SYNTHESIS AND CHARACTERISATION OF CARBOXYMETHYL CELLULOSE FROM VARIOUS AGRICULTURAL WASTES

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Carboxymethyl cellulose (CMC) synthesised from cellulose pulp of six different agricultural wastes was characterised. Spent tea leaves and sugarcane bagasse had the highest moisture content and cellulose yield. Using different concentrations of NaOH to alkalise the cellulose had a variable effect on the CMC yield, but carboxymethyl (CM) content and the degree of substitution (DS) were consistently the highest at 20% NaOH. From the different reaction temperatures tested, the CMC yield was the highest at 60 °C. For the CM content and DS, the highest values were obtained at 50 °C. The CMC yield increased with increasing amounts of sodium monochloroacetate (SMCA) for the etherification process. Maximum CM content and DS were observed at 3 g and 5 g of SMCA, respectively. The optimal conditions of NaOH, temperature and SMCA for deriving maximum yield, CM content and DS from CMC of the various plant materials were determined, and their performance was ranked.

Keywords: agricultural wastes, cellulose yield, CMC yield, CM content, degree of substitution

INTRODUCTION

Most Southeast Asian countries have agro-based economies with oil palm and rubber as major industrial crops, and coconut, cocoa and sugarcane as secondary food crops. These agricultural industries generate large amounts of wastes, particularly during harvesting and replanting. Waste disposal is a major constraint in plantations. In recent years, extensive burning of agricultural residues during the dry season has led to the problem of transboundary haze that blanketed countries in Southeast Asia. The prolonged air pollution has adverse effects on human health and economic activities. It is therefore wise to adopt the concept of 'wealth from waste' by converting some of these plant wastes, which are rich in lignocellulose, into useful bioproducts. The lignocellulosic biomass of agricultural residues comprises cellulose (38%), hemicellulose (32%) and lignin (17%) as major components.[1] One such bioproduct is carboxymethyl cellulose (CMC), which has wide industrial usage.

A derivative of cellulose, CMC is an anionic linear polysaccharide that is highly viscous, non-toxic, non-allergenic and biodegradable.[2,3] The numerous hydroxyl and carboxylic groups in CMC enable its ability to bind and absorb water. The production of CMC is simple, efficient and low-cost, involving etherification of the hydroxyl groups in cellulose under alkaline conditions.[4,5] The process involves an equilibrium reaction between NaOH and the OH groups of cellulose, followed by the formation of carboxymethyl (CM) groups using sodium monochloroacetate (SMCA). The number of CM groups formed (CM content) will determine the degree of substitution (DS) of CMC. The hydro-affinity of CMC increases with the increase in DS. CMC with DS > 0.4 is soluble in water and giving viscosity in solution, whereas that with DS < 0.4 can swell, but is insoluble.[6]

CMC is widely used in detergent, food, paper, paint, textile, pharmaceutical and cosmetic industries.[3,6,7] Water soluble cellulose derivatives, such as CMC, are biocompatible, and can function as thickening, binding, emulsifying, film-forming, lubricating, dispersing, stabilizing and gelling agents, and are especially useful as additives in food, pharmaceutical and cosmetic industries.[8]

Very few studies have been conducted on CMC synthesis from the major agricultural crops in Malaysia. Much of the research on CMC synthesis utilises cellulose from the crops of developed countries, such as wheat, soy and maize, or less important crops, such as sago and durian. All the biomass utilised in this study was derived from major crops listed in the Industrial Crops Statistics published by the Department of Agriculture, Peninsular Malaysia.[9] Oil palm is the most abundant industrial crop and dried duckweed is a by-product from a phytoremediation facility used to treat wastewater from an oil palm estate.

