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Production of Carboxymethyl Cellulose (CMC) From Rubber Seed (*Hevea brasiliensis*) Shells

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ABSTRACT: Carboxymethyl cellulose (CMC) is a cellulose derivative utilized as a thickener in food processing, as well as in non-food items including paints and detergents. In this study, CMC was produced from cellulose which was obtained from rubber seed shells (RSS). The CMC was produced from cellulose by mercerization with 30% sodium hydroxide (NaOH) solution and etherified using monochloroacetic acid. Fourier transform infra-red (FTIR) spectroscopy was used to characterize the CMC produced therein. The amount of cellulose extracted from RSS was 55.15 %. The broad spectrum of the FTIR indicated the presence of hydroxyl, ether and carboxyl functional groups at 3442.00 cm⁻¹, 1420 cm⁻¹, and 1625 cm⁻¹ respectively. These results showed favourable comparisons with the commercial CMC, which demonstrates that RSS is a promising raw material for the manufacture of CMC.

Keywords: Rubber seed shell, *Hevea brasiliensis*, Carboxymethyl cellulose, FTIR Characterization, Spectra

Introduction

Utilizing renewable resources such as wastes for producing industrial goods is very popular nowadays. For sustainable development and environmental preservation, biodegradable materials made from renewable resources have received a lot of attention. Due to the high performance of the resulting composite, the use of natural fibers from renewable resources not only contributes to a healthy environment but also makes them economically appealing for industrial usage (Rohit and Dixit, 2015).

Cellulose (C₆H₁₀O₅) is a natural, renewable, and biodegradable substance that is a high-molecular-weight, linear polymer. It is a glucose polymer that is produced in a variety of ways by solar radiation, and serves as the structural backbone of the plant cell wall (Richardson and Gorton, 2003). Due to its enormous supply, low cost, renewability, biodegradability, and simplicity of chemical modification, cellulose is one of the most alluring and promising sources for biodegradable materials within the larger family of renewable polymers. Anhydroglucose units (AGU) in cellulose are connected at the C-1 and C-4 positions by β-glucosidic bonds, allowing for robust cooperative intra- and intermolecular hydrogen bond patterns (Khazraji and Robert, 2013). The most prevalent organic solvents do not cause cellulose to melt or dissolve, which enhances its usefulness in many different products, such as composites, netting, upholstery, coatings, packaging, and paper (Hattori *et al.*, 2004). An alternate method of using cellulose for industrial purposes is to undergo a chemical derivatization reaction to transform it into a derivative like carboxymethyl cellulose (CMC), which is primarily utilized in synthetic powder-like substances and highly addictive (Singh and Singh, 2012). CMC is water soluble and stable in the pH range of 3 to 10 (Yang and Zhu, 2007). As a result, it has numerous uses in the food sector as well as in detergents, cosmetics, medicines, textiles, paper, adhesives, and ceramics. It is a tasteless, colourless powder that ranges from white to yellow.

According to reports, CMC is made from a variety of plant biomasses that, on a dry basis, comprise 40–50 % cellulose, 25-40% hemicelluloses, and 15-35 % lignin (Singh and Singh, 2012). Many researchers have reported the production of CMC from a variety of agricultural waste cellulose sources, including sugar beet pulp (Togrul and Arsan, 2003), Cavendish banana pseudo stem (Adinugraha, *et al.*, 2005), cashew tree gum (Silva *et al.*, 2004) and sago waste (Pushpamalar *et al.*, 2006).

Rubber (*Hevea brasiliensis*) is one of the most significant trees that is gaining an ever-increasing interest. At around 4-5 years of age, the rubber tree starts to produce fruit that contains three to four seeds, which typically develops and breaks off from the seed pod. About 800 seeds per tree can be produced twice a year (Heuzé and Tran, 2017). The typical size of a rubber seed is 2.0 mm transversely and 15.2 mm longitudinally. The husk, also known as the seed coat, is a hard, lustrous brown to grey colour with numerous darker streaks or mottles on the dorsal surface. According to a survey, Nigeria could produce roughly 42,980 metric tons of the seeds annually (Nwankwo *et al.*, 1985). However, factors such as the weather, genetics, and the disease powdery mildew might have an impact on the seed that is generated (George *et al.*, 2000).

The rubber seed shell is known to have a high cellulose content which can be acquired to create more valuable goods. The celluloses can then be combined to create CMC, a derivative of a cellulosic substance (carboxymethyl cellulose). In this study, the extraction of cellulose from rubber seed shells (RSS) was used to produce CMC through a carboxymethylation process and the chemical properties of CMC produced was compared with commercially available CMC.

