commercial CMC.

From our experiment, the CMCm50 film provided the best mechanical properties. However, as prepared, it was too brittle to use for packaging. Given its underlying mechanical advantages, we introduced glycerol as a plasticizer in an effort to overcome its brittleness, as reported in the next section.

3.3. CMCm50 films: effect of a plasticizer on mechanical properties

Various glycerol concentrations as a plasticizer were introduced into the film forming solutions of CMCm50 in an effort to improve its mechanical properties before casting. Figures 4a and 4b present the TS and EB of the CMCm50-plastisized films, respectively. Increasing glycerol content in the CMCm-plasticized films decreased the TS and increased the EB. The glycerol increased the flexibility of the films due to its ability to reduce internal hydrogen bonding between polymer chains with increasing of a space between the polymers [6, 19]. The increasing flexibility of hydrophilic films with increasing plasticizer content has been reported previously [6, 12, 17, 20].

![Figure 4](image.png)

**Figure 4.** Mechanical properties, (a) TS and (b) EB, of the CMCm50 films plasticized with several amounts of plasticizer.
4. Conclusions
Mulberry paper waste was successfully employed as a raw material to produce carboxymethyl cellulose using MCA as an etherifying agent and isopropanol as a medium under various alkaline conditions. The DS value of the CMCm materials decreased with increasing NaOH concentrations. The CMCm synthesized with 40 g/100 mL NaOH produced the highest DS value of 0.45. As shown in this study, the NaOH concentration used in CMC synthesis directly correlated with the mechanical properties of the CMCm. The CMCm film derived from 50 g/100 mL NaOH had the best mechanical properties. This film was chosen to improve its flexibility by adding glycerol as a plasticizer. The amount of plasticizer, in turn, strongly affected the mechanical properties of the film. The CMCm materials produced here are new biopolymers with potentially broad industrial applications, including as film forming agents, binding agents, gelling agents and/or emulsifying agents.

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