

Carboxymethylation of Cellulosic Material (Average Degree of Polymerization 2600) Isolated from Cotton (*Gossypium*) Linters with Respect to Degree of Substitution and Rheological Behavior

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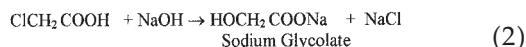
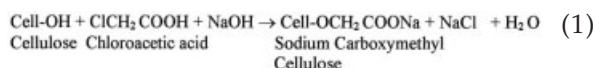
ABSTRACT: Carboxymethylation of cellulosic material (average degree of polymerization 2600) containing 76.5% cellulose and 23.6% xylose isolated from cotton (*Gossypium*) linters was studied under varying reaction conditions with respect to maximum degree of substitution (DS). The influence of reaction conditions on the apparent viscosity of the prepared derivatives was also studied. The conditions optimized were sodium hydroxide concentration 3.75M, monochloroacetic acid concentration 2.05 mol/AGU, carboxymethylation time 3.5 h, and temperature 55°C, to yield car-

boxymethyl cellulose of DS 0.77. Rheological studies of 1 and 2% solutions of the optimized product revealed their non-Newtonian pseudoplastic behavior. Repeating units of the optimized product were also determined by HPLC after complete depolymerization of the polymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1477–1482, 2005

Key words: cotton linters; viscosity; rheology; carboxymethylation; high-performance liquid chromatography (HPLC)

INTRODUCTION

Cellulose, a biodegradable and renewable raw material, can be modified by chemical reaction in many ways to confer novel properties for different purposes.¹ Numerous esters and ethers of cellulose have been reported over the years. Among the cellulose derivatives, cellulose ethers have gained their position in the market because of their multifunctional effects. Among cellulose ethers, carboxymethyl cellulose (CMC) is of special interest because of its versatile properties as a thickener, film former, protective colloid, water-retaining agent, and good compatibility with skin and mucous membranes. CMC is obtained by reacting cellulose with monochloroacetic acid (MCA) in the presence of sodium hydroxide, involving the following two competitive reactions that take place simultaneously²:



Most properties of CMC in actual applications depend, to a large extent, on three key parameters: (1) the molecular weight of the polymer; (2) the average number of carboxymethyl substituents per anhydroglucose unit [AGU; degree of substitution (DS)]; (3) and the distribution of the carboxymethyl substituents along the polymer chain.^{3–5} To achieve the above desirable characteristics, the main reaction conditions influencing the carboxymethylation process include the solvent system, its composition, concentration of alkali, MCA, temperature, and duration of reaction.^{6–9} The chemical composition and rheological characteristics make possible the selection of a modified cellulose to serve special application(s).

This article reports on the investigation of carboxymethylation of the cellulosic material [average degree of polymerization (Av. DP) 2600], derived from cotton linters to obtain the CMC of maximum DS. A search of the literature confirmed the absence of published reports on the carboxymethylation of cellulose of Av. DP 2600. Cotton linters were processed with the aim of isolating α -cellulose of high DP, high purity, and high brightness for its subsequent derivatization into CMC. We also sought to determine the mole fractions of the repeating units and DS of the optimized CMC by HPLC. HPLC analysis of the depolymerized product showed signals of monosubstituted, disubstituted, and unsubstituted xylose in ad-

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dition to the signals of mono-, di-, and unsubstituted glucose, thereby revealing the presence of xylose in the cellulose material isolated from the cotton linters. HPLC analysis of the parent pulp further confirmed the presence of xylose (23.6%) in the pulp. Although the presence of xylose in the cotton linters is surprising, it is supported by the findings of the Buchada et al.,¹⁰ who reported the isolation of different xyloglucans from different types of cotton cells.

The object of the work described in this article, therefore, was to describe the optimization of carboxymethylation of cellulosic material (Av. DP 2600; brightness.82.6%) containing 76.5% cellulose and 23.6% xylose derived from cotton linters, performed in isopropanol solvent medium by varying the concentration of sodium hydroxide, MCA, temperature, and duration of carboxymethylation reaction and studying their effect on the degree of substitution. The influence of these variables on the apparent viscosity (η) of the obtained CMCs was also studied. Based on the values of η , the optimized product was characterized rheologically. To characterize the repeating units of the optimized product, it was subjected to HPLC analysis after complete depolymerization of the polymer.

