Experimental Study on Carboxymethylation of Cellulose Extracted from *Posidonia oceanica*

Chadlia Aguir, M. F. M'Henni

Laboratoire de Chimie Industrielle Appliquée et Environnement, Département de Chimie, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia

ABSTRACT: The production of carboxymethylcellulose (CMC) from bleached cellulose pulps obtained from *Posidonia oceanica* was explored. The optimal reaction conditions were studied for the carboxymethylation of cellulose in organic liquids. The carboxymethylation reaction was carried out with NaOH and monochloroacetic acid (MAC) as the reagent. Different alcohols were compared in terms of the degree of substitution (DS). The highest DS was obtained with *n*-butanol. For this alcohol, the effects of the temperature, alkali concentration, and MAC concentration were studied. The reaction was also carried out in three consecutive steps. The resulting CMC had a DS of about 2.75. The functionalization of cellulose was checked using FTIR spectroscopy and ^{13}C-NMR. The X-ray analysis showed that the crystalline structure of cellulose decreased when the DS increased and the structure was totally amorphous in high DS material. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1808–1816, 2006

Key words: polymer functionalization; carboxymethylation; cellulose; *Posidonia oceanica*; water-soluble polymers
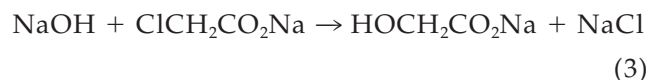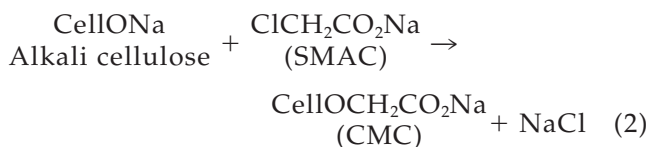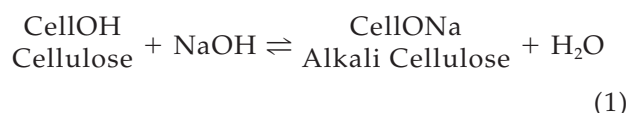
INTRODUCTION

Carboxymethylcellulose (CMC) is one of the most important commercial cellulose ethers. This water-soluble polymer, which was introduced in 1920,[1] is an anionic polyelectrolyte available in several grades and in different types.[2]

Sodium CMC is also labeled as CMC, and the food grade is usually known as cellulose gum. CMC is mainly used as a sizing and printing agent in the textile industry, in detergent,[3] and in the paper industry.[4] It has important effects as a protecting colloid and as an adhesive.[5] CMC is nontoxic and it has an increasing number of applications in the pharmaceutical,[6] medical, and food industries.[7] Most of the CMC uses are based on its rheological properties.[8] The ability of CMC as a thickener[9] depends not only on its degree of substitution (DS) and on its molecular weight, but also on the relative stiffness of the cellulosic backbone.[5] The use of different raw materials for the preparation of cellulose derivatives such as nonwood pulps may meet the specified quality needed for each application.[10] From a technical point of view, nonwood species offer numerous cellulose qualities and can be used in the development of new cellulose pulp derivatives.[11] Annual fiber crops, agricultural residues, and wild plants[12] are used as nonwood species to produce cellulosic pulps. In the present work, we used the plant *Posidonia oceanica* for the same goal. Significant quantities of *P. oceanica* fragments (Fig. 1) are accumulated every summer on the coasts, and the beaches must be cleaned. The valorization of this available biomass can be the solution to this problem.

CMC is produced by etherification of hydroxyl groups with monochloroacetic acid (MAC) or sodium monochloroacetate in the presence of sodium hydroxide:

$$\underset{\text{Cellulose}}{\text{CellOH}} + \text{NaOH} \rightleftharpoons \underset{\text{Alkali Cellulose}}{\text{CellONa}} + \text{H}_2\text{O} \tag{1}$$

$$\underset{\text{Alkali cellulose}}{\text{CellONa}} + \underset{\text{(SMAC)}}{\text{ClCH}_2\text{CO}_2\text{Na}} \rightarrow$$

$$\underset{\text{(CMC)}}{\text{CellOCH}_2\text{CO}_2\text{Na}} + \text{NaCl} \tag{2}$$

$$\text{NaOH} + \text{ClCH}_2\text{CO}_2\text{Na} \rightarrow \text{HOCH}_2\text{CO}_2\text{Na} + \text{NaCl} \tag{3}$$

The amount of carboxymethyl groups fixed on cellulose is determined by the DS, which is defined as the average number of substituents per anhydroglucose unit (AGU). The AGU represents the monomer unit of cellulose (Fig. 2). Each AGU contains three hydroxyl groups, so the theoretical DS value varies between 0 and 3.