EXPERIMENTAL

Plant materials

The plant materials used in this study were agricultural wastes of spent tea leaves, sugarcane bagasse, coconut fibres, oil palm fibres, dried duckweed and palm kernel cake. Spent leaves of Chinese tea were collected from a coffee shop in Taman Connaught, Cheras, Kuala Lumpur, after brewing of tea. The tea leaves were those of Pu-erh, produced from Yunnan in China. Sugarcane bagasse was collected from the Taman Connaught night market, after extraction of the sugarcane juice. The sugarcane was cultivated in Hulu Langat, Selangor. Coconut fibres and oil palm fibres were obtained from the Heng Huat group of companies. Dried duckweed, a patented product, was procured from Chitose Agri Laboratory Sdn. Bhd., which operates a farm in Sandakan, Sabah. Palm kernel cake was obtained from oil palm producers in the Klang Valley, Selangor.

Extraction of cellulose pulp

The extraction of cellulose pulp was performed in accordance with our earlier described technique.[10] The plant materials were oven-dried at 80 °C overnight, blended with a commercial blender and sieved with a 0.5 mm mesh flour strainer. The moisture content of each plant material was calculated by taking the difference in weight before and after drying as percentage of the pre-dried weight. The extraction of cellulose pulp was conducted by bleaching 50 g of dried plant material in 800 ml of 0.5% of acetic acid and 1% sodium chlorite in a stoppered Schott glass bottle under a well-ventilated hood and heated in a shaking water bath at 95 °C for 2 h. After bleaching, the cellulose pulp was filtered and washed with tap water. The bleaching process was repeated thrice to ensure the complete removal of lignin. After washing with 500 ml of deionized water, the cellulose pulp was oven-dried at 80 °C overnight and weighed using an analytical balance. Cellulose yield (%) was calculated as $A/B\times100\%$, where A is the weight of the pulp (g) and B is the weight of the dried plant material (g). Figure 1 shows the three-time bleaching process and the bleached cellulose from sugarcane bagasse.

Production of carboxymethyl cellulose

The procedures used to prepare CMC from sago pulp,[4] and from sugarcane bagasse and palm kernel cake[10] were adapted with some modifications. Firstly, 80 ml of isopropyl alcohol and 10 ml of sodium hydroxide (NaOH) (20%, 30% and 40%) were added into a volumetric flask and shaken well. The mixture was then poured into a 250 ml conical flask containing 5 g of cellulose pulp and allowed to stand for 1 h in a shaking water bath at 40 °C, 50 °C and 60 °C to alkalise the cellulose. Then etherification was initiated by adding different amounts of SMCA (1 g, 3 g and 5 g) and maintained at 60 °C for 3 h.

The solid residue was subsequently filtered and suspended in 100 ml of methanol. The pH of the mixture was neutralised using 10% acetic acid before overnight storage. The purpose of adjusting the pH to 7 was to neutralise any NaOH left in the mixture. The next day, the CMC formed was filtered, washed with aqueous methanol and oven-dried at 80 °C for 3 h to remove any residual alcohol. Derived from 5 g of cellulose pulp, the CMC yield was expressed in grams. Figure 1 shows the dried CMC produced from sugarcane bagasse and palm kernel cake.

Determination of degree of substitution

The DS of CMC was determined by potentiometric back-titration.[10] Prior to titration, the synthesised CMC was acid washed to ensure that its carboxyl groups were completely ion free. About 5 g of CMC was suspended in 60 ml of industrial grade methanol and stirred in a 250 ml conical flask. Subsequently, another 10 ml of 2 M nitric acid was added and allowed to heat in a water bath until boiling. The mixture was swirled in an orbital shaker for 15 min and allowed to cool. The suspended CMC was then filtered and washed with 80% aqueous methanol at 60 °C to remove all traces of nitric acid. Finally, the washed CMC was transferred to a beaker, oven-dried at 105 °C for 3 h and the resultant weight was obtained.

To determine the CM content (%) and DS of CMC, 0.5 g was transferred into a 250 ml conical flask, dissolved in 100 ml of 0.05 M NaOH and brought to boil for 15 min on a hot plate. After cooling for 30 min, the solution was titrated with 0.15 M of HCl using phenolphthalein as indicator. Colour change of phenolphthalein from dark pink to colourless indicates the end-point.