EXPERIMENTAL

Materials

Cellulosic material was isolated from cotton linters as described by Rawat et al.¹¹ Other chemicals (NaOH pellets, MCA, methyl alcohol, isopropyl alcohol, potassium hydroxide, and potassium chlorate) were of laboratory grade.

Methods

Carboxymethylation of α -cellulose

Synthesis of CMC was carried out in two steps: alkalization and etherification of α -cellulose under heterogeneous conditions. Alkalization was conducted at 28°C in which aqueous NaOH (2.5–7.5M) was added to a vigorously stirred slurry of α -cellulose (3 g) in isopropanol (80 mL) over a period of 30 min. Stirring was continued for another 60 min. Then MCA (1.55–2.30 mol/AGU) dissolved in 10 mL isopropanol was added under continuous stirring and the reaction mixture was heated to the desired temperature (35–65°C) and stirred at that temperature for a fixed duration (1.5–4.5 h). After the excess alkali was neutralized with acetic acid, the synthesized CMC samples were filtered, washed with 70% aqueous methanol followed by absolute methanol, and oven-dried at 60°C. Yield: 118–123%. IR (KBr): 1631 cm^{-1} ν_{as} (COO^-); 1417 cm^{-1} ν_{s} (COO^-).

Determination of degree of substitution (DS)

The DS of the prepared CMC samples was determined as reported in the literature.¹²

Determination of apparent viscosity (η)

The apparent viscosity (η) of all the samples was determined, wherever possible, at the shear rate of 3.4 s^{-1} using an RVTD digital viscometer model (Brookfield Engineering Labs, Stoughton, MA). The apparent viscosity of the optimized product was also determined at different shear rates, ranging from 3.4 to 34 s^{-1} . All measurements were made at $25 \pm 1^\circ\text{C}$.

HPLC analysis

HPLC analysis of the optimized product was carried out according to the reported method.¹³ An HPLC system (Jasco, Tokyo, Japan) with refractive index and polarimeter detectors and two Aminex HPX-87H columns (Bio-Rad, Hercules, CA) was used for measurements.

IR spectra

The FTIR spectra were recorded on a Jasco FTIR 5300 using KBr pellets.

RESULTS AND DISCUSSION

Carboxymethylation of cellulosic material, containing 76.5% cellulose and 23.6% xylose isolated from cotton linters, was optimized with respect to DS by varying the process parameters such as concentration of NaOH and MCA, temperature, and duration of reaction. Each of these parameters was varied one at a time, keeping the remaining parameters constant in the reaction (Table I). The apparent viscosity (η) of the products obtained under varied reaction conditions was determined and its dependency on each of the variables was investigated.

Effect of NaOH concentration

The concentration of aqueous NaOH was varied from 2.5 to 7.5M, and results of this effect on DS and η are shown in Figure 1. It was observed that the DS increased with increasing concentration of aqueous

TABLE I
Reaction Parameters for Carboxymethylation

NaOH concentration	2.5–7.5M
MCA, mol/AGU	1.55–2.30
Temperature of carboxymethylation, °C	35–65
Duration of carboxymethylation, h	1.5–4.5

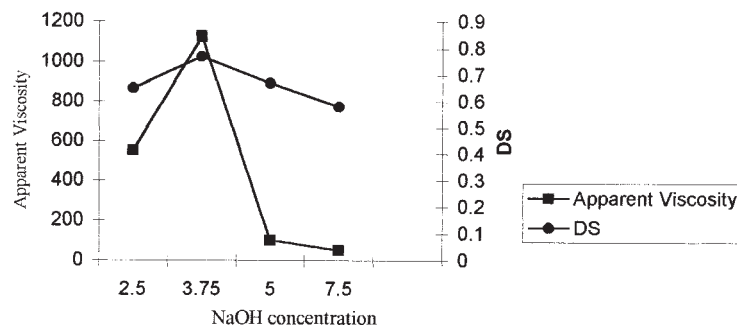


Figure 1 Effect of NaOH concentration on DS and apparent viscosity.

