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Production and Characterization of Carboxymethyl Cellulose from Orange Rind

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Abstract

It is known that orange rind is often discarded as garbage. This research examines the production of carboxymethyl cellulose (CMC) from orange rind. Cellulose was extracted from orange rind (2.0 g) through alkalization. The cellulose was extracted using 1.0 M NaOH at 80 ± 5°C for 60 min. The maximum yield of cellulose was obtained under this condition. The extracted cellulose was then alkalized and etherified to CMC using NaOH and chloroacetic acid after bleaching with H_2O_2. The resulting CMC was characterized through Infrared spectroscopy to determine the functional group of CMC. The presence of carboxyl group (COO^-) at a wavenumber of 1,586 cm^{-1} in the IR spectrum, confirmed the conversion of cellulose to CMC. The surface morphology was also carried out through the SEM technique and the elemental analysis was performed using an EDX method. In addition, the resulting CMC product was coated as a film on banana to observe for various reactions.

Keywords : Carboxymethyl Cellulose; Cellulose; Orange Rind

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1. Introduction

Carboxymethyl cellulose (CMC) is a derivative of cellulose and is a cellulose ether compound. It was developed in Germany during World War I and was used to eliminate re-deposition of soil on fabric during the 1930 [1]. CMC is non-toxic and has high water solubility as well as outstanding light and thermal stability [2]. It exhibits a wide range of potential uses in various applications in many industries. For example; it is used as an inhibitor or sizing agent in fabrics, a water binding agent in foods and a thickening agent in pharmaceuticals and a suspending aid in agriculture and for cosmetics.

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 [3]. In order to decrease this problem, the production of CMC from various waste raw materials has been examined. Authors have continuously reported the conversion of cellulose to CMC from various waste cellulose sources such as palm kernel cake [2], sugar beet pulp [4], office paper waste [6], young coconut husk [7], cassava stem [8], sugarcane bagasse [9], water hyacinth [10], papaya peels [11], pomelo peel [12], durian husk [13] and rice straw pulp [14].

Orange juice is known to be healthy because of the high content of vitamin C and antioxidants. However, the production of orange juice generates orange rind as waste. To add value to this waste, orange rind was used as a cellulose source for the production of CMC in this work.

The objective of this work was to utilize discarded waste orange rind as a raw material for cellulose extraction and then convert the obtained cellulose into CMC. Cellulose was extracted from orange rind using alkalization under optimal conditions, and it was then etherified to CMC. Chemical and physical characterizations of the extracted cellulose and the resulting CMC product were studied. Finally, CMC product was applied as a film coating on banana.

2. Research Methodology

2.1 Materials and Reagents

Orange (Tangerine) rind, waste from an orange juice shop near the Rajamangala University of Technology Krungthep (RMUTK), Bangkok was collected. All chemicals used in this work were analytical grade.

2.2 Methods

2.2.1 Extraction of Cellulose from Orange Rind

After collection, the sample orange rind was cut into small pieces of approxi mately 1-inch in size. It was then dried in sunlight for 2-3 days to obtain a dry sample. Then the remaining moisture was removed in an oven at 50°C for 2-3 hrs. Dried orange rind was ground to

pass a 100-mesh sieve and the orange rind powder was then alkalized in order to separate cellulose from impurities such as lignin and hemicellulose. Various conditions of alkalization; concentration of NaOH (0.5 to 4.0 M), weight of orange rind powder (0.5 to 2.5 g) and extraction time (30 to 120 min) were investigated at 80 ±5°C and it was found that the optimal condition for cellulose extraction was to treat 2.0 g of orange rind powder with 1.0 M NaOH at 80±5°C for 60 min. The extracted cellulose powder was filtrated and then dried at 70°C for 90 min in an oven. The extracted cellulose powder was weighed and the cellulose yield was calculated from equation (1).

$$\%\,\text{cellulose yield} = \frac{\text{weight of extracted cellulose (g)}}{\text{weight of dried orange rind (g)}} \times 100 \quad (1)$$

