NEW ROUTE FOR CARBOXYMETHYLATION OF CELLULOSE: SYNTHESIS, STRUCTURAL ANALYSIS AND PROPERTIES

SURENDRA S. BISHT,[*] K. K. PANDEY,[*] GYANESH JOSHI[**] and SANJAY NAITHANI[**]

[*]*Institute of Wood Science and Technology, Bengaluru-560003, Karnataka, India*
[**]*Forest Research Institute, Dehradun-248001, Uttarakhand, India*
✉ *Corresponding author: Surendra S. Bisht, ssbisht@icfre.org, ssbchem@gmail.com*

An efficient and new route for the synthesis of carboxymethyl cellulose (CMC), a most widely used biopolymer for various applications, has been developed. Cellulose was converted into cellulose triacetate (CTA) intermediate, which was then converted to CMC by deprotection, followed by etherification using NaOH and $ClCH_2COONa$ in the tetrahydrofuran-water (THF-H_2O) solvent system. Reaction parameters were optimized and a maximum degree of substitution (DS) of 1.02 was achieved at 50 °C within 1 h with 0.95 M and 1.1 M concentration of NaOH and $ClCH_2COONa$, respectively. The rheological characterization of the 1-3% aqueous solution of optimized CMC product showed non-Newtonian pseudo-plastic behavior. The 2% aqueous solution of CMC had a maximum viscosity of 40 cP. The reaction products (CTA and CMC) were characterized by Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. [1]H and ^{13}C chemical shift assignment of the anhydroglucose units (AGUs) that comprise sodium carboxymethyl cellulose with a degree of substitution of 1.02 was performed using 2D NMR spectra obtained from COSY and TOCSY experiments. In the 2D COSY and TOCSY spectra, there were four correlation networks for the H1 to H6 atoms of AGU; the four types of AGUs with H1 resonances appearing at 4.96, 4.94, 4.90 and 4.88 ppm, are referred to as residue A, B, C and D, respectively.

Keywords: cellulose triacetate, carboxymethyl cellulose, degree of substitution, viscosity

INTRODUCTION

Carboxymethyl cellulose (CMC) is a non-toxic, biodegradable and biocompatible polysaccharide obtained from cellulose. It is water soluble cellulose ether, also known as cellulose gum, sodium cellulose glycolate or sodium carboxymethyl cellulose.[1] It has colloidal, binding, thickening, absorbing, stabilizing and film-forming properties, due to which it is used in the diversified fields of food technology,[2] pharmaceuticals,[3] paper,[4] cosmetics, paints, thickeners, emulsion stabilizers, water-retention agents *etc*.[1]

CMC is produced commercially by reacting cellulose with sodium monochloroacetate in an alcohol-water-NaOH system,[5] which has an excess of alcohol.[6] There exist several methods for preparing cellulose ethers, including homogeneous carboxymethylation,[7] rotating drum technique,[8] fluidized bed technique,[9] sheet carboxymethylation,[10] Werner-Pfleiderer type mixers,[11] and also a solventless method using a double screw press,[12] and a paddle reactor.[13]

Physical and chemical properties of CMC are mainly dependent on the degree of substitution (DS), distribution pattern and degree of polymerization (DP). DS has the greatest influence on the solubility, shearing stability, thermal stability and viscosity of the CMC solution. The DS range for commercially available CMC is generally in between 0.4-1.5.[5]

Earlier efforts have been made by various researchers to improve the DS of CMC using different methods. These methods include dissolving of the cellulose in dimethylsulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF),[14] by dissolving cellulose in DMAc/LiCl or via hydrolytically unstable cellulose intermediates.[15] However, a maximum DS of about 0.4-1.5 could be achieved by one-step reaction. DS values of more than 1.5 could not be obtained by the usual heterogeneous reaction. Moreover, direct chemical modification of cellulose is often challenging because of its high stability and hydrophilicity.[16]

Several protecting group techniques have been developed for synthesis of CMC and other cellulose derivatives with respect to regio-selective substitution and high DS. The commonly used protective groups are the triphenylmethyl (trityl), thexyldimethylsilyl,[17,18] dichloroacetates[19] and trifluroacetate.[20] The most widely used tritylation was attempted in different media, such as in N-ethylpyridinium chloride melts,[21] DMSO/N$_2$O$_4$, DMA/LiCl, and DMSO/SO$_2$/diethylamine,[22] while trifluroacetate (CFTA) was the most exploited for subsequent functionalization in homogeneous phase, giving a O-3 selectivity of the sulphation,[20] carboxymethylation[23] and a variety of other organic esters, inorganic esters, carbamates, and ethers with specific distributions of functional groups.[24] One of the major disadvantages in the first two protecting groups (triphenylmethyl and thexyldimethylsilyl) is the deprotection step, which is usually carried out with HCl or other strong acids, resulting in a significant degradation of the polymer chains, while the trifluroacetate (TFA) protecting group technique has several disadvantages, such as its strong acidic nature, and corrosivity of the reagents. Therefore, alternative protecting groups techniques, which can overcome these disadvantages, are still of interest.