NaOH from 2.5 to 3.75M and decreased substantially thereafter. The increase in DS (0.77) to 3.75M is attributed to the predominance of the reaction [eq. (1) over its competitive reaction eq. (2)] and, above this concentration, the side reaction [eq. (2) between NaOH and MCA] becomes more significant, consuming NaOH to form sodium glycolate, and thus lowering the DS. These findings are in accordance with those reported in the literature.⁶ The value of η also increased from 550 to 1125 cps on increasing the concentration of aqueous NaOH from 2.5 to 3.75M. This increase in apparent viscosity can be attributed to the increase in hydrodynamic volume arising from the introduction of carboxyl groups, as evidenced by the increasing value of DS. However, further increases in the concentration of aqueous NaOH beyond 3.75M led to a sharp decline in the value of η . These results suggest that during carboxymethylation, with further increases in the concentration of NaOH, a significant degradation of cellulose molecules occurs, causing a decline in the molar masses and consequently a decrease in the viscosities.

Effect of MCA concentration

The effect of MCA concentration on DS and η was examined by varying the MCA concentration from 1.55 to 2.30 mol/AGU. The results are plotted in Fig-

ure 2. It was observed that the DS increased from 0.59 to 0.75 with increasing MCA concentration and reached a maximum (0.77) at the molar ratio of MCA to AGU of 2.05. An increase in the concentration of monochloroacetic acid seems to enhance the availability of the acid molecules in the proximity of the cellulose hydroxyls, thus facilitating the carboxymethylation. Further increases in MCA concentration resulted in a slight decrease in DS (0.76). This may probably be attributed to the nonavailability of enough cellulose-alkoxide for reaction with MCA.¹⁴

The η values also increased from 362.5 to 1125 cps with increasing MCA content to 2.05 mol/AGU and decreased to a value of 1000 cps when the MCA content was increased to 2.30 mol/AGU. The increase in η value with increasing DS may be explained by the hydrodynamic volume enhanced by the increased number of carboxyl groups introduced.

Effect of temperature

The effect of temperature of carboxymethylation, varied from 35 to 65°C, on DS and η is shown in Figure 3. A gradual increase in DS (from 0.66 to 0.77) was observed with the increase in temperature from 35 to 55°C, followed by a decrease in DS at 65°C (0.72). The increase in DS to 55°C could be linked with the advantageous effect of temperature on swellability of

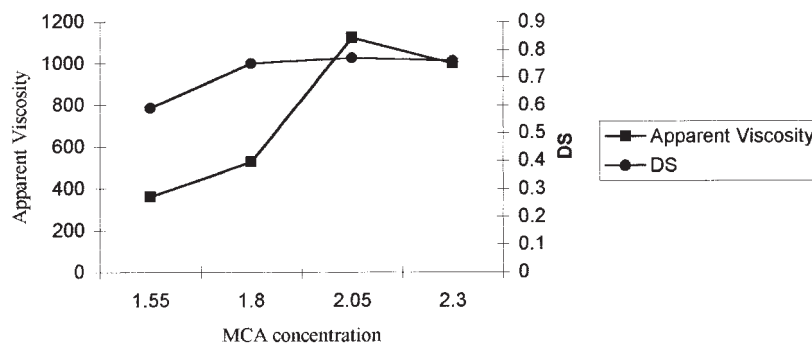


Figure 2 Effect of MCA concentration on DS and apparent viscosity.

