

# Carboxymethyl Cellulose (CMC) from Oil Palm Empty Fruit Bunch (OPEFB) in the new solvent Dimethyl Sulfoxide (DMSO)/Tetrabutylammonium Fluoride (TBAF)

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**Abstract.** The surplus of Oil Palm is the most galore wastes in Malaysia because it produced about half of the world palm oil production, which contributes a major disposal problem. Synthesis from an empty fruit bunch produced products such as Carboxymethyl Cellulose (CMC), could apply in diverse application such as for paper coating, food packaging and most recently, the potential as biomaterials has been revealed. In this study, CMC was prepared by firstly dissolved the bleached pulp from OPEFB in mixture solution of dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF) without any prior chemical modification. It took only 30 minutes to fully dissolve at temperature 60<sup>0</sup>C before sodium hydroxide (NaOH) were added for activation and monochloroacetate as terrifying agent. The final product is appeared in white powder, which is then will be analyzed by FTIR analysis. FTIR results show peaks appeared at wavenumber between 1609 cm<sup>-1</sup> to 1614 cm<sup>-1</sup> proved the existence of carboxymethyl groups which substitute OH groups at anhydroglucose (AGU) unit. As a conclusion, mixture solution of DMSO/TBAF is the suitable solvent used for dissolved cellulose before modifying it into CMC with higher Degree of Substitution (DS). Furthermore, the dissolution of the OPEFB bleached pulp was easy, simple and at a faster rate without prior chemical modification at temperature as low as 60<sup>0</sup>C.

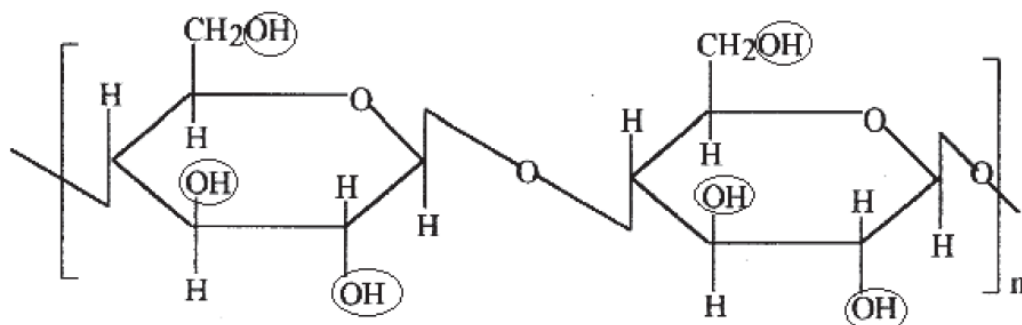
## 1. Introduction

World palm oil production in 1990 doubled to 11.0 million tonnes from 5.0 million tonnes in 1980, and by the year 2000, the production doubled to 21.8 million tones [1]. Malaysia produced about half of the world palm oil production (10.8 million tonnes), thus, making Malaysia as the world's largest producer and exporter of palm oil during this period [2]. Palm oil surplus such as fronds and empty fruit bunches can be used in many process industries until recently Cellulose Phosphate (CP) one of the product synthesized from empty fruit bunch was used as material for biomedical applications because it has the potential due to its biocompatibility and ability to induce the formation of apatite nuclei [3]. CP has high Ca binding capacity, associated with lack of toxicity and indigestibility, has been used for decades in the treatment of Ca metabolism-related diseases [4 – 6]. Due to the reason, CP was then investigated for orthopaedic application to improve the osseointegration of cellulose [7].

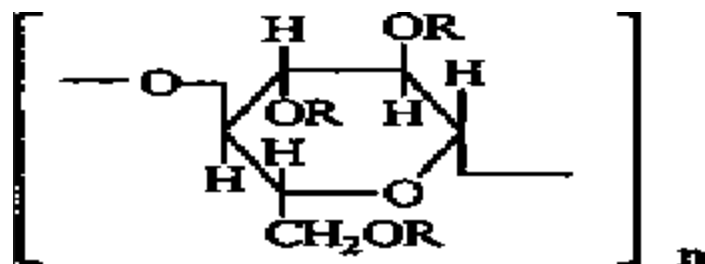
Carboxymethyl Cellulose (CMC) is rarely used as a biomaterials. Conventionally, it was used in wide application of food, pharmaceuticals, toothpaste, detergents, oil drilling mud, paper coating and others [8]. Nowadays, CMC is used to enhance the viscosity, to control rheology of a solution, to avoid separation of water from a suspension and to improve surface or barrier properties [9]. Of late, it has been also investigated for its potential use as biomaterials [10].