Materials and methods

Chemicals: Analytical grade n-hexane, sodium hydroxide, hydrogen peroxide, 37 % hydrochloric acid (HCl), isopropanol, ethanol, methanol in commercial grade, and analytical grade chloroacetic acid (ClCH₂COOH), acetic (CH₂COOH), and 70 % nitric acid obtained from Merck, Darmstadt, Germany were the chemicals used for extraction.

Collection and preparation of rubber seeds: Rubber seeds (*Hevea brasiliensis*) were obtained from the Rubber Plantation at Ovir-Okpe in Okpe Local Government Area of Delta State, Nigeria.. The rubber seed shells (RSS) were manually separated from the seed and allowed to air dry for two days. The RSS were then grounded and purified using n-hexane solvent in a soxhlet extractor. The resulting material was refrigerated for storage after being dried at 100 °C for 18 h.

Extraction of cellulose from RSSs: A two-step modified liquid phase oxidation process developed by Mae *et al.* (2000) was used to extract the cellulose from RSS. The hot water treatment step of the cellulose extraction process involved putting 40 g of crushed RSS in a beaker with 400 mL of boiling distilled water. The reaction was then stopped by soaking the reactor for 30 minutes in cold water. The processed RSS was thoroughly cleaned using distilled water and ethanol until a clear filtrate was produced. It was then dried, crushed (with a pestle and mortar), and sieved through a 300 mm mesh.

In order to preserve the pure cellulose in the pretreated RSS, liquid phase oxidation was used to remove any remaining residue material, such as solid residue and organic compounds like lignin. This was accomplished by combining pre-treated RSS and 30% H₂O₂ in a 1:10 reaction mixture in a flask. For almost 10 hours, the reaction was stirred at 700 rpm under reflux at a temperature of 75 °C. A surplus of cold water was added to the mixture to stop the oxidation reaction after the reaction period had passed. The mixture was filtered, thoroughly rinsed with distilled water and ethanol to produce a clear filtrate, and then dried at 70 °C.

The obtained cellulose was ground into powder. Equation (1) was used to calculate the percentage yield of cellulose.

$$\% \text{ Yield of cellulose} = \frac{\text{weight of cellulose}}{\text{weight of RSS}} \times 100 \quad (1)$$

The cellulose from RSS was employed as a precursor in the etherification reaction to create CMC.

Synthesis of carboxymethyl cellulose (CMC)

Etherification reaction and characterization: The method of Hong (2003) was used for etherification of cellulose. 150 mL of isopropanol was weighed out, and the solution was continuously stirred as 5 g of RSS cellulose was added. 15 mL of a 30 % w/v NaOH solution was added and the mixture was agitated for 1 h at 25 °C. 6.0 g of monochloroacetic acid was added and mixed for 1 hour at room temperature. The mixture was placed in an oven, covered with aluminum foil, and heated to 60 °C for 4 h. The produced solid was then immersed in 100 mL methanol overnight. The pH of the slurry formed was adjusted to 7 the following day using 90 % (v/v) acetic acid, after which it was filtered through a sintered funnel and washed with ethanol and methanol, respectively. The CMC formed was purified by repeatedly soaking in 80 % (v/v) methanol. The percent yield of CMC was determined using equation (2).

$$\% \text{ Yield of CMC} = \frac{\text{weight of CMC}}{\text{weight of cellulose}} \times 100 \quad (2)$$

Characterization of CMC

Titration estimation of degree of substitution of CMC: The reverse titration method was used to calculate the degree of substitution (DS) of CMC. A 0.5 g sample of CMC of oven-dry sample was soaked in a 20 mL solution of HNO₃ and methanol for 3 hours, after which it was filtered, washed with 70 % methanol, and dried at 550 °C for 1 h.

20 mL of distilled water and 3 mL of 1 M NaOH were used to dissolve 0.2 g of the dried CMC. 1M HCl was then used to titrate the mixture with phenolphthalein indicator. The average amount of HCl used during each of the three titrations was noted.

The DS of CMC was calculated using equations (3) and (4):

$$\% \text{ Carboxymethyl content} = \frac{(V_o - V_n) \times M \times 0.059}{m} \times 100 \quad (3)$$

$$\text{Degree of substitution (DS)} = \frac{162 \times \%CM}{(5900 - (58 \times \%CM))} \quad (4)$$

Where: V_o= ml of hydrochloric acid used to titrate blank
 V_n= ml of hydrochloric acid used to titrate samples
 M= molar concentration of hydrochloric acid used
 m= sample mass (g)

162 g/mol is the molar mass of the anhydroglucopyranose unit (AGU), and 59 g/mol is the molar mass of -CH₂COOH (Elomaa, *et al.*, 2004). 58 is the Net increment in the anhydrous glucose unit for every substituted carbxy methyl group.