The CM content and DS of CMC were calculated as $[(V_o-V_n)\times0.15\times58/1000\times100]/M$ and $(162\times\%CM)/[100\times58-(58-1)\times\%CM]$, respectively, where V_o is the amount (ml) of HCl used to titrate the blank, V_n is the amount (ml) of HCl used to titrate the samples, 0.15 is the normality of HCl used, 58 is the molecular weight of the CM group, M is the amount

(g) of the sample and 162 is the molecular weight of the anhydroglucose unit.[10,11]

Fourier transform infrared spectroscopy

The functional groups of the CMC synthesized from the various plant materials were determined using a Thermo Scientific Nicolet iS5 FT-IR Spectrometer. The CMC samples were dried in an oven at 60 ºC to remove any moisture. About 0.2 mg of sample and 2.0 mg of potassium bromide were mixed and finely ground before the mixture was compressed to form a transparent pellet. The infrared spectra were measured in the transmission wavelength range of 4000 cm^{-1} to 400 cm^{-1}.

Figure 1: Bleaching process (top left) to extract cellulose (top right) from sugarcane bagasse, and dried carboxymethyl cellulose (CMC) from sugarcane bagasse (bottom left) and palm kernel cake (bottom right)

Experimental design and statistical methods

The experimental design of this study comprised three phases, *i.e.* procurement of six types of agricultural wastes, extraction of cellulose pulp, and production of CMC under different NaOH concentrations (20%, 30% and 40%), temperatures (40 °C, 50 °C and 60 °C) and amounts of SMCA (1 g, 3 g and 5 g). When a given parameter was studied, the other two parameters were kept constant at 20% for NaOH, 50 °C for temperature and 5 g for SMCA.

Analysis involved determination of moisture content, yield of cellulose and CMC, and characterisation of the CMC produced. All analyses were conducted in triplicate, and the results were presented as means ± standard deviations. Data were analysed using the Tukey honestly significant difference (HSD) one-way analysis of variance (ANOVA) with significant difference at $p < 0.05$.

RESULTS AND DISCUSSION

Moisture content and cellulose yield

Of the six different plant materials, spent tea leaves and sugarcane bagasse had the highest moisture content (85% and 65%) and cellulose yield (57% and 46%), respectively (Table 1). Significantly lower moisture content and cellulose yield were found in coconut fibres, oil palm fibres and dried duckweed. Interestingly, palm kernel cake with the lowest moisture content (2.8%) produced a cellulose yield (45%) that was comparable to that of sugarcane bagasse (46%). Ranking based on moisture content was: spent tea leaves > sugarcane bagasse > coconut fibres ~ oil palm fibres > dried duck weed > palm kernel cake. At the time of sample collection, both spent tea leaves and sugarcane bagasse were moist and this may explain their high moisture content. The other plant materials were already dried when obtained. Ranking based on cellulose yield was: spent tea leaves > sugarcane bagasse ~ palm kernel cake > oil palm fibres ~ dried duckweed > coconut fibres.

In this study, the moisture content and cellulose yield of sugarcane bagasse were 65%

and 46%, and those of palm kernel cake were 3% and 45%, respectively. In our earlier study, we reported values of 53% and 43% for sugarcane bagasse, and 3% and 26% for palm kernel cake, which were comparable or lower.[10] Earlier studies reported values of 46-52% for moisture content[12] and 27-54% for cellulose content[13] for sugarcane bagasse.

CMC yield, CM content and DS

Using different concentrations of NaOH (20%, 30% and 40%) to alkalise the cellulose pulp appeared to have a variable effect on the CMC yield (g) of the plant materials (Table 2). For oil palm fibres, coconut fibres and sugarcane bagasse, the yield of CMC increased with increasing NaOH concentrations. The highest CMC yield was observed at 30% NaOH for dried duckweed (6.1 g) and palm kernel cake (6.2 g), and at 20% NaOH for spent tea leaves (3.8 g). In terms of CM content and DS, there was a consistent trend for all the plant materials. The highest values were observed at 20% NaOH with the CM content ranging from 17 g for sugarcane bagasse to 22 g for coconut fibres, and with the DS ranging from 0.60 for oil palm fibres to 0.73 for spent tea leaves and palm kernel cake.