The usage of CMC as a biomaterials base for the reason that the product is from polysaccharide group containing cellulose structural. Cellulose is a linear macromolecule in which anhydroglucose unit (AGU) are linked by  $\beta$ -1,4-glucosidic bonds [8]. AGU are presented from three reactive hydroxyl groups: the primary OH on C(6) and the two secondary OHs on C(2) and C(3) [8, 11]. Fig. 1 shows the general chemical structure of the cellulose presenting AGU unit and next the chemical structure of CMC (Fig. 2) after etherification process where OH groups are etherified with a carboxymethyl group.



**Figure 1:** Chemical structure of cellulose. AGU units are circled at carbon number 2, 3 and 6.

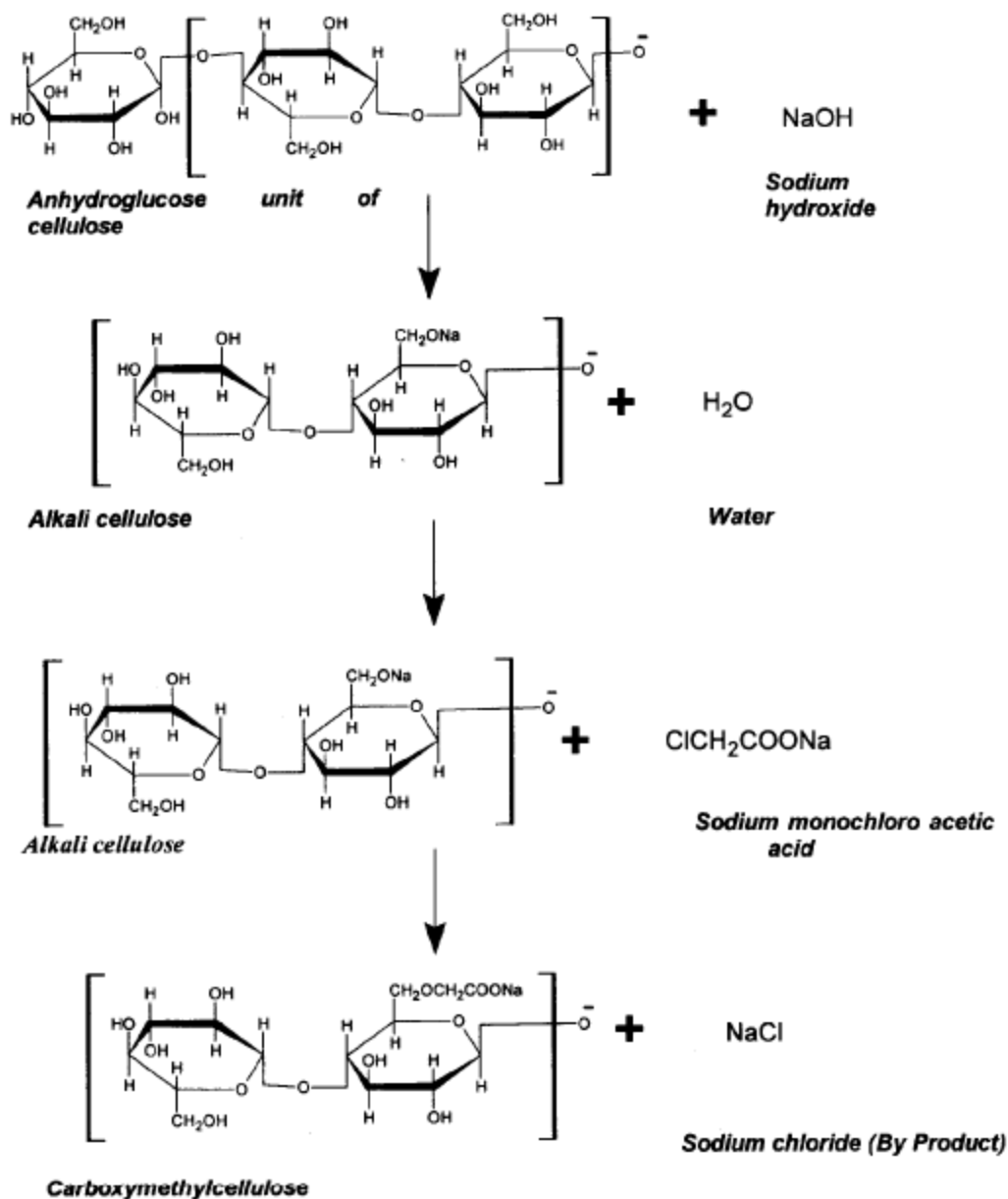


**Figure 2:** Carboxymethyl cellulose chemical structure. The OH group at C(2), C(3) and C(6) are substituted with Sodium Carboxymethyl groups where  $R = CH_2CO_2Na$ .

## 2. Carboxymethylated from various natural sources

CMC is produced by conversion of alkali cellulose in an organic liquid/aqueous NaOH with monochloroacetic acid or its sodium salt as etherifying agent [12] as illustrated in fig. 3. The sources of CMC were a lot