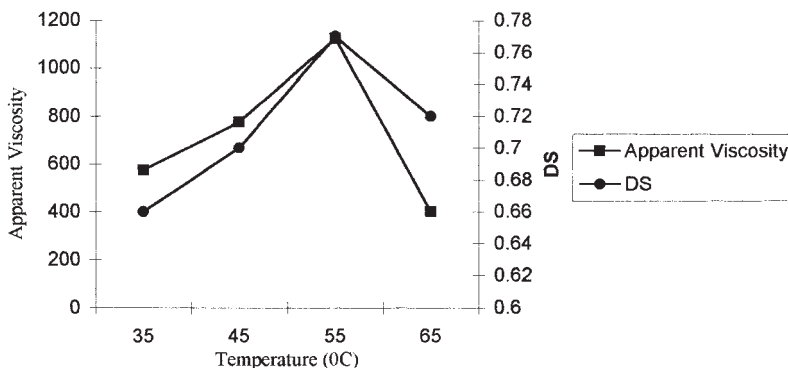


Figure 3 Effect of temperature of carboxymethylation on DS and apparent viscosity.

cellulose fibers as well as diffusion and adsorption of MCA, thereby facilitating the reaction between MCA and the cellulose molecules. The decrease of the DS beyond 55°C could be attributed to the degradation of carboxymethylated cotton cellulose under the influence of atmospheric oxygen. Similar observations have been reported for the carboxymethylation of cellulose.^{6,8} With increasing temperature of carboxymethylation (35–55°C), values of η (575–1125 cps) changed in a parallel fashion, which could be attributed to the hydrodynamic volume enhanced by the increased carboxymethyl contents. A decreased value of η (400 cps) was observed on further increasing the temperature to 65°C. This decrease in apparent viscosity could be interpreted as a consequence of the corresponding decline in the molar mass resulting from the atmospheric oxidative degradation of the CMC.⁸

Effect of time

The effect of duration on DS and η was investigated by performing carboxymethylation for different periods of time (1.5 to 4.5 h). The values of DS and η for the obtained products, as a function of duration of carboxymethylation, are illustrated in Figure 4. On increasing the carboxymethylation time from 1.5 to 3.5 h DS

was found to increase from 0.61 to 0.77. However, a further increase in the time resulted in a lowering of DS (0.65). The increment in DS on increasing the carboxymethylation time is the result of better contact between MCA and the immobile cellulose hydroxyls essential for diffusion; the adsorption processes involved in the reaction and the lowering of DS on prolonging the carboxymethylation time may be attributed to the atmospheric oxidative degradation of CMC. A similar influence of duration of reaction on DS of carboxymethylated flax cellulose was reported by Hebeish et al.⁸

The values of η when carboxymethylation was performed for a period from 2.5 to 3.5 h showed an increase from 600 to 1125 cps and then decreased to 837.5 cps (4.5 h). The η of the sample resulting from the reaction carried out for 1.5 h could not be determined because of its insolubility in water. The increase in apparent viscosity with increasing carboxymethylation time may arise from the increase in hydrodynamic volume because of the introduction of carboxyl groups, as evidenced by the increasing value of DS. The decrease in apparent viscosity could be interpreted as a consequence of the corresponding decline in the molar mass, resulting from the atmospheric oxidative degradation of the carboxymethylated cellulose.

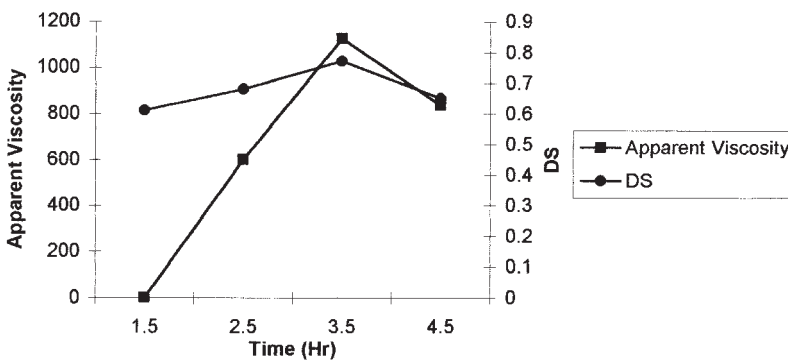


Figure 4 Effect of time of carboxymethylation on DS and apparent viscosity.