2.2.2 Production of CMC from Cellulose

In order to convert extracted cellulose to CMC, the extracted cellulose powder from section 2.2.1 was first bleached in a solution of 5.0% (v/v) of H_2O_2 (from 30 % H_2O_2) for 10 min at pH 11-12, and then the pH of cellulose powder was adjusted to 8-9 after bleaching. Cellulose powder was then dried in an oven at 70°C for 1.5 hrs. The production of CMC was performed fol lowing the method of Rachtanapun *et al.* [10] and Bunsiri *et al.* [12]. Conversion of cellulose to CMC contained two reactions: alkalization and etherification. First, the alkalization treatment was performed by mixing 1.5 g cellulose powder with 40% (w/v) NaOH (5.0 mL) and stirring for 15 min at room temperature. Second, the etherification reaction was carried out by adding 1.8 g of chloroacetic acid into 45.0 mL of isopropyl alcohol. The solutions from alkalization and etherification were mixed and stirred for 10-15 min at room temperature. The mixing solution was heated in an oven for 2 hrs at 50°C. A slurry product was then obtained and soaked in 70% methanol solution. The slurry was later neutralized using glacial acetic acid, and was then washed in 70% ethanol solution. Later, it was cleaned with methanol to remove undesirable by- products before filtration. The solid residue was collected from filtration and then dried at room temperature for 24 hrs. The obtained CMC was weighed and calculated for the yield from equation (2). The CMC synthesis process is described by a block flow diagram, as shown in **Fig. 1**.

$$\%\,\text{CMC yield} = \frac{\text{weight of CMC (g)}}{\text{weight of extracted cellulose (g)}} \times 100 \quad (2)$$

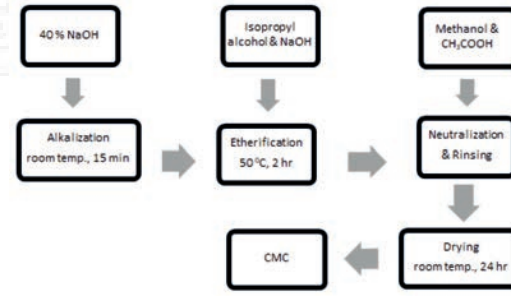

Fig. 1 Procedure for synthesis of CMC

2.2.3 Characterization of Extracted Cellulose and CMC Product

The surface morphologies of the extracted cellulose and CMC product were examined by SEM (Scanning electron microscopy). The Energy dispersive X-ray spectroscope (EDX), coupled to SEM, was used to determine the elemental composition (SEM-EDX model HITACHI S-3400 N, Japan). The functional groups of extracted cellulose and CMC product were analyzed using Fourier transform infrared spectroscopy, FT-IR (Model 6700, Thermo Electron Corporation USA). All measurements were carried out using the KBr method. The sample and KBr were mixed and ground finely, and the mixture was compressed to form a transparent disk. The infrared spectra were recorded for wave numbers 4,000-400 cm^{-1}.

2.2.4 Application of the Resulting CMC Product

The CMC product was utilized as a film coating on a banana sample to observe for degradation. A mixture of 1.5 g CMC product in 50 mL of water was prepared. The mixture was boiled at 80°C for 10 min or until the slurry product was obtained, and it was used to coat on banana sample when its temperature was decreased to 50°C. The banana sample was cut and divided into 3 groups; 1) coated with CMC product, 2) coated with commercial CMC and 3) non-coated (as the control). Each sample was dipped in the slurry solution of the CMCs (CMC product and the commercial CMC) for 2 min. The thickness of the coating film was controlled by the dipping time which was fixed at 2 min. The banana samples were placed in plastic baskets and stored in a refrigerator at 20±5°C for 3 days. The banana samples of each group were observed every day for their physical properties (Firmness, Decay, Color Change and Smell).

3. Results and Discussion

3.1 Extraction of Cellulose from Orange Rind

Before extraction of the cellulose from the orange rind, dried brown powder of orange rind was prepared and its appearance is shown in **Fig. 2**. Extraction of cellulose from orange rind powder was done via alkalization to solubilize and remove lignin and hemicellulose from cellulose. Various factors for alkalization, including amount of orange rind, concentration of NaOH and extraction time were studied and all measurements were performed in triplicate. Finally, an optimal condition using 1.0 M NaOH at 80 ± 5°C for 60 min was used for further experiments.