such as from sisal [12], cotton linters [12, 13, 14] viscose staple fibre [13], spruce sulfite pulp [13], rayon grade wood pulp [14], durian rind [15], banana pseudo stem [16] and most recently from oil palm waste, empty fruit bunch [17].

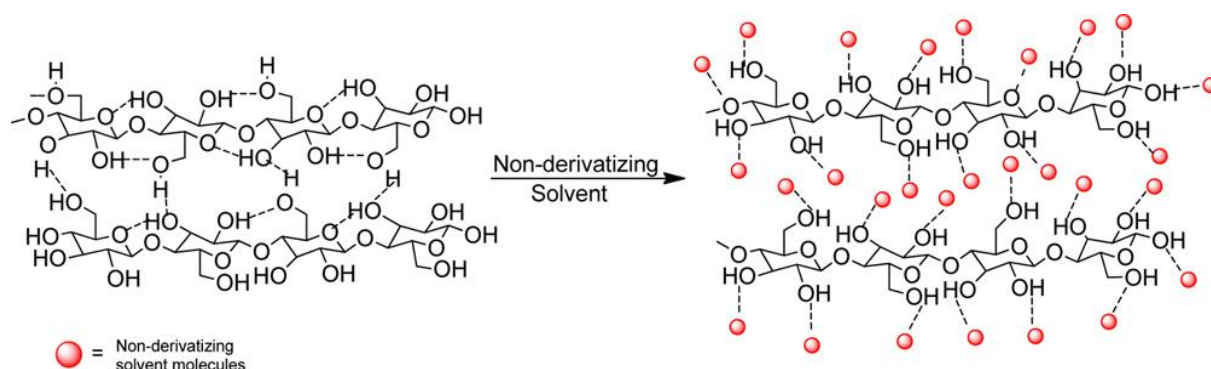
Synthesization of CMC is simple and easy that commonly followed conventional way to produce it. The bleached pulp of OPEFB is treated with NaOH at a certain temperature, and the alcohol usually ethanol or isopropanol. This treatment is required as a swelling and impregnation stage and facilitates penetration of the NaOH into the cellulose structure. The product produced at this stage is called alkali cellulose (Na-cellulose) which is highly reactive towards monochloroacetic acid (MCA), or its sodium salt that normally carried out at about  $50^{\circ}C$  to  $70^{\circ}C$ , were added in the following etherification stage. The method has been practically used since 1920's [8] and already used frequently to produce CMC from various sources [8, 9, 11], [18].



**Figure 3:** The reaction for the synthesis sodium carboxymethylcellulose [14] which shows reaction occur at Carbon number 6 [C(6)].