In this paper, we report a new protecting group technique for the synthesis of CMC by using economical, mild acidic and non-corrosive agents. The hypothesis was the conversion of cellulose triacetate (CTA), an organic solvent soluble intermediate, into CMC by reaction with chloroacetic acid. CTA (DS 2.95) was prepared and used as starting material. The synthesized CMC is expected to have a high degree of substitution and better physical and chemical properties without polymer degradation. The elucidation of the substituent distribution is important to understand the structure-property relationships. Therefore, the assignment of ring carbon and proton resonances in the NMR spectra of CMC was performed *via* 2D NMR experiments, including COSY and TOCSY on CMC with the degree of substitution (DS) = 1.02.

EXPERIMENTAL
Materials
Microcrystalline cellulose (DP 270) was purchased from Sigma Aldrich, and dried under vacuum at 50 °C overnight before use. Chloroacetic acid, acetic acid, acetic anhydride, pyridine, laboratory grade solvents and reagents were purchased from HiMedia Laboratories Pvt. Ltd., and Sisco Research Laboratories Pvt. Ltd., India. Double-distilled water was used throughout the experiments.

Methods
Synthesis procedure of cellulose triacetate (CTA)
A typical acetylation procedure was adopted according to published procedure.[25] A mixture of 10 grams dry cellulose and 200 grams acetic acid (mixture A) was heated in a round-bottom flask at 45 °C with continuous stirring using a magnetic stirrer. Another mixture of acetic acid (57 wt%), acetic anhydride (43 wt%), and 0.5 grams of sulfuric acid (mixture B) was added to a 500 mL round-bottom flask, which was set on a hot plate at 45 °C. Mixture A was added to mixture B and the acetylation process was carried out at 40-45 °C for 2 h with continuous stirring. After 2 h, the reaction mixture was quenched by the addition of magnesium acetate and an excess of acetic acid. The reaction mixture was then precipitated in 20% aqueous NaCl solution, followed by washing with water. The solid mass was obtained and dried at 60 °C in a hot air oven. The product was characterized by FTIR and NMR spectroscopy.

Synthesis procedure of carboxymethyl cellulose (CMC)
The cellulose triacetate (CTA, 1 g) was dissolved in 15-20 mL of solvent, followed by the addition of the sodium salt of chloroacetic acid (0.67-1.20 M). The NaOH (0.95-1.25 M) was added fraction-wise to the reaction mixer at room temperature. The reaction mixture was heated up to the desired temperature (40-60 °C) and stirred for the desired duration (0.5-2 h). After completion of the *in situ* etherification reaction, the excess alkali was neutralized with acetic acid (5N). The excess amount of solvent was evaporated by a Rotavapor. The jelly mass was subjected to washing by methanol, water and a mixture of water:methanol (80:20%). The solid mass was obtained and dried at 60 °C in an oven. The final product was characterized by FTIR and NMR spectroscopy. The yield of CMC was calculated on oven dry weight basis. The net dry weight of CMC was calculated as per the following formula:

Yield (%) = [Weight of dried CMC/Oven dried weight of CTA] x 100   (1)

Determination of degree of substitution (DS)
The DS of the prepared CMC samples was determined by the ASTM standard method.

Determination of apparent viscosity (η)
The apparent viscosity (η) of the optimized CMC product (1, 2 and 3% solution in water), was determined at different shear rates, using a Brookfield Digital Viscometer model DV ULTRA-III USA as per the standard conditions.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were recorded on a Bruker Tensor 27 FT-IR using the KBr pallet technique. Absorbance spectra were measured in the 4000-400 cm^{-1} region at a spectral resolution of 4 cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on a Bruker AV400 and 500 High Resolution Multinuclear FT-NMR spectrometer (^{1}H frequency of 400.23 MHz and 500.15 MHz, ^{13}C frequency of 100.64 MHz). ^{1}H NMR spectra of CTA were recorded in CDCl$_3$, while for CMC in D$_2$O at 298.0 K and 343.0 K, respectively.