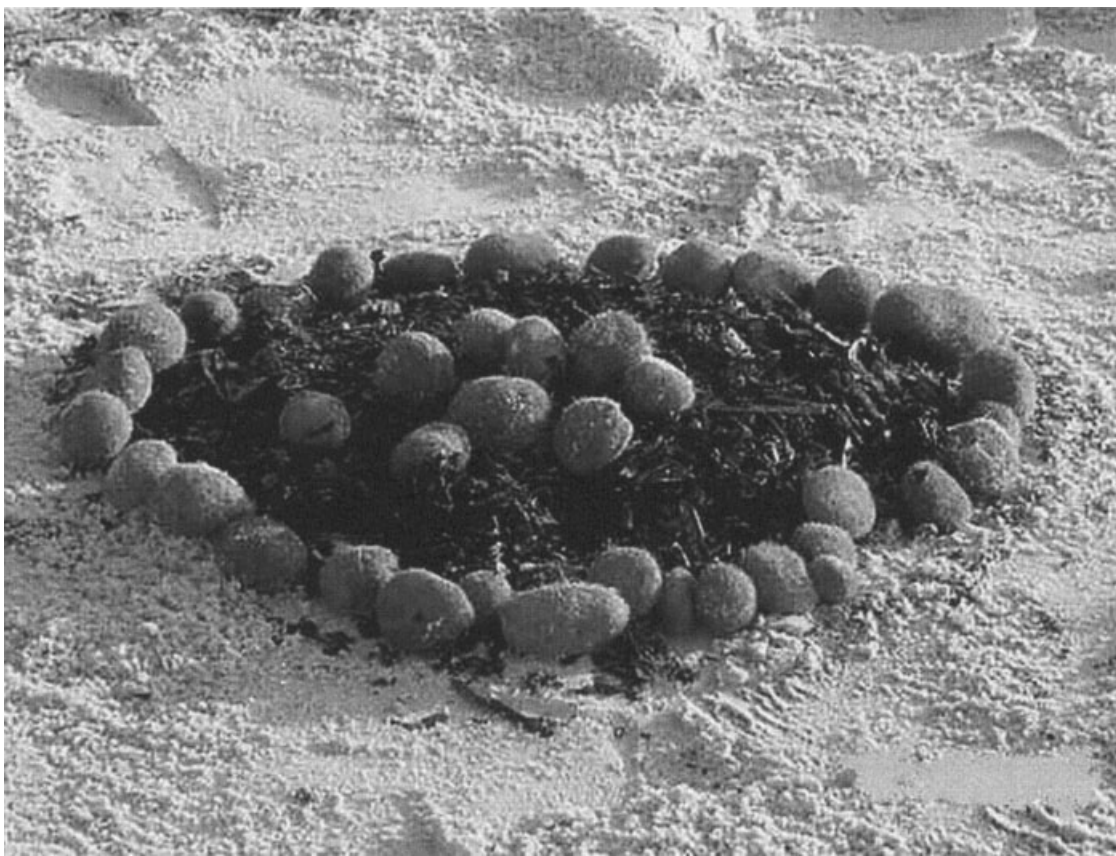*Correspondence to:* C. Aguir (aguirc@yahoo.ca).

Figure 1 The *Posidonia oceanica* plant.

Numerous studies discussed the influence of the reaction conditions, for example, the reagent concentration, reaction medium, and temperature, on the carboxymethylation of different kinds of cellulose. The influence of the reagent concentration on an organic medium was investigated by several groups.[13–19] In all cases, the higher the MAC concentration was, the higher the DS of the product up to a constant value. An increasing NaOH concentration gives an optimum DS value from which an increase in the concentration of NaOH leads to a decrease in the DS.