Fig. 2 Ground orange rind

3.1.1 Effect of Amount of Orange Rind on Cellulose Extraction

To study on this effect, 0.5 to 2.5 g of orange rind powder was used for cellulose extraction in 1.0 M NaOH (50 mL) at 80±5°C for 60 min. From the results, we found that the cellulose yield increased with increasing the weight of orange rind from 0.5 to 2.0 g, and yield was later dropped at 2.5 g as shown in **Fig. 3**. An excess amount of cellulose at 2.5 g of orange rind wound found under the conditions. The ratio of amount of rind powder and volume of NaOH may be improper in this case. Thus, the saturated concentration of extraction phase was occurred. The orange rind residue increased by increasing the weight of the orange rind. Moreover, it was obvious (by eyes) that the color of the cellulose powder became darker after increasing the weight. A 2.0 g of orange rind with the maximum yield of extracted cellulose as 23.50% was selected for further study. A Two-way ANOVA was run on a study to examine the effect of orange rind weight and yield of cellulose. There was significantly different between the orange rind weight and yield of cellulose F_{crit} was less than $F_{0.95,2,4}$. So, different weights of orange rind have different effects on yield at the 0.5 level. The ANOVA analysis was shown on **Table 1**.

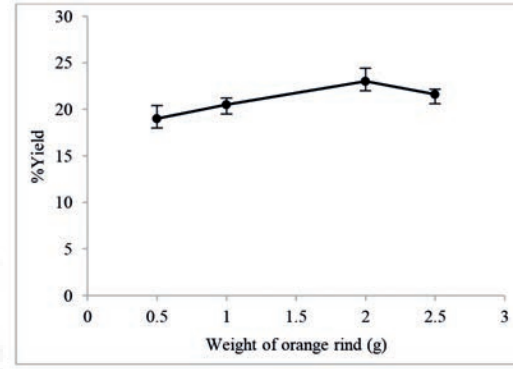

Fig. 3 Effect of amount of orange rind (0.5-2.5 g) on cellulose extraction

Table 1 The result of ANOVA for study the effect of amount of orange rind

Source of Variance	SS	df	MS	F	P-value	F_{crit}
Weight	0.895	2	0.447	0.534	0.622	6.944
Yield	8.428	2	4.214	5.030	0.080	6.994
Error	3.351	4	0.837			
Total	12.675	8				

3.1.2 Effect of NaOH Concentration on Cellulose Extraction

The effect of the concentration of NaOH (0.5 to 4.0 M) on the extraction of cellulose was tested by using the weight of the dried powder sample at 2.0 g. It was observed that the darker color and higher viscosity of mixture (Orange peel powder and NaOH solution) were related to the higher concentration of NaOH. Considering the yield of cellulose, it was increased with NaOH concentration from 0.5 M to 1.0 M. The cellulose yield reached a maximum value (40.50%) at 1.0 M NaOH after

which it started declining as shown in **Fig. 4**. This result can be explained by the cellulose molecule hydrolyzing at a maximum yield of 1.0 M NaOH. A Two-way ANOVA for study the effect of NaOH concentration on the yield of cellulose, F_{crit} was less than $F_{0.95,2,4}$. Then, there was significantly different between the concentration of NaOH and yield of cellulose. So, the concentrations have different effects on yield. The ANOVA result was shown in **Table 2**.

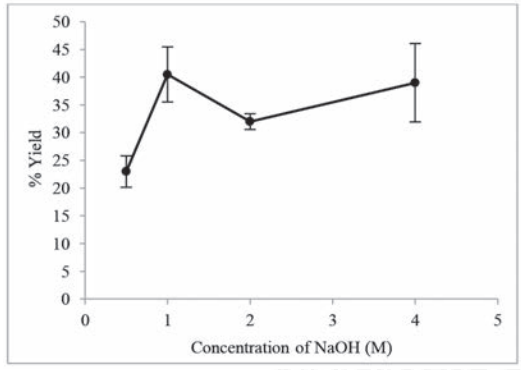

Fig. 4 Effect of NaOH concentration (0.5-4.0 M) on cellulose extraction

Table 2 The result of ANOVA for study the effect of NaOH concentration

Source of Variance	SS	df	MS	F	P-value	F_{crit}
Conc.	90.486	2	45.243	2.972	0.161	6.944
Yield	124.62	2	62.31	4.094	0.107	6.994
Error	60.873	4	15.218			
Total		8				