A 5 mg sample of CMC dissolved in 0.6 mL of D$_2$O was taken in a 5 mm NMR tube and NMR spectra were recorded at 343 K on a Bruker BioSpin AVIII 500 spectrometer (1H frequency of 500.15 MHz) equipped with a 2-channel BBO probe incorporating a z-gradient coil. Using this spectrometer, the following experiments were performed: 1D 1H, 1D 13C, water-suppressed 2D 1H-1H COSY using gradient pulse for selection,[26] water-suppressed 2D 1H-1H TOCSY using the MLEV17 sequence for TOCSY spinlocking.[27] In the COSY experiments, a total of 256 t1 acquisitions with 32 scans per increment were collected. In the TOCSY experiments, the mixing times were 50, 100, or 180 ms, and a total of 256 t1 acquisitions with 64

RESULTS AND DISCUSSION

The reaction scheme for the synthesis of CMC from cellulose is shown in Scheme 1. Cellulose was acetylated to obtain CTA, which was subsequently converted into CMC. The reaction parameters for the synthesis of CMC from CTA were optimized. The process parameters were: the type of solvent (water, methanol, ethanol, IPA, THF, dichloromethane and chloroform), reaction temperature 40-60 °C, and reaction period (1-3 h), amount of monochloroacetic acid sodium salt, and concentration of NaOH.

The proposed reaction mechanism is shown in Scheme 2. The reaction proceeds *via* the formation of alkali cellulose III intermediate through transition state II, resulting from the reaction between the triacetate cellulose I and hydroxide ($^-$OH) ion. In the second step, the alkali cellulose III intermediate undergoes a nucleophilic substitution (SN) reaction with chloroacetic acid sodium salt at the methylene carbon atom to yield carboxymethyl cellulose (CMC).
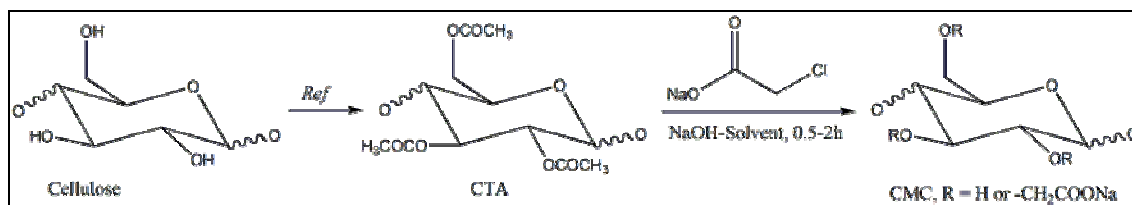
Scheme 1: Carboxymethylation of cellulose *via* cellulose triacetate (CTA)
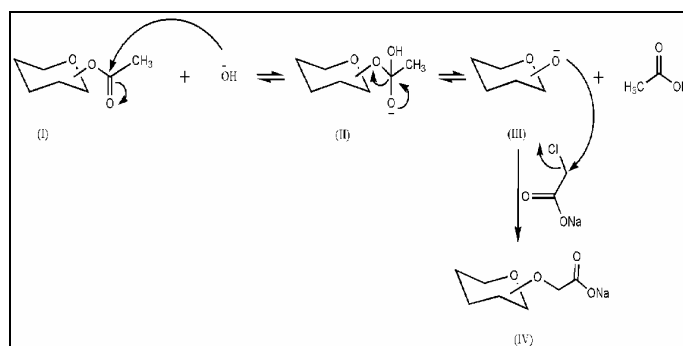
Scheme 2: Proposed reaction mechanism of carboxymethylation of cellulose triacetate (CTA)

Optimum reaction conditions for synthesis of CMC

Cellulose triacetate (CTA, 1 g) was dissolved in the appropriate solvent, followed by addition of

chloroacetic acid sodium salt (1.00M). The NaOH (1.1 M) was added fraction-wise to the reaction mixer at room temperature. The reaction mixture was heated up to the desired temperature (55-60

°C) and stirred at that temperature for a fixed duration (2 h). After completion of the etherification reaction, the excess alkali was neutralized with acetic acid (5N). The excess amount of solvent was evaporated by a rotavapor. The jelly mass was subjected to washing by methanol, water and a mixture of water:methanol (80:20%). The desired solid mass was obtained and dried at 60 °C in an oven.

Table 1 shows the effect of different solvent media on the yield of CMC. A maximum yield of 95-98% was obtained in THF and isopropyl alcohol with the water solvent system. Among the solvents used, THF or isopropyl alcohol with water in the presence of NaOH were found to be the most suitable combination to afford the maximum yield of the desired compound, CMC. The differences in the extent of carboxymethylation can be explained by taking into consideration their solvent polarities and the formation of alkaline cellulose. THF or IPA with water was the best choice. No reaction was observed in THF, CH_2Cl_2 and $CHCl_3$ solvents, while a very poor yield of CMC was obtained in other solvents and combinations of solvents.

In situ deprotection and carboxymethylation of the above cellulose triacetate (CTA) was carried out separately at 40-60 °C in the presence of NaOH in different solvent systems. To optimize the reaction conditions, the etherification (carboxymethylation) of CTA in different organic solvents and water under the influence of a base was carried out. Further, the reaction parameters, such as concentration of NaOH, sodium monochloroacetate (SMCA), temperature and time, were performed in THF and the water solvent system (Table 2).