### 3. Cellulose dissolution in Tetrabutylammonium fluoride (TBAF)/Dimethyl sulfoxide (DMSO)

TBAF/DMSO is a powerful solvent for cellulose with a degree of polymerization as high as 650 can be dissolved without any pre-treatment within 15 minutes [19]. It is well known that cellulose is not soluble in conventional solvents, due to its supramolecular structure formed by inter- and intramolecular hydrogen bonds [20] – [26]. The cellulose dissolution power of the TBAF/DMSO system is essentially due to the strong ion-dipole interaction between fluoride ions from TBAF and the hydroxyl groups of cellulose [26]. The highly electronegative fluoride ion from hydrogen bonds with the cellulose hydroxyl groups deconstructing the hydrogen-bonded cellulose network [27]. Fig. 4 illustrates mixture solvents of TBAF/DMSO react with cellulose in disrupting the hydroxyl groups.



**Figure 4:** Non-derivatizing solvent of TBAF/DMSO reacts in disrupting the hydroxyl groups of cellulose [27].

The preparation of CMC from OPEFB is slightly different in this research where the bleached pulp was firstly dissolved in TBAF/DMSO mixture solution. This is due to the observation that CMC produced without prior dissolution, will not appear in powder form like CMC commercial. The product required to be appeared in powder form in order to suit with the requirement for biomaterial application. Fig. 5 shows different physical appearance between CMC without prior dissolution and CMC with prior dissolution.



**Figure 5:** CMC produced (a) without prior dissolution and (b) with prior dissolution

## 4. Materials and Methods

### 4.1 Materials

OPEFB was supplied by SABUTEK (M) Sdn. Bhd, and all the chemicals were bought from BGOilchem, Penang, Malaysia. All the experimental work was done at School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia.

### 4.2 Extraction of bleached pulp from OPEFB

For this investigation, oil palm empty fruit bunch (OPEFB) cellulose was prepared using the environmentally benign process [28, 29]. This procedure involves water pre-hydrolysis of the OPEFB, followed by soda-anthraquinone pulping. Then the unbleached pulp was bleached using a totally chlorine-free (TCF) sequence of oxygen (O), ozone (Z) and peroxide (P) to a kappa number of 1.4.

### 4.3 Synthesis

#### 4.3.1 Dissolution of bleached pulp of OPEFB in TBAF/DMSO

Cellulose (bleached pulp of OPEFB) was immersed in a mixture solution of 60ml DMSO and 6.6g TBAF. Stirred evenly by magnetic stirrer for 30 minutes at temperature 60°C for 30 minutes in fume chamber, resulting in a clear solution of cellulose.

#### 4.3.2 Carboxymethylation of OPEFB bleached pulp in TBAF/DMSO

Following previous application [12], to the cellulose solution, 4.94g of NaOH which was suspended in 10ml of DMSO, and subsequently 10.78g of monochloroacetate were added under vigorous stirring using magnetic stirrer leading to gelation and partly precipitation of the cellulose. The temperature was raised to 70°C. After 4h, the mixture was cooled to room temperature and put into 300ml isopropanol. The solid product was filtered off, dissolved in 40ml of distilled water, neutralized with either NaOH if too acidic or with acetic acid if the alkali solution, and precipitated into 300ml of ethanol. After filtration, the product was washed with 90% (v/v) ethanol and dried in an oven at 50°C. Finally, to obtain fine white powder, the product was grind by using stone and mortar and kept in desiccators.

### 4.4 Characterization of Sodium Carboxymethylcellulose by FTIR analysis

Product of CMC was analyzed by using FTIR analysis with OMNIC software.

## 5. Results and Discussions

FTIR analysis using OMNIC software was done on the bleached pulp of OPEFB, CMC commercial, CMC with prior dissolution in TBAF/DMSO and CMC without prior dissolution in TBAF/DMSO, wavenumber between 4000cm<sup>-1</sup> to 400cm<sup>-1</sup>. Fig. 6 is attached here as the comparison for FTIR result obtain for CMC synthesized from OZP-pulp of OPEFB. From fig. 6 and fig. 7, it shows obvious different pattern of graph and the existence peaks. It proves the attendance of new group when the pulp was synthesized to CMC, the water dissolved cellulose.