Various organic liquids have been used for the carboxymethylation of cellulose such as DMSO,[20] isopropyl alcohol,[21,22] propyl alcohol,[23] butyl alcohol,[23] ethyl alcohol,[13,23,24] and acetone.[25]
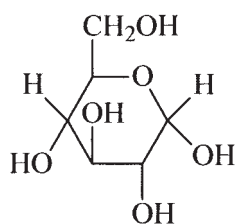

Figure 2 The anhydroglucose unit (AGU) structure.

The first major aim of this work is to investigate the use of bleached nonwood cellulose pulps from *P. oceanica* for CMC production. The second aim is to determine the influence of certain parameters to routinely produce CMC with an important DS from the raw material. In order to achieve this, a systematic experimental plan, using several organic liquids and various reaction conditions, has been carried out.

EXPERIMENTAL

Extraction of cellulose pulps from *P. oceanica*

Pulping experiments were carried out using biomass of *P. oceanica* harvested on the coasts of Tunisia. Five hundred grams of the cleaned and crushed raw material were delignified in two stages. First, impregnation with an alkali solution was performed at room temperature overnight, using charges of 10% (w/v) NaOH. Second, the sample was bleached after washing with an equivolumic mixture of sodium hypochlorite solution and buffer solution at pH 4.7. The bleaching bath was changed every 2 h. This treatment was repeated until complete bleaching of the sample. The pulp was then rinsed and lyophilized.

TABLE I
Values of Various Parameters to Calculate degree of polymerization (DP_V) of Cellulose from *Posidonia oceanica*

t_0 (s)	t (s)	η_{sp}	C^* (g/L)	$[\eta]$	DP_V
140	141.48	0.0717	0.1	6	80

Extracted cellulose characterization

The degree of polymerization (DP_V) of cellulose is determined by measuring the intrinsic viscosity in cupriethylene–diamine solution in a capillary viscometer using the standard NFT 12-005 methods.

Carboxymethylation reaction of extracted cellulose

Cellulose was suspended in organic liquids under magnetic stirring at room temperature. During the experiments, continued N_2 flushing was performed to prevent any reaction of NaOH with CO_2 in the air. A reflux cooler was used to avoid the loss of organic liquid. After 1 h the desired amount of NaOH was taken from a 40% aqueous NaOH solution and added to the reaction mixture. The flask was heated and left overnight under stirring to assure equilibrium between the cellulose and the sodium hydroxide. MAC was then added to the mixture. The reaction was stopped by the addition of acetic acid. CMC was recovered by filtration and washed several times with a large amount of an 80/20 (v/v) ethanol/water mixture. Finally, the product was washed with pure methanol and oven dried at 50°C for 24 h.

Carboxymethylation characterization

Determination of DS

In this work, a dosage method was used to determine the DS. This technique was described in the literature for CMC from wood.[22] The sample was first mineralized at 600°C for 4 h and then cooled to room temperature. The ash that was obtained, which contained Na_2O, was then dissolved in hot distilled water (80°C). Next, the solution was titrated with $0.1N$ ($0.05M$) H_2SO_4 in the presence of methyl orange. The reddish solution thus obtained was heated to remove dissolved CO_2 until it became yellow. A second titration was performed with H_2SO_4. The total consumption volume of the acid (V_{tot}) was in milliliters.

If the weight of the initial sample is denoted by m_{CMC} (g), we can define a ratio B as the following:[25]

$$B = 0.1 V / m_{CMC} \qquad (4)$$

where 0.1 is the normality of the solution. The DS was obtained from the formula[22,32]

$$DS = \frac{0.162B}{1 - 0.008B} \qquad (5)$$

where 0.162 is the molar mass of the glucose units (kg/mol) and 0.08 is the molar mass (kg/mol) of the group ($CHCOO^-Na^+$) substituted on the cellulose.