Some studies on the synthesis of carboxymethyl cellulose from various biomass, like bamboo (DS 0.98),[28] cotton litter (DS 0.77),[29] textile waste (DS 0.86),[30] palm kernel cake (DS 0.67),[31] sago waste (DS 0.82),[32] sugar beet pulp (DS 0.67),[33] have been published, but all these methods report a lower DS value than the DS achieved in the present study (DS 1.03). In order to achieve a high DS, the optimized reaction parameters are shown in Table 2.

Table 2, column 2 shows the effect of NaOH concentration (0.65 to 1.25 M) on the DS of CMC. It was observed that the DS increased with increasing the concentration of aqueous NaOH and thereafter decreased significantly. The concentration of SMCA (0.87 M), reaction time (1 h) and temperature (50 °C) was kept constant during the optimization of NaOH concentration with respect to DS for carboxymethylation. The average DS of the products thus formed has values varying from 0.71 to 0.88.

Maximum DS (0.88) was achieved when the experiment was performed with 0.95 M NaOH and 0.87 M SMCA at 50 °C temperature for 1 h reaction time. The increase in DS (0.88) is due to the predominance of the main carboxymethylation reaction over its competitive side reaction, that is, formation of sodium glycolate by the reaction of sodium hydroxide with SMCA. Above this concentration, the side reaction between NaOH and SMCA becomes more substantial by consuming NaOH to form sodium glycolate, which leads to lowering the DS (0.71). The same behavior was reported in carboxymethylation earlier.[34]

Table 1
Optimization of CTA carboxymethylation with different NaOH-solvent systems at 55-60 °C for 2 h

Entry	Solvent-base system	Isolated yield (%)
1	Water-NaOH	57
2	MeOH-NaOH	30
3	EtOH-NaOH	54
4	IPA-NaOH	60
5	IPA-Water-NaOH	95
6	THF-NaOH	NR
7	THF-Water-NaOH	98
8	CH_2Cl_2-NaOH	NR
9	$CH2Cl_2 + H_2O$-NaOH	45
10	$CHCl_3$-NaOH	NR
11	$CHCl_3 + H_2O$-NaOH	40

Table 2
Reaction parameters for carboxymethylation of CTA

Entry	NaOH (M)	SMCA (M)	Temperature (°C)	Average DS	Reaction time (h)
1	0.65		50	0.87	
2	0.95	0.87	50	0.88	1
3	1.25			0.71	
4		0.76		0.45	
5		0.88		0.83	
6		0.97	50	0.97	
7	0.95	1.10		1.02	1
8		1.20		0.98	
9			40	0.93	
10		1.10	50	1.02	
11			60	0.92	
12			50	0.98	0.5
13	0.95	1.10	50	1.02	1
14			50	1.01	2

The effect of SMCA concentration on the DS of CMC was evaluated by varying SMCA concentration from 0.76 to 1.20 M (Table 2). The concentration of NaOH (0.95 M), reaction time (1 h) and temperature (50 °C) was kept constant throughout the course of the reaction. Table 2 reveals that DS increased from 0.45-1.02 with increasing the SMCA concentration. Maximum DS was achieved at 1.1 M SMCA concentration. An increase in the concentration of SMCA seems to enhance the availability of acid molecules in the proximity of the cellulose hydroxyls, facilitating thereby the carboxymethylation. No significant increase in DS occurred on further increase in SMCA concentration. Moreover, further increase in the concentration of SMCA resulted in a decrease in DS. This may be due to the non-availability of enough cellulose-alkoxide for the reaction.[35]

The effect of temperature of carboxymethylation was studied on DS by varying the temperature from 40 to 60 °C (Table 2). All the reactions were performed with 0.95 M NaOH, 1.1 M SMCA at different temperatures (40-60 °C) for 1 h reaction time. Maximum DS (1.02) was achieved at 50 °C. The increase in DS up to 50 °C could be linked with the effect of temperature on the swellability of cellulose, diffusion and adsorption of MCA, which facilitated the reaction between MCA and the cellulose. Further increase in temperature resulted in a decrease in DS, which is in agreement with earlier similar observations.[36]

The reactions for time optimization with respect to DS were carried out with 0.95 M NaOH and 1.1 M SMCA concentration at 50 °C for different time intervals (0.5-2 h). Table 2 shows the increase in DS (1.02) with respect to time, which may be due to the fact that there is a better reaction environment created and a prolonged time available for carboxymethylation. This may lead to better reaction efficiency and higher DS of the final product. Moreover, further increase in temperature up to 60 °C resulted in a decrease in DS. The lowering of DS on prolonging the carboxymethylation time may be attributed to the atmospheric oxidative degradation of CMC. A similar effect of temperature on DS during the carboxymethylation of flax cellulose has been reported by Hebeish et al.[36] The performances of the reactions under drastic reaction conditions (higher temperature, NaOH and SMCA concentration) lead to more degradation of polymer chains and formation of side reaction products.