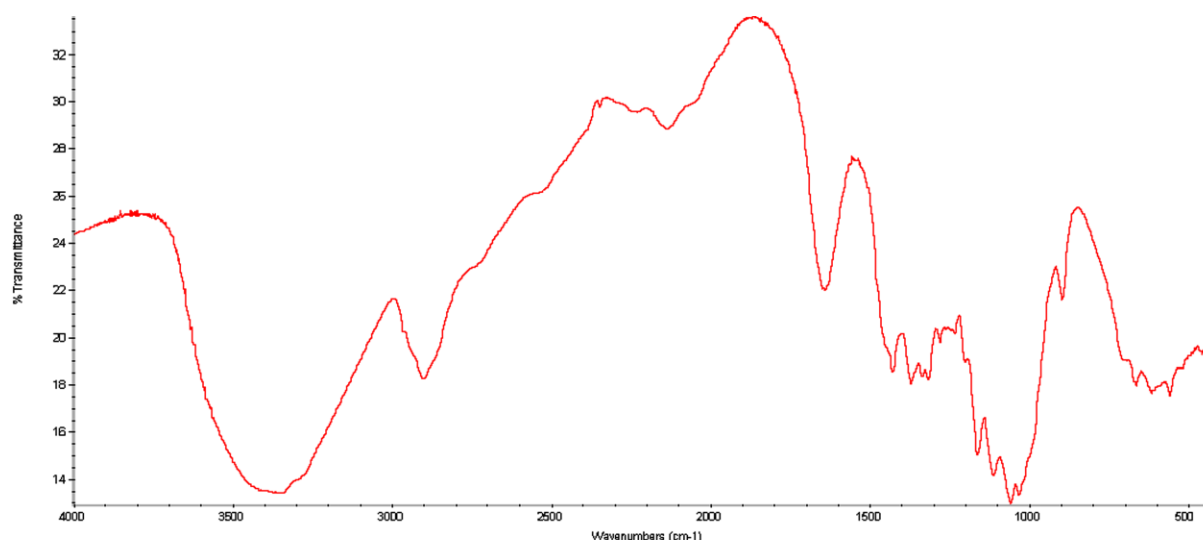
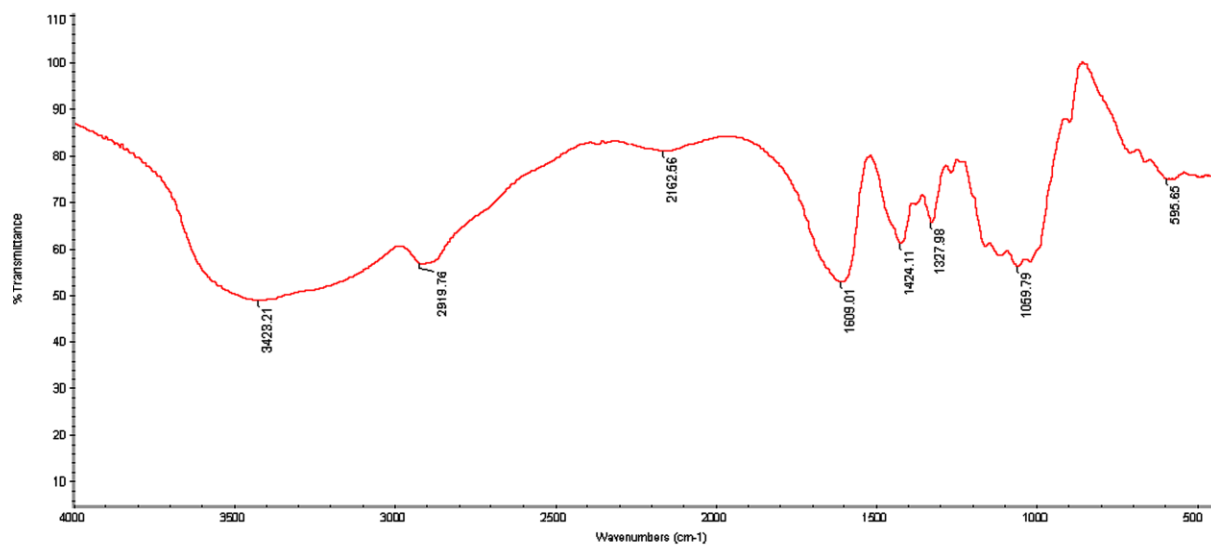
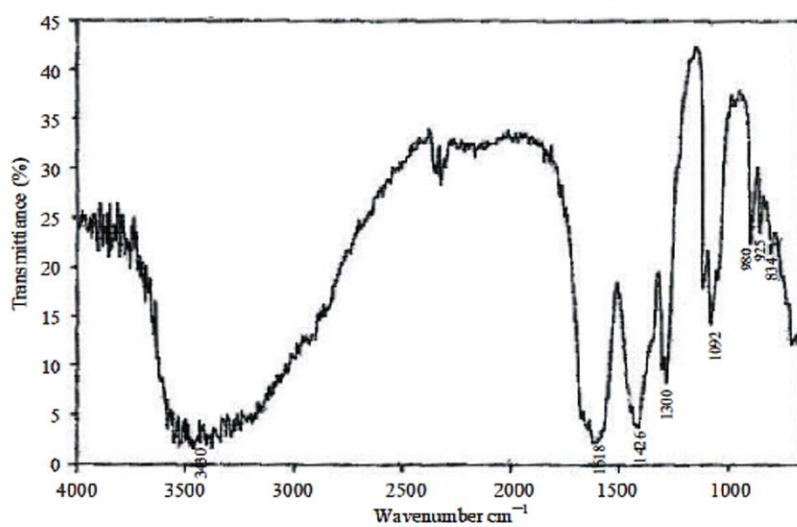