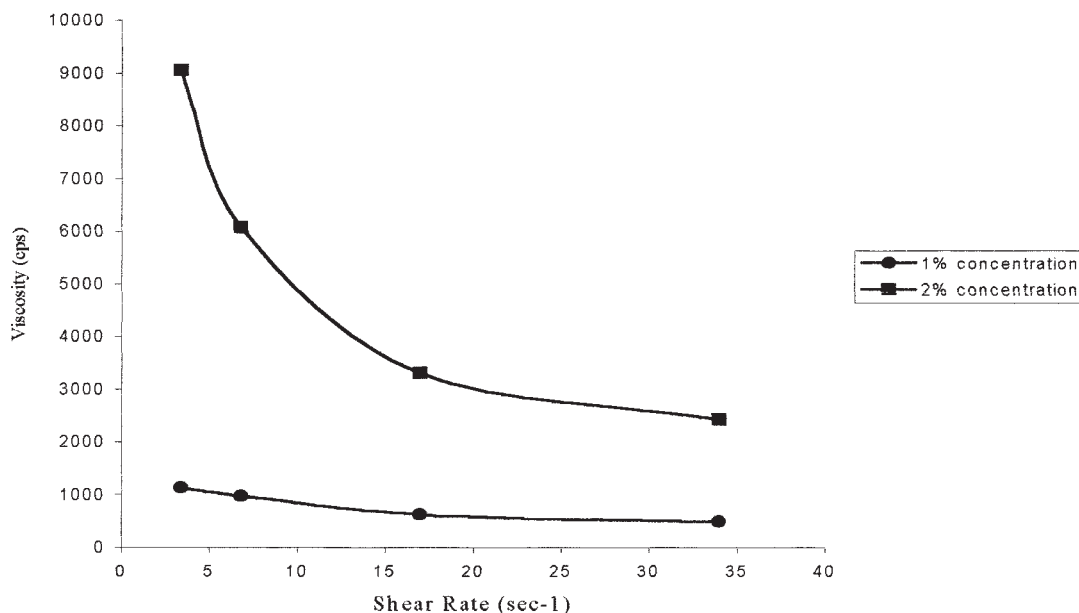


Figure 5 Effect of shear rates on the apparent viscosity of the aqueous solutions (1%, 2%) of the optimized CMC.

Rheological characterization

The wide range of practical applications of CMC uses its ability to modify the properties of an aqueous environment and control the rheology of hydrated systems. In an aqueous solution, it represents a complex rheological system as it forms aggregates and associations, and thus higher-level structures.¹⁵ Preparation and use of its solutions involve a wide range of shearing conditions. CMC is a common polymer used for turbulent flow experiments¹⁶ as well as for studying the effects of shear-dependent flow properties and viscoelasticity on the hydrodynamics in mixing operations, performed in a laminar flow regime.¹⁷ Rheological properties of CMC are highly influenced by the polymer concentration, temperature, salt content, molecular structure, and the presence of surfactants.^{1,18,19} Thus it is important to understand the rheological properties of CMC solutions.

Rheological studies of the optimized carboxymethylated cellulose, reported herein, were carried out by measuring the apparent viscosity of its 1 and 2% aqueous solutions. A plot of η values of the aqueous solutions (1 and 2%) of the optimized CMC versus shear rates (Fig. 5) shows that values of η of both solutions of the optimized product are dependent on shear rate and decrease with increasing shear rate. Thus both solutions of the optimized product exhibit non-Newtonian pseudoplastic behavior. The rate of reduction in the apparent viscosity of these solutions with increasing shear rate is different. The rate of decrease in viscosity of the 2% solution is greater than that of the 1% solution at each increased shear rate. When the shear rate was increased from 3.4 to 6.8 s⁻¹, the percentage reduction in viscosity of the 1% solution was

22.2% and 32.9% for the 2% solution. In the case of the 2% solution, the viscosity was decreased by 63.5 and 73.2% under the influence of shear rate increasing by five- and tenfold of the original shear rate (i.e., 3.4 s⁻¹), respectively, whereas the viscosity of the 1% solution was decreased by 45.3 and 57.5% on increasing the shear rate by the same amount. The difference in the rate of lowering of viscosity of both solutions could be attributed to the following.