3.1.3 Effect of Extraction Time on Cellulose Extraction

The effect of extraction time (30 min to 120 min) on the extraction of cellulose was also examined in this chapter. The increasing of the extraction times from 30 to 120 min did not make a significant difference on the cellulose yield. It was found to be a small increase of the yield (from 20.0 to 22.50%) with the increasing of time where the 30 min extraction time provided the lowest yield. The longer period provided the higher viscosity of solution and thus 120 min was improper. The maximum yield was obtained at 60 min and this extraction of time was then selected.

3.2 Preparation of CMC

Under the optimal condition of cellulose extraction (A 2.0 g of orange rind was extracted by 1.0 M NaOH at 80±5°C for 60 min). The extracted cellulose of a dark brown color was found as shown in **Fig. 5(a)**. The cellulose powder was bleached with 5% H_2O_2 (from 30% H_2O_2) before it was converted to CMC. After bleaching, the color of the powder changed from dark brown to yellow as shown in **Fig. 5(b)**. After that the cellulose powder was then modified to CMC through alkalization and etherification processes. In these two reactions, extracted cellulose was suspended in a mixture of alkali-water-alcohol system at a room temperature with an excess of alcohol (Isopropanol) to ensure good mixing efficiency. In alkalization, cellulose is modified by NaOH to produce sodium cellulosate which is an available form

for etherification, as shown in equation (3). This alkaline condition causes the substitution of the hydroxyl (-OH) group of cellulose molecules to form alkali cellulose. In etherification, firstly, chloroacetic acid dissolves in NaOH to form sodium chloroacetate, as shown in equation (4). Then, the chlorine in sodium chloroacetate reacts with the sodium cellulosate to generate carboxymethyl cellulose, as equation (5) [15].

$$[C_6H_7O_2(OH)_3]_n + n\ NaOH \rightarrow n\ H_2O + [C_6H_7O_2(OH)_2ONa]_n \quad (3)$$

$$ClCH_2COOH + NaOH \rightarrow ClCH_2COONa + H_2O \quad (4)$$

$$[C_6H_7O_2(OH)_2ONa]_n + n\ ClCH_2COONa \rightarrow [C_6H_7O_2(OH)_2OCH_2COONa]_n + n\ NaCl \quad (5)$$

Under the modified condition, a 0.80 g of CMC product was obtained at a yield of 53.33. The yellow to brown color of CMC product is shown in **Fig. 5(c)**.

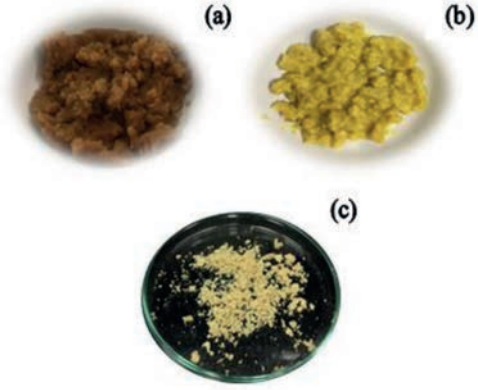

Fig. 5 Extracted cellulose from orange rind (a) before bleaching (b) after bleaching and (c) CMC product from-orange rind

3.3 Characterization of Cellulose and CMC Product from Orange Rind

3.3.1 Elemental Analysis

Elemental analysis of the extracted cellulose was carried out by EDX. The results in **Fig. 6** showed that the orange rind contained a high amount of C (56.33%) and O (39.67%). These two elements are the main composition of cellulose ($C_6H_{10}O_5$). The tiny amounts of Fe, Al, K and Ca were found at 4%.