Fourier transforms infrared spectroscopy: Fourier transform infrared spectroscopy was used to determine the functional groups of the CMC-synthesized cellulose. Before the mixture was crushed to produce a recorded pellet, the mixture was combined and grouped with around 0.2 mg of sample and 2 mg of potassium bromide. These samples' infrared spectra were assessed during transmission at wavelengths between 4000 and 400 cm⁻¹.

Results

The percentage yield of cellulose extracted from the RSS 55.2 %. The cellulose was yellow in colour (Figure 1). The percentage yield of CMC synthesized was 135.2 % while the degree of substitution obtained from this work was 0.5. The extracted cellulose from the RSS and its FTIR spectra are shown in Figures 1 and 2 respectively while the FTIR spectra of the CMC obtained from this study and that of commercial CMC are shown in Figures 3 and 4 respectively.



Figure 1: Cellulose extracted from RSS

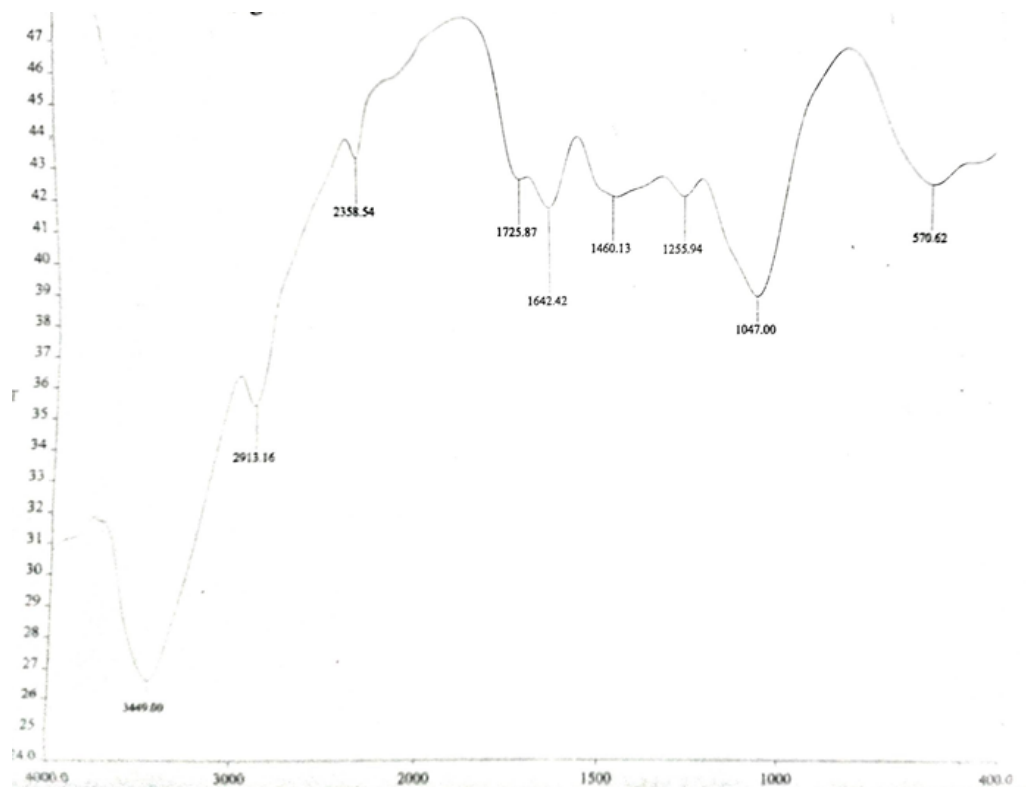


Figure 2: FTIR spectra of the synthesised cellulose from the RSS

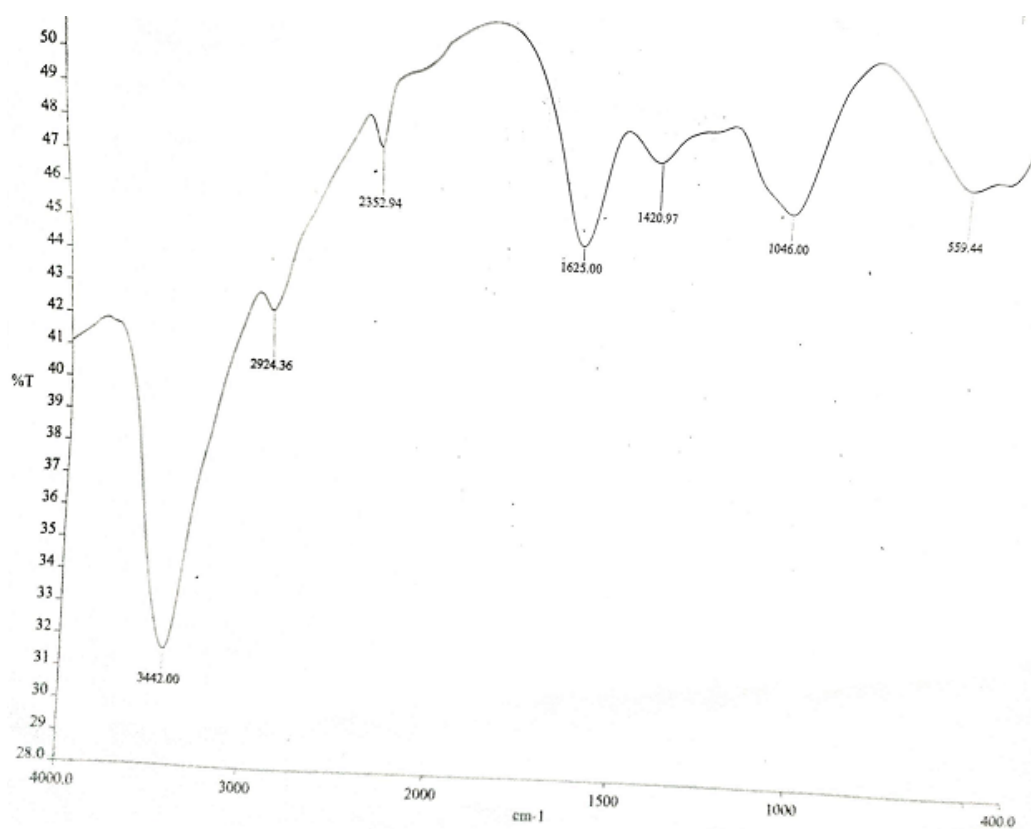


Figure 3: FTIR spectra of CMC obtained in this study

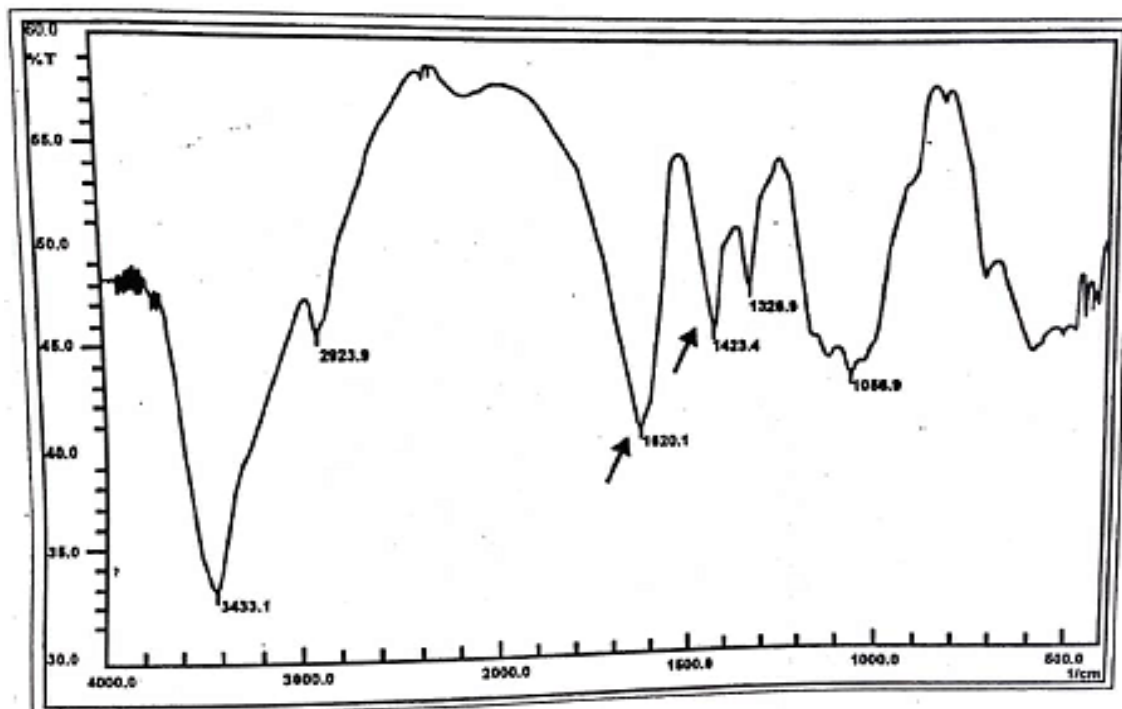


Figure 4: The FTIR spectra of commercial CMC

Discussion

Percentage output of cellulose and carboxyl methyl cellulose: Based on the dry weight principle, the yield of cellulose recovered from the RSS and the yield of CMC produced were both measured. Equation was used to determine the yield of cellulose, expressed as a percentage, based on the quantity of RSS. Moreover, the yield of CMC was determined by dividing the net dry weight of CMC with 5g of dry cellulose. From the measurement, water pre-treatment followed by liquid phase oxidation using hydrogen peroxide recovered 55.2% of RSS cellulose. The high yield of CMC synthesized with 30% NaOH was due to the quantity of NaOH and monochloroacetic acid used. The output percentage was 135.2%. The reaction becomes more acidic as the concentration of NaOH rises, replacing the hydroxyl group and giving rise to a greater mass (Selke *et al.*, 2004).