In the 2% solution, polymer-polymer interactions (entanglements) are greater in number than that in the 1% solution and, at higher polymer concentration, these entanglements become the main factor influencing the viscosity of the solution.¹ At higher concentration Na-CMC chains overlap and undergo a coiling process, thereby causing the formation of a network structure in the concentrated regime. Under the influence of increased shear rate coil expansion is increased, thus enhancing the orientation of the molecules in the direction of flow and, consequently, a steep decline in the viscosity occurs.

HPLC analysis of the optimized product

HPLC analysis of the optimized product was carried out for the determination of the repeating unit for which the polymer chains were completely depolymerized by the treatment of the polymer with HClO₄. The HPL chromatogram showed the signals of di-O-CMG, mono-O-CMG, and unsubstituted glucose with their areas of 8.447, 32.427, and 44.418%, respectively. In addition, signals were also identified for xylose (5.308%), mono-O-CMX (8.450%), and di-O-CMX

(0.949%). From these data mole fractions were determined and the DS_{CMC} and DS_{CMX} values were calculated to be 0.58 and 0.70, respectively.

However, the DS value determined by HPLC does not agree with that determined by the conventional acid–base titration method and the value of the latter is 16.8% higher than the former. This can probably be explained by the systematic errors encountered by the distorting influence of purity and moisture content during the titration.

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References

1. Kulicke, W.-M.; Kull, A. N.; Kull, W.; Thielking, H. *Polymer* 1996, 37, 2723.
2. Mark, H. F.; Gaylord, N. G.; Bikales, N. M. *Encyclopedia of Polymer Science and Technology*, Vol. 3; Wiley: New York, 1965; p 520.
3. Kamide, K.; Okajima, K.; Kowsaka, K.; Matsui, T.; Nomura, S.; Hikichi, K. *Polym J* 1985, 17, 909.
4. Reuben, J.; Conner, H. T. *Carbohydr Res* 1983, 115, 1.
5. Baar, A.; Kulicke, W.-M. *Macromol Cell Phys* 1994, 195, 1483.
6. Barai, B. K.; Singhal, R. S.; Kulkarni, P. R. *Carbohydr Polym* 1997, 32, 229.
7. Youssef, M. A. M.; Nada, A. M. A.; Ibrahim, A. A. *Cellulose Chem Technol* 1989, 23, 505.
8. Hebeish, A.; Abou-Zied, N. Y.; Waly, A.; Higazy, A. *Cellulose Chem Technol* 1984, 22, 591.
9. Tijsen, C. J.; Kolk, H. J.; Stamhuis, E. J.; Beenackers, A. A. *Carbohydr Polym* 2001, 45, 219.
10. Buchada, A. J.; Genoud, T.; Roulin, S.; Matter, K. S. *Acta Bot Neeri* 1993, 42, 213.
11. Rawat, R.; Naithani, S.; Singh, S. V.; Soni, P. L. In: *Trends in Carbohydrate Chemistry*, Vol. 7, Soni, P. L., Ed.; Surya International Publications: Dehra Dun, India, 2001; p 131.
12. Green, J. W. In: *Methods in Carbohydrate Chemistry*, Vol. III, Whistler, R. L., Ed.; Academic Press: New York, 1963; p 322.
13. Heinze, T.; Pfeiffere, K. *Angew Makromol Chem* 1999, 226, 37.
14. Sharma, B. R.; Kumar, V.; Sharma, P.; Soni, P. L. *J Appl Polym Sci* 2003, 89, 3216.
15. Kulicke, W.-M.; Reinhardt, U.; Fuller, G. G.; Arendt, O. *Rheol Acta* 1999, 38, 26.
16. Escudier, M. P.; Gouldson, I. W.; Pereira, A. S.; Pinho, F. T.; Poole, R. J. *J Non-Newtonian Fluid Mech* 2001, 97, 99.
17. Florjancic, U.; Zupancic, A.; Zumer, M. *Chem Biochem Eng Q* 2002, 16, 105.
18. Ghannam, M. T.; Esmail, M. N. *J Appl Polym Sci* 1997, 64, 289.
19. Edali, M.; Esmail, M. N.; Vatistas, G. H. *J Appl Polym Sci* 2001, 79, 1787.