Rheological properties and water solubility of synthesized CMC

To assess the importance and feasibility of the CMC product for its application, its viscosity profile is an important parameter. Viscosity is due to friction between neighboring parcels of the fluid that are moving at different velocities.

The rheological properties of CMC depend upon the DS, as reported by other authors.[37] The DS not only influences the solubility of the CMC molecule, but also affects the solution characteristics. The higher the DS, the clearer will be the CMC solution achieved. The rheological properties of CMC solutions are much more

documented and all these report non-Newtonian and pseudoplastic flow behavior of CMC solutions.[38,39] In this connection, the rheological property of 1, 2 and 3% aqueous solutions of the optimized CMC product (DS 1.02) was examined with respect to shear rate, apparent viscosity (η) and shear stress. Figure 1 shows the effect of shear rate of CMC on its viscosity. A plot of η values of the aqueous solutions (1, 2 and 3%) of the optimized CMC *versus* shear rates (Fig. 1)

shows that the values of η for all the solutions of the optimized product rely upon the shear rate and decrease with increasing shear rate. No time effects were detected and the viscosity obtained with decreasing the rate was identical with that obtained with increasing the shear rate. Therefore, all the solutions of different concentration of the optimized product exhibit non-Newtonian pseudoplastic behavior.
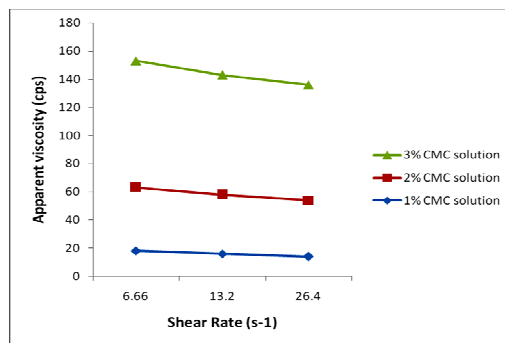
Figure 1: Effect of shear rates on apparent viscosities of aqueous solutions (1, 2 and 3%) of optimized CMC

The results are in good accordance with the results reported by Varshney *et al.*[35] The commercial range for medium viscosity CMC is 20-50 cP in 2% solution concentration. The optimized 2% aqueous solution of CMC from CTA has a maximum viscosity of 40 cP. The measurements of viscosity reveal that this grade of CMC may be a viable option for medium viscosity application, such as paper coating.

The solubility of CMC is another important parameter in order to assess the quality of CMC. In this regard, the solubility of all the CMC samples in distilled water has been investigated. All the samples were found soluble in water up to 96-98% by forming a clear transparent solution. The solution of CMC with a high DS was clearer, compared to the solution of CMC with a lower DS value. Increasing DS makes CMC more hydrophilic, or water-loving, hence solutions having highly substituted CMC are more readily disaggregated in water.

Spectroscopic characterization of CTA and CMC
FTIR characterization
The CTA was characterized by FTIR spectroscopy (Fig. 2). The comparison of the FTIR spectra of cellulose and CTA shows a

significant decrease in intensity of the OH band at 3346 cm^{-1} in CTA due to the acetylation process. This is accompanied with the appearance of a strong band at 1750 cm^{-1}, characteristic of C=O stretching. This indicates the successful conversion of cellulose into CTA. The formation of CTA was further confirmed by ^{1}H NMR analysis.

The structure of CMC was established on the basis of spectroscopic data (Fig. 3). Its FT-IR spectrum shows the peaks corresponding to the backbone of the cellulose molecule at 3435 cm^{-1} (broad absorption band due to stretching of –OH groups and intermolecular and intramolecular hydrogen bonds), 2916 cm^{-1} (C–H stretching), 1422 cm^{-1} (–CH$_2$ scissoring), 1327 cm^{-1} (–OH bending) and 1061 cm^{-1} (CH–O–CH$_2$ stretching). The peak at 1601 cm^{-1} corresponds to COO$^-$ in the FTIR spectrum of CMC. In conclusion, the FT-IR spectrum of CMC indicates the successful conversion of CTA into CMC.

^{1}H NMR characterization
The ^{1}H NMR spectrum of the sample shows all the characteristic features, as reported previously (Hiroyuki *et al.*),[40] which further indicates that the cellulose was fully converted to CTA. A typical ^{1}H NMR spectrum indicated

complete conversion of the cellulose to CTA (Fig. 4). Three signals of methyl protons assigned to the acetyl moieties appeared at δ 1.94, δ 2.0 and δ 2.14, while the methylene protons H-6 and H-6′ were observed at δ 4.07 and δ 4.36. All the sugar ring protons (H-2, H-3, H-4 and H-5) appeared at their respective position. The ^{1}H NMR spectrum of CTA was found in full agreement with reported data.[40]