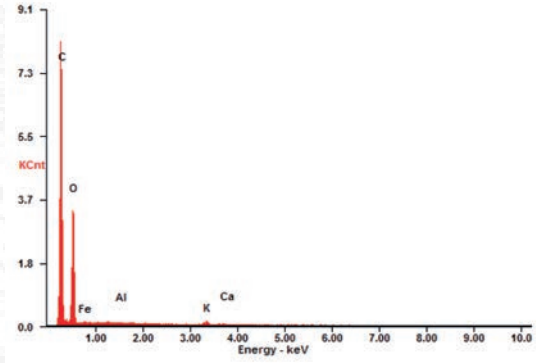

Fig. 6 Elements found in cellulose extracted from orange rind

EDX is related to the K-shells (that is not the valence shell). The %H is not valued because H has only a K shell that is a valence shell. Then, the H 1s electrons are only electron that is shared for bonding, and the valence orbits often appear broad band of spectrum. So, the signal from H would overlap with signals from excitation of valence electrons from other atoms. It is not possible to distinguish between H 1s valence electron and valence electrons of other elements. Then, H do have characteristic in X-ray, and it cannot be analyzed by EDX.

3.3.2 Surface Analysis

SEM was employed to determine the surface morphology of the orange rind powder, extracted cellulose and CMC product. From the result, a micro porous structure of orange rind powder existed as shown in **Fig. 7(a)**, compared to the extracted cellulose. The surface of the extracted cellulose appeared to be smoother (as shown in **Fig. 7(b)**) than the orange rind powder. This was due to the alkalization treatment improved the surface roughness. For the CMC product, the surface roughness was slightly decreased as shown in **Fig. 7(c)** when compared with the extracted cellulose. It is due to the etherifying agent causes to modify the cellulose molecule and result into swelling of surface.

3.3.3 Functional Group Analysis

The spectrum of extracted cellulose showed an absorption band in the range of 3,500 to 3,200 cm^{-1}. This is an indication of –OH stretching vibration, inter-molecular and intra-molecular hydrogen bonds in cellulose molecules. The peak wave number of 1,084 cm^{-1} is due to –CH-O-CH. A C-H stretching vibration at a peak wave number range of 2,900-2,800 cm^{-1} attributed to the bending of the C-H in the lignin was disappeared. Moreover, the 2 peaks of lignin located at 1,500 (C=C stretching of the aromatic ring of lignin) and 1,300 cm^{-1} (C-O stretching of the aromatic ring of lignin) were eliminated after bleaching. The bands at 1,420 cm^{-1} and 1,319 cm^{-1} were assigned to $–CH_2$ scissoring and –OH bending vibration. The extracted cellulose spectrum is shown in **Fig. 8(a)**.

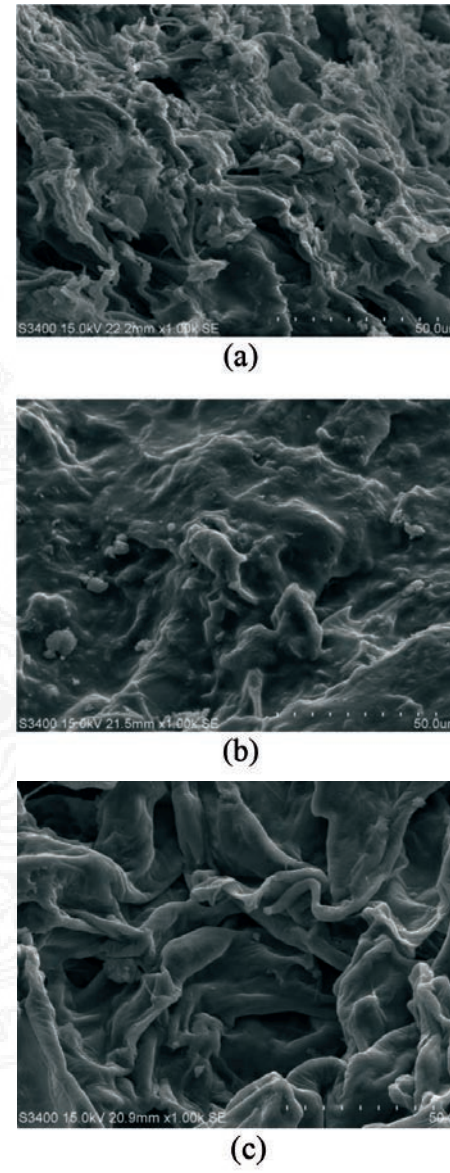

Fig. 7 Surface morphology (at 50 mm resolution and 1.00 k magnification) of (a) orange rind powder, (b) extracted cellulose and (c) CMC product from orange rind