FTIR analysis

The FTIR analysis spectra were obtained using a Bio-Rad spectrometer. The spectral resolution was 4 cm^{-1} and the scanning range was from 500 to 4000 cm^{-1}. The spectra of the samples were obtained in solid suspension with anhydrous KBr.
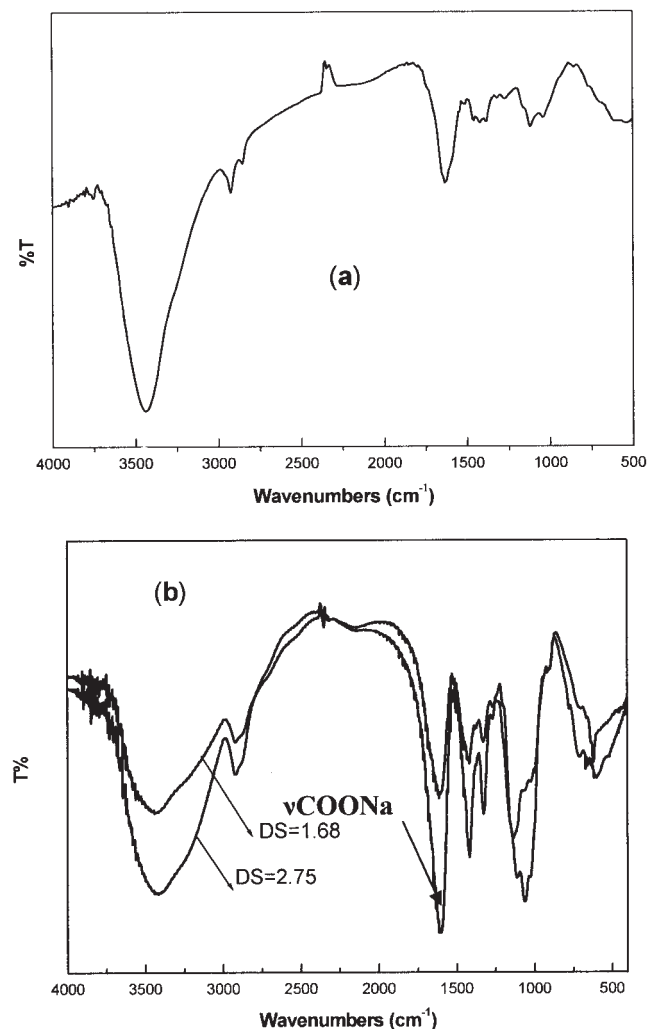

Figure 3 FTIR spectra of (a) an untreated cellulose and (b) a CMC sample prepared in *n*-butanol with degrees of substitution of 1.68 and 2.75.
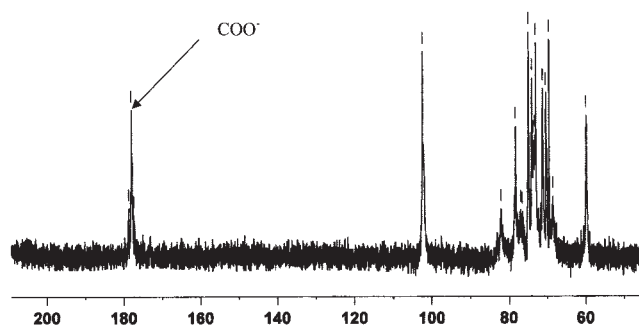
Figure 4 The ^{13}C-NMR spectrum of CMC with a degree of substitution of 0.7.

^{13}C-NMR analysis

The ^{13}C-NMR spectra with proton decoupling were recorded at 25°C in D$_2$O on a Bruker DMX-300FT-NMR spectrometer at a frequency of 75.47 MHz and with 12,000 scans.

X-ray analysis

The X-ray diffractograms of cellulose and CMC were recorded on a Rontgen Universal HZG 4/A diffractometer. The test conditions were Cu Kα, radiation with a 35-kV tube voltage and a 25-mA tube current.

RESULTS AND DISCUSSION

Materials characterization

Extracted cellulose characterization

The specific viscosity (η_{sp}) was calculated using the following formula:

$$\eta_{sp} = \frac{t_0 - t}{t_0} \tag{6}$$

where t is the flow time of the dilute polymer solution and t_0 is the flow time of the solvent. The intrinsic viscosity (η) was determined using the standard NFT 12-005 method.

The DP$_V$ is related to the η by

$$\eta = K(\overline{DP_V})^\alpha \tag{7}$$

For cupriethylene–diamine as a solvent, the constants are $K = 7.5 \times 10^{-3}$ and $\alpha = 1$. The parameters evaluated to calculate the DP$_V$ are illustrated in Table I.