Table 1
Moisture content and cellulose yield of various plant materials

Plant material	Moisture content (%)	Cellulose yield (%)
Oil palm fibres	9.60 ± 1.98^{c}	37.6 ± 0.58^{c}
Dried duckweed	3.50 ± 0.12^{d}	33.6 ± 2.17^{c}
Coconut fibres	11.0 ± 0.57^{c}	28.9 ± 1.29^{d}
Sugarcane bagasse	65.2 ± 1.05^{b}	46.4 ± 4.86^{b}
Spent tea leaves	84.7 ± 1.57^{a}	56.5 ± 3.15^{a}
Palm kernel cake	2.80 ± 0.53^{e}	45.1 ± 1.80^{b}

Data are in means ± standard deviations. Cellulose yield (%) was produced from 50 g of plant material. Within a given column, different superscripts (a–e) are significantly different as $p < 0.05$, as measured by the Tukey HSD test. Values are in alphabetic order and those with the same superscripts are comparable

Table 2
Yield, CM content and DS of CMC produced from various plant materials using different concentrations of NaOH

Plant material	NaOH (%)	CMC yield (g)	CM content (%)	DS
	20	5.91	21.6 ± 0.08^{a}	0.60 ± 0.02^{a}
Oil palm fibres	30	6.60	17.0 ± 1.15^{b}	0.57 ± 0.04^{ab}
	40	8.13	15.7 ± 0.80^{b}	0.52 ± 0.03^{b}
	20	5.86	20.7 ± 0.93^{a}	0.54 ± 0.02^{a}
Dried duckweed	30	6.14	15.6 ± 0.62^{b}	0.52 ± 0.02^{a}
	40	5.66	13.2 ± 0.73^{c}	0.43 ± 0.03^{b}
	20	5.98	22.3 ± 1.23^{a}	0.65 ± 0.02^{a}
Coconut fibres	30	6.12	17.9 ± 0.69^{b}	0.61 ± 0.03^{a}
	40	6.51	18.1 ± 0.43^{b}	0.62 ± 0.01^{a}
	20	5.81	16.9 ± 0.73^{a}	0.69 ± 0.02^{a}
Sugarcane bagasse	30	6.30	16.7 ± 0.43^{a}	0.56 ± 0.02^{b}
	40	6.67	15.7 ± 0.09^{b}	0.52 ± 0.00^{c}
	20	3.80	20.8 ± 0.31^{a}	0.73 ± 0.02^{a}
Spent tea leaves	30	3.68	21.6 ± 0.09^{a}	0.77 ± 0.03^{a}
	40	3.22	18.6 ± 0.26^{b}	0.64 ± 0.01^{b}
	20	4.68	20.7 ± 0.28^{a}	0.73 ± 0.02^{a}
Palm kernel cake	30	6.19	11.7 ± 0.60^{b}	0.37 ± 0.02^{b}
	40	6.02	11.0 ± 0.87^{b}	0.34 ± 0.03^{b}

CMC yield (g) was derived from 5 g of cellulose pulp. The experiment was done at a reaction temperature of 50 °C using 5 g of SMCA. Within a column, different superscripts (a–c) are significantly different as $p < 0.05$ as measured by the Tukey HSD test. ANOVA does not apply between plant materials. Values are in alphabetic order and those with the same superscripts are comparable

Finding that the CM content and DS were highest at 20% NaOH and lowest at 40% NaOH for all the plant materials is in agreement with reports stating that high concentrations of NaOH tend to degrade the cellulose chains by alkaline hydrolysis and form sodium glycolate, causing a reduction in DS.[14-16]