^{1}H and ^{13}C NMR spectra of CMC in D_2O were recorded at 343 K. Each AGU contains seven protons, *i.e*., H1-H6, in the glucose ring and additional methylene protons in the substituted carboxymethyl groups. In the 1H spectrum shown in Figure 5, a plethora of 1H resonances from the

AGUs that compose the CMC structure overlap in the narrow region between 5.0-3.5 ppm. However, in the expanded spectrum, an anomeric proton (H1) was observed from δ 4.88-4.96 ppm, while other protons (H2-H7) appeared at their usual chemical shift values, which was in good agreement with previously assigned values by Kono.[41] The ^{13}C NMR spectrum in Figure 6 reveals the carbonyl carbons of the substituent groups, C1 and C6 of the glucose ring appearing at 180-178, 104-102, and 72-61 ppm, respectively. The resonances for the ring carbons in the C2-C5 positions appear as complex spectral lines in the region of 85-73 ppm, which is in good concordance with previous results.[42]
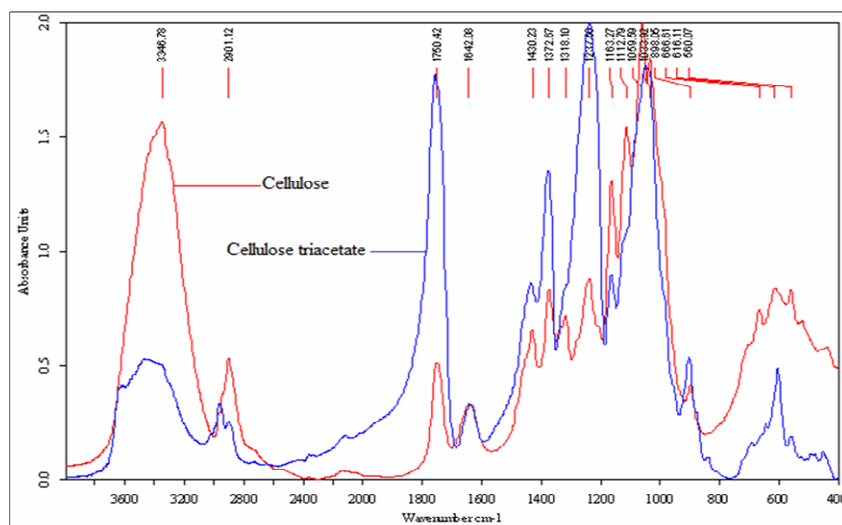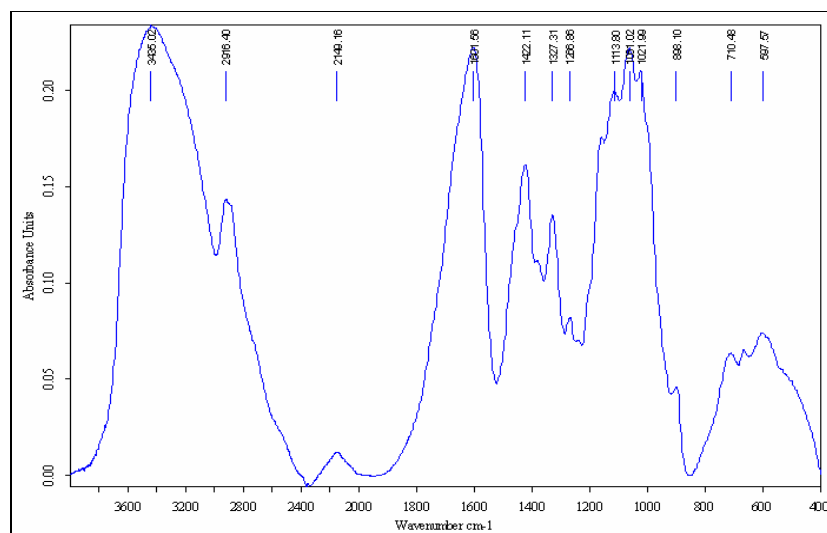

Figure 2: FT-IR spectra of cellulose and CTA

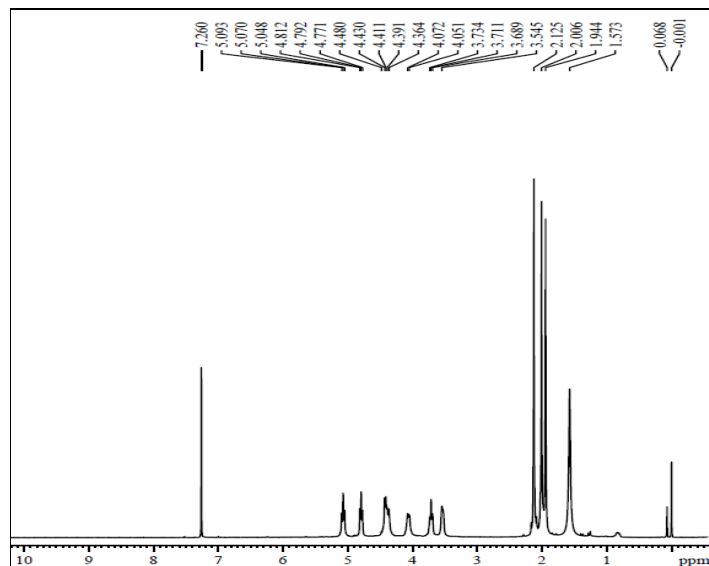Figure 3: FTIR spectrum of optimized CMC product with DS 1.02