CMC characterization

FTIR analysis. Figure 3(a) shows the IR spectra of the starting cellulose, and Figure 3(b) illustrates the IR
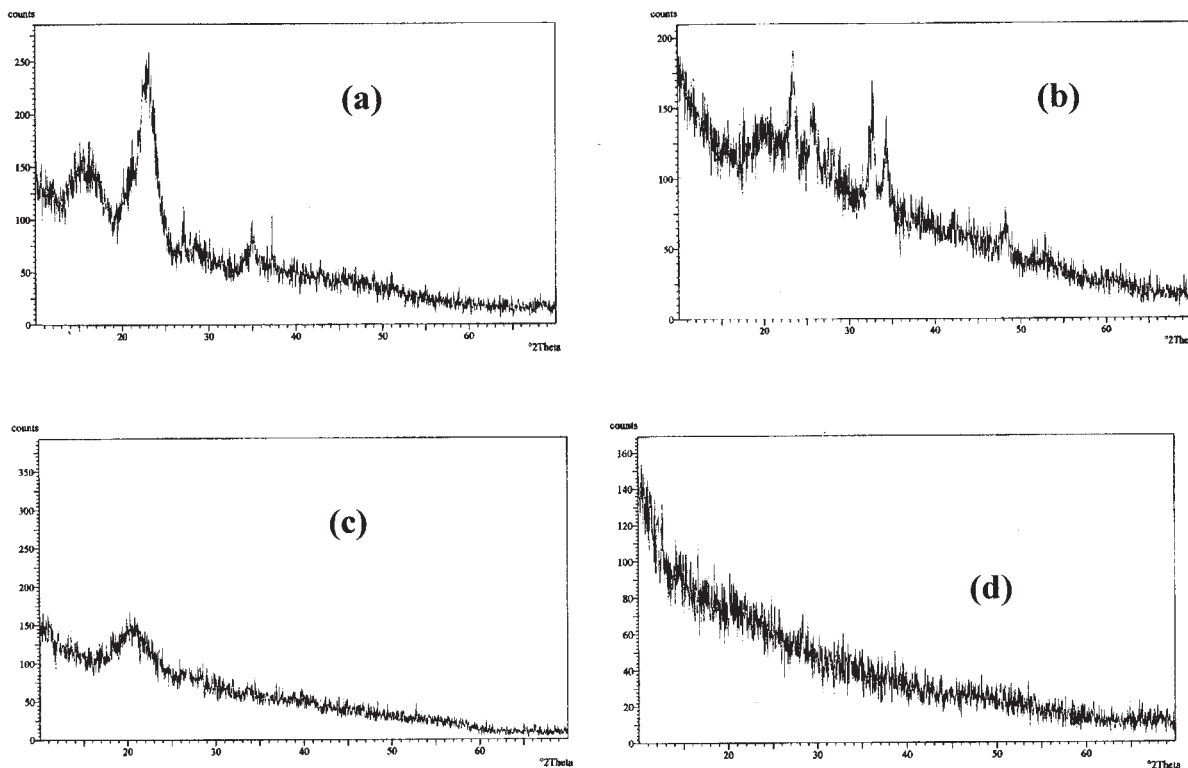

Figure 5 X-ray diffractograms of (a) cellulose and (b–d) carboxymethylcellulose with degrees of substitution of (b) 0.7, (c) 1.68, and (d) 2.75.

TABLE II
Standard Reaction Conditions

Amount of org. liq. (mL)	Temp. (°C)	Mass of cellulose (g)	Cellulose/NaOH (mol/mol)	Cellulose/MAC (w/w)	DS_{th} (mol/mol)
60	45	3	1/3	1/0.583	1

DS_{th}, theoretical degree of substitution, is the value obtained for complete conversion of the limiting reactant and depending on the ratio of cellulose/MAC, where $DS_{th} = n_{A'0}/n_{AGU,0}$, $n_{A'0}$ is the initial amount of moles of MAC, and $n_{AGU,0}$ represents the initial number pattern of anhydroglucose units.

spectra of CMC with two DS values (1.68 and 2.75). The carboxylate anion COO^- absorption band appears at 1610 cm^{-1}, confirming the formation of carboxylic acid salt. The absorption bands at 1318 and 1420 cm^{-1} are attributed to the C—O stretching in CO_2H and binding in —CH_2, respectively.