The cellulose pulp alkalised at different reaction temperatures (40 °C, 50 °C and 60 °C) had a consistent effect on the CMC yield of the plant materials (Table 3). The highest values were obtained at 60 °C, ranging from 5.0 g for spent tea leaves to 6.4 g for oil palm fibres. Palm kernel cake was the only exception in that the highest value of 5.7 g was at 40 °C. Based on the CM content and DS, the highest values were obtained at 50 °C for all the plant materials. Dried duckweed and spent tea leaves were the only exceptions in that the highest values were observed at 60 °C. In the case of dried duckweed, its CM content and DS at 60 °C were comparable to the values at 50 °C. According to the data in Table 3, the increase in the CM content and DS from 40 °C to 50 °C might be due to a better reaction environment for carboxymethylation. The values culminated at 50 °C and declined or remained unchanged at 60 °C. Possible explanations have been attributed to the degradation of cellulose caused by chemical elimination of water and inter-molecular elimination of hydroxyl groups, which are necessary for carboxymethylation.[3,17]

Using different amounts of SMCA (1 g, 3 g and 5 g) for the etherification process showed that the CMC yield increased with increasing amounts of SMCA for all plant materials, *i.e.* the highest values were obtained with 5 g of SMCA (Table 4). Palm kernel cake was the only exception where 3 g of SMCA yielded the highest value (5.8 g). For dried duckweed and palm kernel cake, the highest CM content and DS were obtained with 3 g of SMCA. Although oil palm fibres, coconut fibres, sugarcane bagasse and spent tea leaves had the highest values with 5 g of SMCA, the values of coconut fibres and spent tea leaves were comparable to those using 3 g of SMCA. In general, maximum CM content and DS were observed for 3 g or 5 g of SMCA (Table 4). For oil palm fibres and sugarcane bagasse, where maximum CM content and DS were at 5 g of SMCA, the positive correlation might be due to greater availability of acetate ions, active alkoxides and functional groups at higher concentrations of SMCA.[3,16,18]

Table 3
Yield, CM content and DS of CMC produced from various plant materials at different temperatures

Plant material	Temp (°C)	CMC yield (g)	CM content (%)	DS
	40	5.69	14.5 ± 0.56^{b}	0.47 ± 0.02^{b}
Oil palm fibres	50	5.90	19.0 ± 0.00^{a}	0.65 ± 0.00^{a}
	60	6.44	15.2 ± 0.30^{b}	0.50 ± 0.03^{b}
	40	5.15	14.8 ± 0.96^{a}	0.48 ± 0.04^{b}
Dried duckweed	50	5.37	16.1 ± 0.52^{a}	0.54 ± 0.02^{a}
	60	5.65	16.7 ± 0.93^{a}	0.56 ± 0.04^{a}
	40	5.65	15.6 ± 1.16^{b}	0.49 ± 0.05^{b}
Coconut fibres	50	5.94	18.0 ± 0.16^{a}	0.61 ± 0.02^{a}
	60	6.32	15.7 ± 0.27^{b}	0.52 ± 0.02^{b}
	40	5.57	15.5 ± 0.48^{b}	0.51 ± 0.02^{b}
Sugarcane bagasse	50	6.15	20.0 ± 0.11^{a}	0.70 ± 0.00^{a}
	60	6.33	19.9 ± 0.12^{a}	0.69 ± 0.01^{a}
	40	4.67	21.4 ± 0.74^{b}	0.76 ± 0.03^{b}
Spent tea leaves	50	3.56	21.2 ± 0.04^{b}	0.75 ± 0.00^{b}
	60	4.99	23.3 ± 0.65^{a}	0.85 ± 0.03^{a}
	40	5.70	10.7 ± 0.79^{b}	0.33 ± 0.03^{b}
Palm kernel cake	50	5.13	20.7 ± 0.28^{a}	0.63 ± 0.04^{a}
	60	4.72	9.97 ± 1.41^{b}	0.31 ± 0.05^{b}

CMC yield (g) was derived from 5 g of cellulose pulp. The experiment was done using 20% NaOH and 5 g of SMCA. Within a column, different superscripts (a–c) are significantly different as $p < 0.05$ as measured by the Tukey HSD test. ANOVA does not apply between plant materials. Values are in alphabetic order and those with the same superscripts are comparable