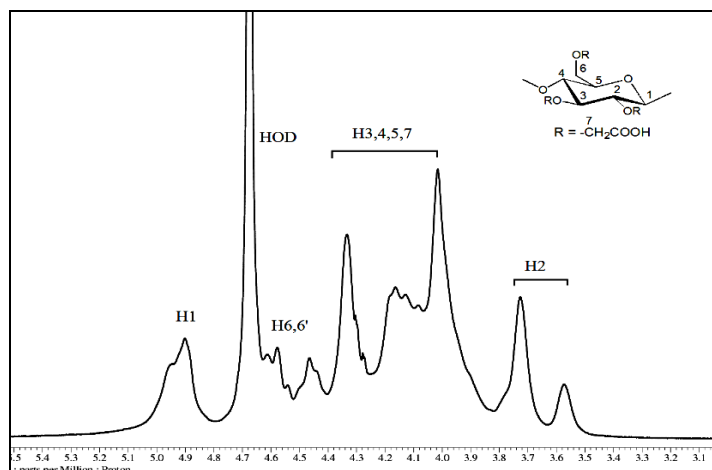Figure 4: ^{1}H NMR spectrum of CTA in CDCl$_3$ recorded at 298.0 K

Figure 5: ^{1}H NMR spectra of CMC (DS = 1.02) in D$_2$O recorded at 343K

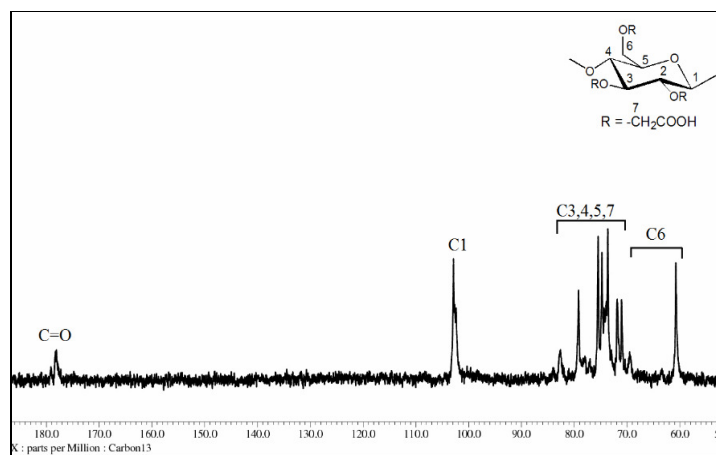
Figure 6: ^{13}C NMR spectra of CMC (DS = 1.02) in D$_2$O recorded at 343K

The distribution of the substituent at the C2, C3, and C6 positions leads to the possibility of eight different types of AGUs in the newly synthesized CMC. The total eight AGUs may

have 2,3,6-tri-O-, 2,3-di-O-, 2,6-di-O-, 3,6-di-O-, 2-mono-O-, 3-mono- O-, 6-mono-O-, and un-carboxymethylated substitution patterns in the modified polymer chain. In order to find out the different types of AGUs in CMC, the 2D NMR experiment, correlation spectroscopy (COSY) and total correlation spectroscopy (TOCSY) have been carried out.

Figure 7 shows the contour plot of a COSY spectrum, which identifies direct ^{1}H–^{1}H couplings. In the COSY spectrum, at least four different H1-H2 couplings were detected, although the correlation peaks partially overlapped. Here, the four types of AGUs with H1 resonances appearing at 4.96, 4.90, 4.88 and

4.94 ppm are referred to as residue A, B, C and D, respectively.