^{13}C-NMR analysis. Figure 4 shows a representative ^{13}C-NMR spectrum of CMC with a DS value of 0.7. This spectrum proves the molecular structure of CMC. Indeed, there are typical signals of the modified AGU in the range of 60–105 ppm, as mentioned by Capitani et al.[27] and Hunze et al.[28] The signals at 178 ppm are assigned to the carbon of the carboxyl group (sodium salt).[28]

X-ray analysis. Three typical peaks of natural cellulose from *P. oceanica* at diffraction angles of 16.1°, 22.4°, and 34° appear in Figure 5(a). This confirms that the cellulose form is cell-I.[15,29] The highest intensity peak is caused by the cellulose crystalline fraction, whereas the amorphous portion causes the background noise line.[22] Figure 5 shows that the peaks corresponding to the crystalline form disappear progressively while the DS increases. The sample corresponding to a DS of 2.75 is totally amorphous. These results are similar to those in the literature.[29,30]

Influence of operating conditions

The effect of the reaction conditions on the carboxymethylation was studied by varying the parameters one at a time and keeping the other parameters constant at the standard conditions given in Table II.

Influence of organic media

Figure 6 shows the evolution of the DS as a function of the reaction time in different organic liquids, which are ethyl alcohol, isopropyl alcohol, *n*-butanol, 2-butanol, and isobutyl alcohol.

All the curves have a similar shape and for a reaction time longer than 6 h the reaction rate decreases considerably and the DS goes toward a limit value, as Figure 6 indicates. A decreasing order of the efficiency of the organic media was established as follows: *n*-butanol, 2-butanol, isobutyl alcohol, isopropyl alcohol,

and ethyl alcohol. After a 10-h reaction time the DS values are 0.86 for *n*-butanol, 0.75 for 2-butanol, 0.71 for isobutyl alcohol, 0.6 for isopropyl alcohol, and 0.5 for ethyl alcohol. Thus, under these reaction conditions (Table II), *n*-butanol has the highest DS. As a result, in the following it is used as the adequate organic medium.

The role of the solvent in the carboxymethylation reaction is to provide accessibility of the etherifying reagent to the reaction center of the cellulose chain.[19] These differences in the DS values can probably be explained by taking into consideration the polarities and stereochemistries of these solvents. The polarity index values of *n*-butanol, 2-butanol, isobutyl alcohol, isopropyl alcohol, and ethyl alcohol are 3.9, 4, 3.4, 4.3, and 5.9, respectively. This implies that the lower the polarity of the solvent is, the higher the DS, except for isobutyl alcohol. These results confirm those reported in the literature.[18,19] Isobutyl alcohol has two bulky methyl groups that may provide steric hindrance to the reacting groups. This probably explains the low DS obtained with isobutyl alcohol as a solvent during the carboxymethylation process, in spite of its relatively low polarity.
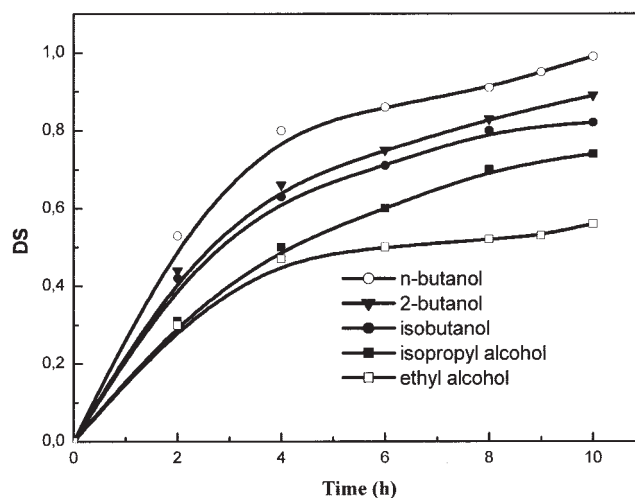