Table 4
Yield, CM content and DS of CMC produced from various plant materials using different amounts of SMCA

Plant material	SMCA (g)	CMC yield (g)	CM content (%)	DS
	1	3.04	9.27 ± 0.71^{c}	0.29 ± 0.02^{c}
Oil palm fibres	3	5.67	14.7 ± 0.63^{b}	0.48 ± 0.02^{b}
	5	5.84	18.7 ± 0.53^{a}	0.64 ± 0.02^{a}
	1	4.09	11.0 ± 0.07^{c}	0.35 ± 0.01^{c}
Dried duckweed	3	4.57	15.4 ± 0.29^{a}	0.51 ± 0.01^{a}
	5	4.83	14.4 ± 0.61^{b}	0.47 ± 0.02^{b}
	1	4.61	8.86 ± 1.08^{b}	0.27 ± 0.04^{b}
Coconut fibres	3	5.24	17.2 ± 0.49^{a}	0.58 ± 0.02^{a}
	5	5.64	17.8 ± 0.92^{a}	0.60 ± 0.03^{a}
	1	4.12	10.7 ± 1.86^{c}	0.34 ± 0.06^{c}
Sugarcane bagasse	3	5.41	15.8 ± 0.59^{b}	0.52 ± 0.02^{b}
	5	5.87	19.4 ± 0.79^{a}	0.67 ± 0.03^{a}
	1	4.12	16.8 ± 0.64^{b}	0.56 ± 0.03^{b}
Spent tea leaves	3	4.56	18.7 ± 0.50^{a}	0.65 ± 0.02^{a}
	5	4.95	20.0 ± 0.85^{a}	0.70 ± 0.04^{a}
	1	5.45	20.8 ± 0.26^{a}	0.73 ± 0.01^{a}
Palm kernel cake	3	5.83	20.9 ± 0.35^{a}	0.73 ± 0.02^{a}
	5	4.68	14.8 ± 0.06^{b}	0.48 ± 0.01^{b}

CMC yield (g) was derived from 5 g of cellulose pulp. The experiment was done using 20% NaOH at reaction temperature of 50 °C. Within a column, different superscripts (a–c) are significantly different as $p < 0.05$ as measured by the Tukey HSD test. ANOVA does not apply between plant materials. Values are in alphabetic order and those with the same superscripts are comparable

Table 5
Optimal conditions for generating the maximum yield, CM content and DS of CMC from various plant materials

Plant material	NaOH	Temp.	SMCA	NaOH	Temp.	SMCA	NaOH	Temp.	SMCA
	CMC yield (g)			CM content (%)			Degree of substitution		
OPF	40 (8.13)	60 (6.44)	5 (5.84)	20 (21.6)	50 (19.0)	5 (18.7)	20 (0.60)	50 (0.65)	5 (0.64)
DD	30 (6.14)	60 (5.65)	5 (4.83)	20 (20.7)	50 (16.1)	3 (15.4)	20 (0.72)	50 (0.54)	3 (0.51)
CF	40 (6.51)	60 (6.32)	5 (5.64)	20 (22.3)	50 (18.0)	3 (17.2)	20 (0.65)	50 (0.61)	3 (0.58)
SB	40 (6.67)	60 (6.33)	5 (5.87)	20 (16.9)	50 (20.0)	5 (19.4)	20 (0.69)	50 (0.70)	5 (0.67)
STL	20 (3.80)	60 (4.99)	5 (4.95)	30 (21.6)	60 (23.3)	3 (18.7)	20 (0.77)	60 (0.85)	3 (0.65)
PKC	30 (6.19)	40 (5.70)	3 (5.83)	20 (20.7)	50 (20.7)	3 (20.9)	20 (0.73)	50 (0.63)	3 (0.73)

Abbreviations: OPF, oil palm fibres; DD, dried duckweed; CF, coconut fibres; SB, sugarcane bagasse; STL, spent tea leaves; PKC, palm kernel cake; NaOH, sodium hydroxide; CMC, carboxymethyl cellulose; CM, carboxymethyl and SMCA, sodium monochloroacetate. Values of NaOH, temperature and SMCA are in %, °C and g, respectively. Figures in brackets are actual values of CMC yield (g), CM content (%) and DS under optimal conditions of NaOH, temperature and SMCA