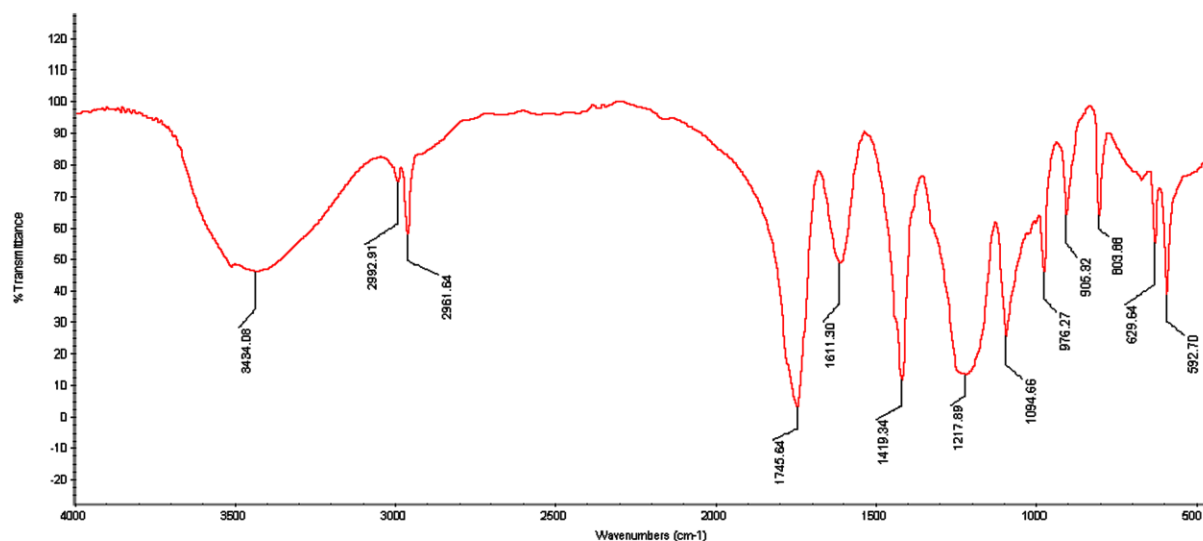
Figure 6: OZP-pulp



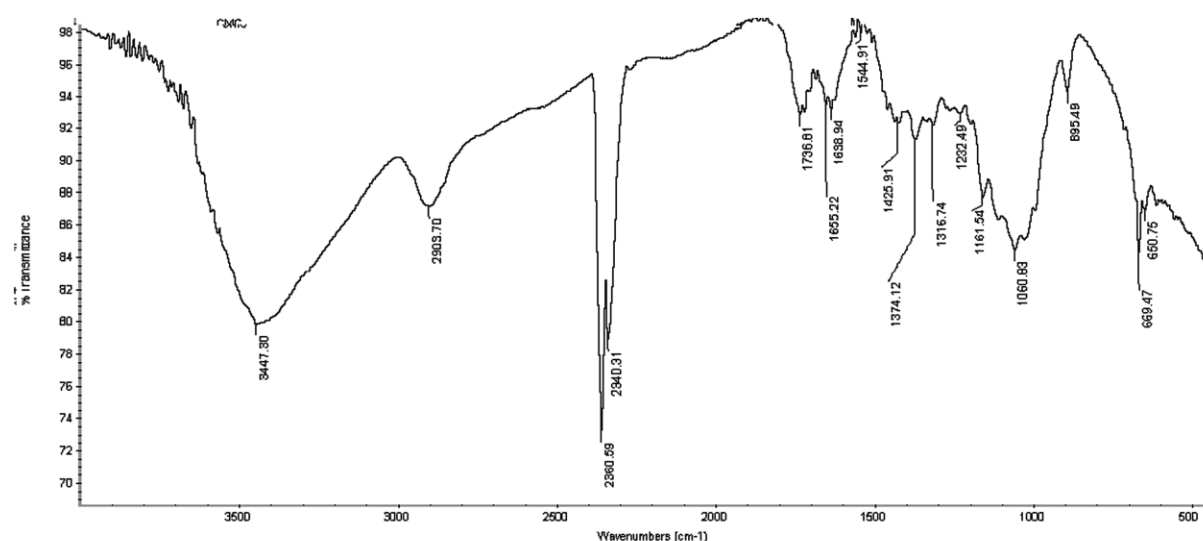
**Figure 7:** CMC commercial



**Figure 8:** FTIR spectrum of synthesized CMC sample [30]



**Figure 9:** CMC from OPEFB with bleached pulp prior dissolution



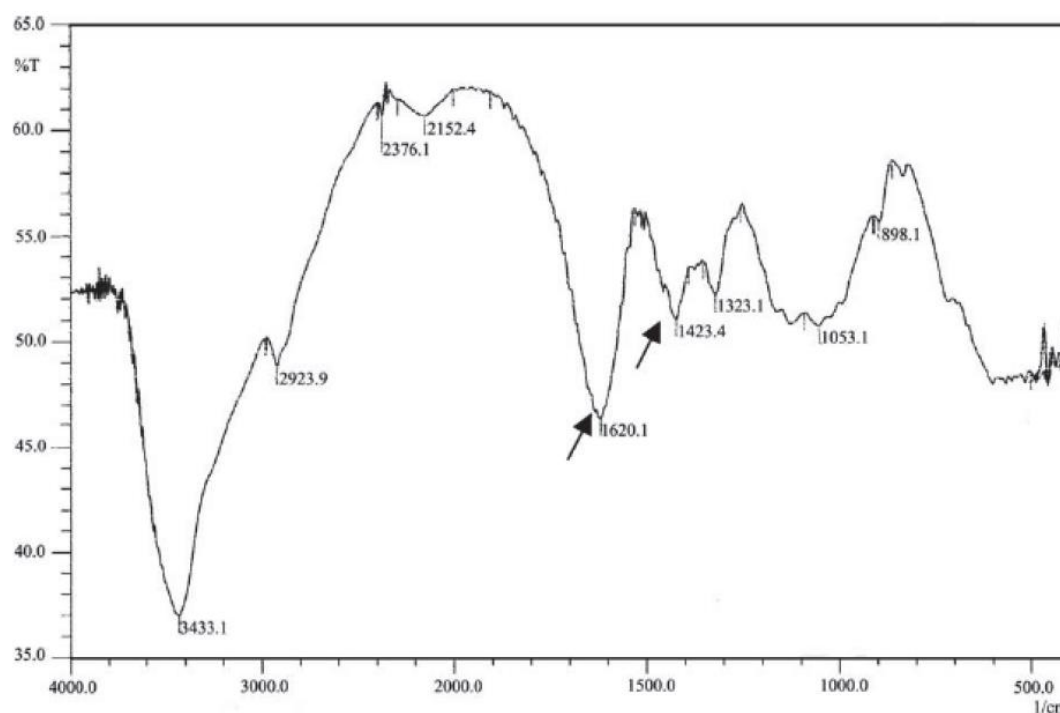
**Figure 10:** CMC from OPEFB without bleached pulp prior dissolution