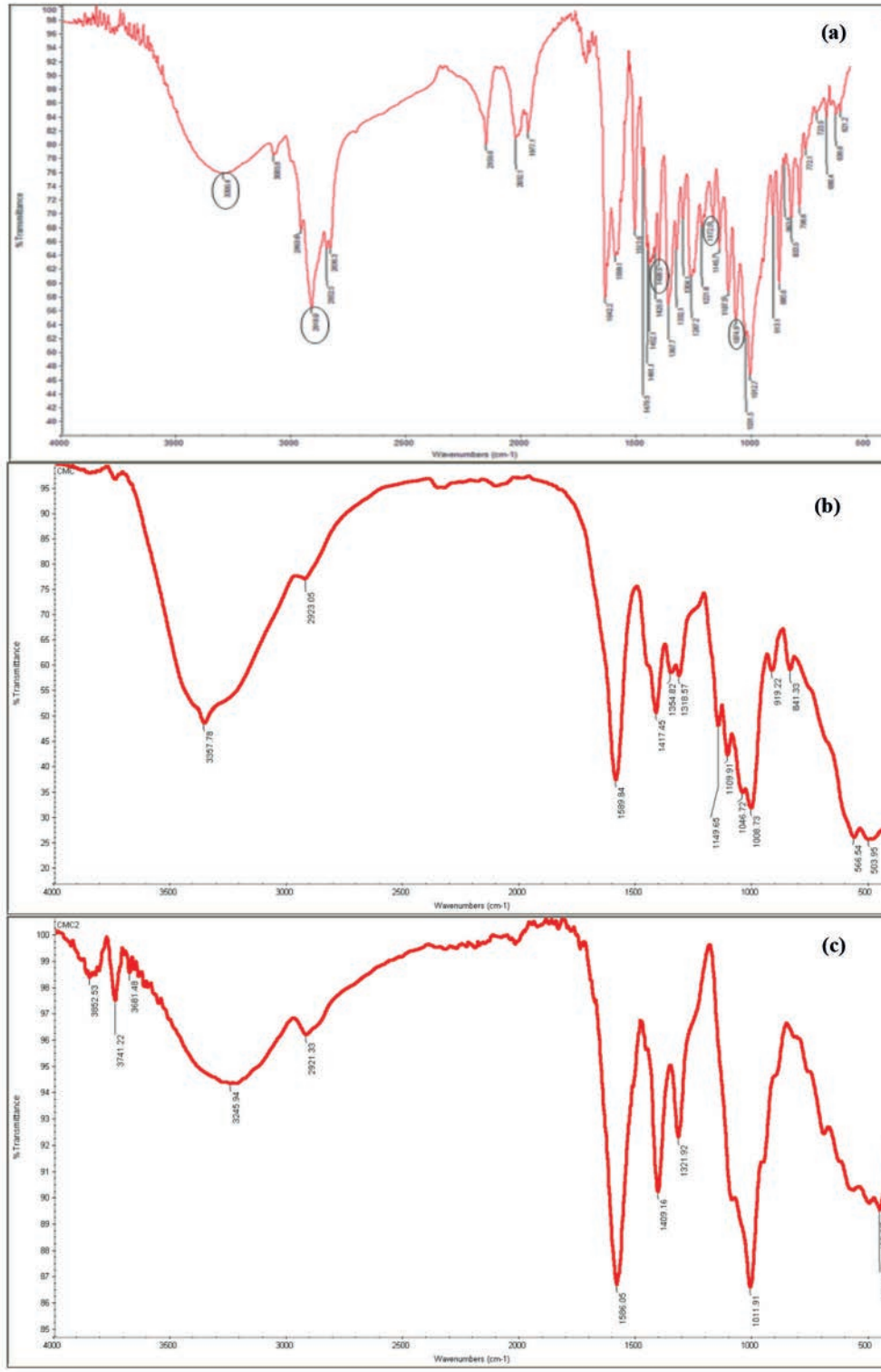

Fig. 8 IR-spectrum of extracted cellulose (a) commercial CMC (b) and CMC product from orange rind (c)