For dried duckweed, coconut fibres, spent tea leaves and palm kernel cake, where maximum CM content and DS were at 3 g of SMCA, the reaction efficiency might have culminated at 5 g of SMCA due to the formation of sodium glycolate.[3,16]

Optimal conditions

Table 5 summarises the optimal conditions of NaOH (%), temperatures (°C) and SMCA (g) for deriving maximum yield, CM content and DS from CMC of the various plant materials. From the actual values under optimal conditions, it was possible to rank the performance of the various plant materials. In terms of average CMC yield, the ranking was: oil palm fibres (6.8 g) > sugarcane bagasse (6.3 g) ~ coconut fibres (6.2 g) > palm kernel cake (5.9 g) > dried duckweed (5.5 g) > spent tea leaves (4.6 g). In terms of average CM content, the ranking was: spent tea leaves (21%) ~ palm kernel cake (21%) > oil palm fibres (20%) ~ coconut fibres (19%) ~ sugarcane bagasse (19%) > dried duckweed (17%). In terms of average DS, the ranking was: spent tea leaves (0.75) > palm kernel cake (0.70) ~ sugarcane bagasse (0.69) > oil palm fibres (0.65) > coconut fibres (0.61) > dried duckweed (0.59).

In our earlier study,[10] we reported that sugarcane bagasse and palm kernel cake had CMC yields of 27 g and 14 g, respectively. The CM content and DS of sugarcane bagasse were 12% and 0.40, while palm kernel cake had values of 19% and 0.70. For comparison, our study also quoted values of the CM content and DS of 25% and 0.91 in the low-viscosity commercial CMC, and 32.1% and 1.31 in the high-viscosity commercial CMC. Commercial CMC has been reported to have a DS in the range of 0.4 to 1.4.[19]

Cellulose from some agricultural wastes, such as sugarcane bagasse, spent tea leaves and palm kernel cake reacted very readily with SMCA to yield CMC with high DS. In contrast, cellulose from dried duckweed, oil palm fibres and coconut fibres yielded relatively lower DS even with increased SMCA concentrations. The DS remained low for these agricultural wastes even when the etherification process was repeated in an attempt to increase their DS.

The DS of the CMC polymer has important implications in its applications. A higher DS results in better viscosity and cation exchange ability. Additional carboxyl groups provide more sites for cross-linking by multivalent cations. A high DS also enhances covalent cross-linking *via* electron beam irradiation.[20] It has been reported that irradiation of 10% w/v CMC solution with a DS of 0.7 resulted in degradation of the polymer, while CMC with higher DS of 1.32 resulted in good cross-linking and high gel fraction. A higher DS also allowed cross-linking at lower radiation doses.

Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was used to verify the successful etherification of cellulose. CMC synthesized from all the agricultural wastes showed similar FT-IR spectra. As an example, the FT-IR spectrum of CMC from sugarcane bagasse displayed a broad absorption band at 3326 cm^{-1} due to the stretching frequency of the –OH group and another band at 2894 cm^{-1} due to C–H stretching. The presence of a strong absorption band at 1588 cm^{-1} was attributed to C=O stretching confirmed the presence of the –COO group, indicating successful etherification of cellulose.

CONCLUSION

Of the plant materials, oil palm fibres, dried duckweed, coconut fibres and spent tea leaves were studied for the first time. Along with sugarcane bagasse and palm kernel cake, they all have the potential to be converted into CMC. However, they differed in terms of their cellulose content and maximum DS. Sugarcane bagasse, spent tea leaves and palm kernel cake are particularly attractive plant materials for conversion into CMC due to their high cellulose content and their CMC has the ability to achieve a high DS. The next phase of our research would be to cross-link CMC from these sources into hydrogels for use as biosorbents and root-targeted delivery systems.

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