Fig. 8 shows the FTIR spectrum of the sample with a rising peak of carboxyl, methyl and hydroxyl functional groups which are found at wavelength of 1618, 1426 and 1300  $\text{cm}^{-1}$  [30]. Comparing with fig. 9, the CMC from OPEFB with bleached pulp prior dissolution shows almost the same wavenumber as shown in fig. 7, CMC commercial and also in fig. 8, CMC from other publication. From the traced peak, the product is assumed to have higher degree of substitution (DS) because it contain sharp and long peak at wavenumber of carboxyl and methyl groups. Fig. 10 is CMC from OPEFB without bleached pulp prior dissolution shows peaks which also having almost identical wavenumber with fig. 8 but with larger value differentiation. The product also having the possibility to have lower DS due to the weak peak appears at carboxyl and methyl groups.

According to reported data, the peaks at wavelength of 1620 and 1423  $\text{cm}^{-1}$  represented two different functional groups in CMC [16, 31]. But, when referring to fig. 10, eventhough the peaks are appeared but not as sharp as wavelengths showed in fig. 9 at wavelength 1638 $\text{cm}^{-1}$  and 1425 $\text{cm}^{-1}$ . Fig. 11 shows



the additional peaks at wavelength of 2152 and 2376  $\text{cm}^{-1}$  might be done to the existence of the contamination from impurities or combination band with water [16]. It is obvious that broad absorption band at 3432 $\text{cm}^{-1}$  is due to the stretching frequency of the hydroxyl group ( $-\text{OH}$ ). The band at 2909 $\text{cm}^{-1}$  is due to carbon-hydrogen bond ( $\text{C}-\text{H}$ ) stretching vibration. The presence of a strong absorption band at 1603 $\text{cm}^{-1}$  confirmed the presence of carboxyl group ( $-\text{COO}$ ). The bands around 1423 and 1325  $\text{cm}^{-1}$  are assigned to  $-\text{CH}_2$  scissoring and hydroxyl group ( $-\text{OH}$ ) bending vibration, respectively. The band at 1061 $\text{cm}^{-1}$  is due to  $>\text{CH}-\text{O}-\text{CH}_2$  stretching [32]. All the data presented from previous publication supported the CMC attributed produced from OPEFB either with or without prior bleached pulp dissolution.



**Figure 11:** FTIR spectra of CMC made from cavendish banana pseudo stem cellulose with DS of 0.75 which was synthesized using 15% NaOH and 6 g of NaMCA (carboxyl groups substituent are indicates by arrows) [16].

## 6. Conclusion

The synthesis of CMC from OPEFB could easily be done in a laboratory at low temperature and in a short period. The fabrication method is conventional and mostly practical from many researchers before and is not dangerous. Commonly, one fabricates CMC without prior dissolution of the sources, which is usually in pulp form. From the experimental work done, CMC without prior dissolution is not suitable to be used as biomaterials for all applications. The simplest way in dissolving OPEFB bleached pulp was by the mixture solution of TBAF/DMSO where the process only took about 30 minutes at temperature 60°C to be finished, resulting in a clear solution of cellulose. FTIR analysis showed a better result compared with CMC without prior dissolution and the result was also discussed with comparing with other works to strengthen the obtained FTIR data analysis. As a brief conclusion, CMC produced with prior dissolution of bleached pulp of OPEFB is better in terms of its appearance, DS and also its application could be more diverse especially in the biomaterials field.



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