In Figure 8, a TOCSY spectrum reveals through-bond long-range ^{1}H-^{1}H couplings for correlations from H1 to all protons in each AGU, which was recorded with spin-lock times of 180 ms. Further, 1D spectra from row slices along the horizontal axis of the TOCSY spectrum were recorded and these slices were taken at the diagonal peaks of the resonances to see the relative intensities and appearance of all protons in four AGUs, A-D (Fig. 9). In these spectra, it was clearly visible that the intensities and chemical shift values for all protons in AGUs (A-D) were significantly different from each other.
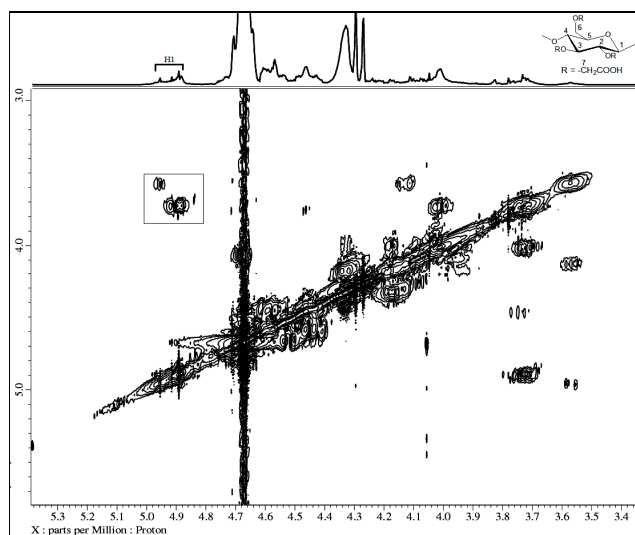

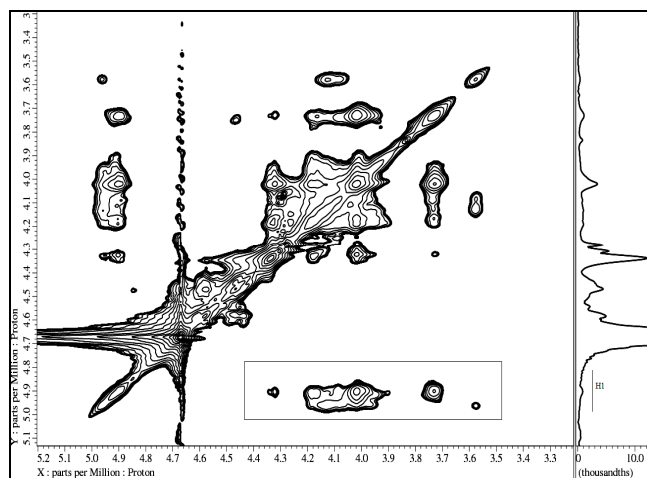Figure 7: COSY contour plot of CMC (DS = 1.02) in D$_2$O recorded at 343K

Figure 8: TOCSY contour plot of CMC (DS = 1.02) in D$_2$O recorded with spin lock time of 180 ms at 343K

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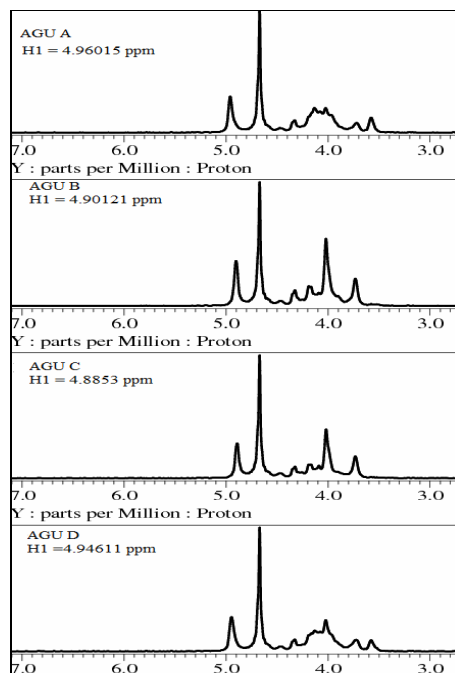Figure 9: [1]D spectrum from row slices along the horizontal axis of the TOCSY spectrum recorded with lock time of 180 ms, taken at the diagonal peaks of the resonances of AGUs A-D

From the above 1D and 2D NMR analysis, it is clear that out of eight different possible AGUs, only four types of substitution were observed in CMC. Further using higher magnetic field and sensitivity of NMR measurements would enable full assignment of ambiguous and overlapping signals, which will make complete the assignment as well as the substitution distribution at C2, C3 and C6 of CMC. The synthesis of CMC *via* the new route opens up new opportunities.

CONCLUSION

An alternative new route for the synthesis of CMC has been developed. The CTA obtained by acetylation of cellulose was converted into CMC. A maximum DS value of 1.02 for CMC was obtained under optimum reaction conditions. The optimized 2% aqueous solution of CMC from CTA had a maximum viscosity of 40 cP. The CMC was characterized by FTIR and NMR spectroscopy. Totally, four different types of substitution distribution for AGUs with H1 resonances at 4.96, 4.94, 4.90 and 4.88 ppm were observed in the 2D COSY and TOCSY spectra. The study of NMR measurements using higher magnetic field and sensitivity is further required to elucidate the complete assignment and the substitution distribution of CMC.

Abbreviations:
CMC – carboxymethyl cellulose
CTA – cellulose triacetate
SMCA – sodium salt of monochloroacetic acid
DS – degree of substitution
DP – degree of polymerization
COSY – Correlation spectroscopy
TOCSY – Total correlation spectroscopy
AGU – anhydroglucose unit

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