Degree of Substitution: The absolute degree of substitution obtained from this work was 0.5. The maximum ratio of NaOH concentration to MCA concentration would result in an increase in the absolute degree of substitution achieved from this work, which is 0.5. The DS steadily rises with each increase in NaOH concentration, and after reaching its maximum value, it gradually falls. The function of the organic solvent in the carboxy methyl cellulose process is to act as a medium for the replacement of the CMC functional groups. The miscibility of the solvent system and its capacity to dissolve the etherifying agents into the cellulose structure determine how the solvent system affects the process (Silva *et al.*, 2004). The carboxymethylation of the cellulose molecule was made easier by the polarity of the organic solvent. Isopropanol has a lower polarity than water does. The effectiveness of the methylation reaction increases as the polarity of the aqueous medium decreases. The concentration of NaOH has an impact on the degree of substitution. Since the DS value is 0.5, adding more NaOH concentration could increase or decrease the DS value. The sodium gluconate form, which is known as a by-product in the synthesis of CMC, was probably to blame for it. Several earlier studies have demonstrated that DS declines as the reaction temperature is increased past the point at which its maximum value is reached (Varshney *et al.*, 2006). If carboxymethylation is continued, it could lead to the oxidative destruction of CMC.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis: FTIR spectroscopy was widely employed in cellulose research because it offers a quick and easy way to get information directly on the chemical changes that take place after different chemical treatments (Ristolainen *et al.*, 2002). The FTIR spectra of grounded RSS cellulose and CMC from the RSS cellulose are shown in Figures 2 and 3 respectively.