The spectrum of the commercial CMC presented a strong absorption band at 1,586 cm^{-1}. This is due to the carboxyl group (COO^-) where the hydroxyl group was replaced with the carboxyl group after etherification. A C-H stretching vibration was at 2,900-2,800 cm^{-1} where the C-H bending in the lignin disappeared. In addition, a strong peak at 1011 cm^{-1} indicates the C-O-C pyranose ring stretching vibration. The CMC product spectrum is shown in **Fig. 8(b)**. The spectrum of the commercial CMC was also determined as shown in **Fig. 8(c)**. The program compared a relative spectrum of the CMC product and the commercial CMC which provided a 52.40% match. This result confirmed that the resulting CMC product could be synthesized from orange rind.

3.4 Application of CMC Product

During 3-day storage of uncoated and CMC coated bananas, the results showed that the changes (firmness, decay, color change and smell) of banana clearly varied during this study period. The uncoated banana (as the control) showed a decrease in firmness over the study period, and it also increased in degradation. Both CMC coatings (Commercial CMC and resulting CMC coatings) could delay the browning and putrid smell of the banana. The coating can provide better preservation than the non-coating one. Pictures of the testing results were shown in **Fig. 9**.

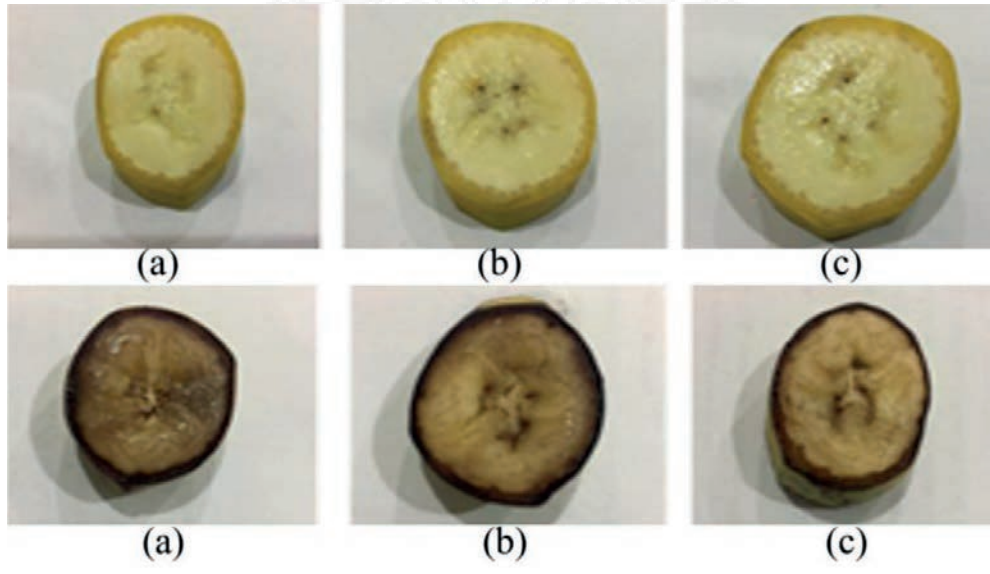

Fig. 9 The appearance of banana before (above) and after (below) storage for 3 days (a) non-coating, (b) coating with commercial CMC and (c) coating with CMC product

4. Conclusion

Orange rind has been used as a cellulose source from waste discarded from the market. Cellulose was extracted from orange rind powder through alkalization. The extracted cellulose was etherified to CMC and showed the CMC yield at 52.4% of dried cellulose. The characterizations of the CMC product were investigated to show the physical and chemical properties. The presence of carboxyl (COO^-) group at wavenumber of 1,586 cm^{-1} in IR spectrum, confirmed the conversion of cellulose to CMC. The relation of spectrums between the CMC product and commercial CMC were matched at 52.40%.

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