The IR spectrum is comparable to the cellulose standard library. The stretching frequency of the -OH group as well as intramolecular and intermolecular hydrogen bonding in a cellulose are what cause the absorption band at 3449.00 cm^{-1} (Pushpamalar *et al.*, 2006). Peaks are caused by $>\text{CH}_2\text{-O-CH}_2$ at wave number 1047.00 cm^{-1} within an anhydroglucose ring stretching. The tiny band between 2896 and 2913 cm^{-1} is attributed to the C-H molecule stretching and vibrating (Biswal and Singh, 2004). The H bending of adsorbed water may be seen in the stretching at 1642.42 cm^{-1} . While the band 1460.13 cm^{-1} , which is attributed to the $-\text{CH}_2$ bending vibration, was another proof of the presence of cellulose.

The trend in the FTIR spectra of the CMC obtained in this study was similar that of the commercial CMC (Figure 4). This demonstrated that RSS is a promising raw material for the manufacture of CMC. The stretching frequency of the -OH group is what causes the absorption band at 3442 cm^{-1} . The COO-group is responsible for the presence of a brand-new, powerful absorption band at 1625 cm^{-1} . The presence of a carboxymethyl substituent is indicated by the existence of two peaks at wave numbers between 1400 and 1450 cm^{-1} and 1600 cm^{-1} and its salts. The bands in the 1350–1450 cm^{-1} range are also the result of symmetrical deformations of the CH_2 and OH groups. Bands in the fingerprint area that depict the ether bonds in CMC are 1420.97 cm^{-1} and are attributed to the carboxyl groups that they salt.

Conclusion and Recommendation

In this study, RSS was successfully used to make CMC. The yield was 135.32%, and the DS value was 0.5. The cellulose from RSS was removed using a typical bleaching and delignification procedure comprising hot water treatment and hydrogen peroxide. To prepare carboxymethylation from shells, reaction conditions should be optimized in order to find the best circumstances that would provide the highest yield. DS value and viscosity should also be assessed. Isopropanol should be avoided at all costs; instead, choose another solvent.

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