Figure 6 The degree of substitution of carboxymethylcellulose in various alcohols as a function of the reaction time in different organic liquids: ethyl alcohol, isopropyl alcohol, *n*-butanol, 2-butanol, and isobutyl alcohol.
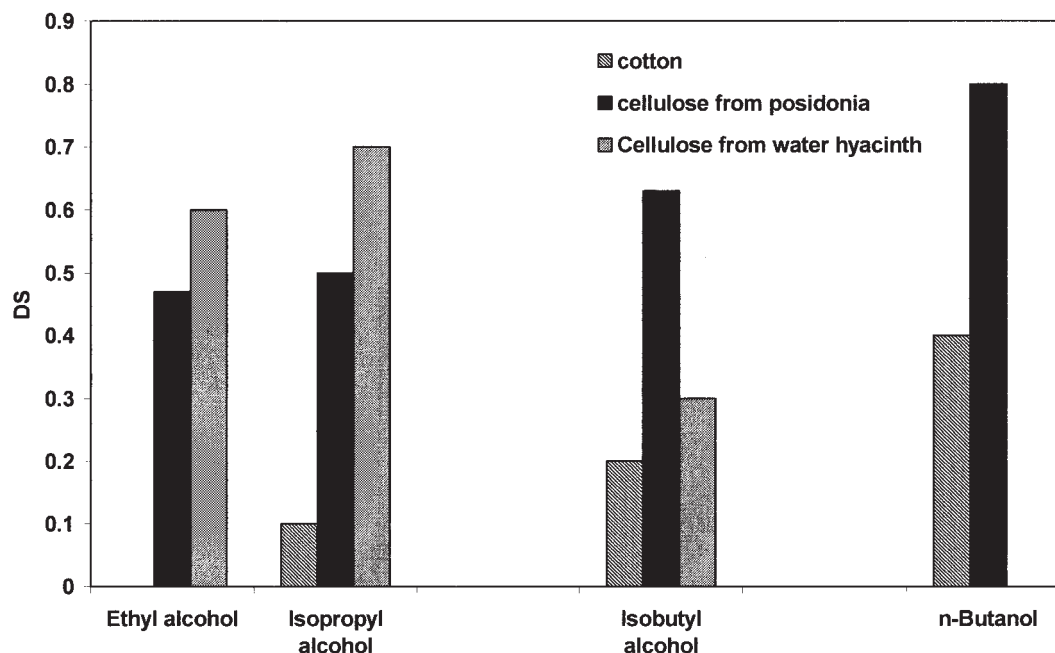
Figure 7 The effect of various organic liquids on the degree of substitution in carboxymethylcellulose from different kinds of cellulose.

For the five different organic media, the performance obtained in this work was compared (Fig. 7) to the one obtained in the carboxymethylation of different kinds of cellulose reported by others. Figure 7 shows that the highest DS (0.8) is obtained for *Posidonia* cellulose in *n*-butanol. With isobutyl alcohol, *Posidonia* cellulose gives the highest DS (0.63). In the case of isopropyl alcohol and ethyl alcohol, *Posidonia* cellulose gives the lowest DS. The significant difference between the results is most likel caused by the different reaction conditions and the experimental methods used. Table III gives an overview of the various reactions conditions that were applied.

Influence of temperature

The influence of the reaction temperature on the DS is shown in Figure 8. As expected, the highest reaction rate can be seen with the highest temperature. An interesting result is that after a 10-h reaction time all curves converge to the same DS value, which is about 0.9. In this last reaction condition, the DS appeared to be independent of the reaction temperature.

The effect of the temperature on carboxymethylation was studied for different kinds of cellulose[18,19,22] and similar conclusions were reported. The highest temperature used in the carboxymethylation of cellulose from water hyacinth[18] was 75°C and the one used for carboxymethylation of cotton[17] was 55°C. This indicates that the optimal reaction temperature depends on the type of cellulose and the reaction conditions.

Influence of sodium hydroxide concentration

Using *n*-butanol as the solvent medium, the effect of the alkali concentration (for the carboxymethylation of cellulose) on the DS was studied. Figure 9 shows the evolution of the DS as a function of time for the three carboxymethylation reactions with cellulose/NaOH (mol/mol) ratios of 1/1.5, 1/3, and 1/4.5. For every reaction time, the highest DS was obtained for a cellulose/NaOH ratio equal to 1/3. The DS behavior as a

TABLE III
Overview of Experimental Conditions Used for Comparison of DS Given in Figure 6

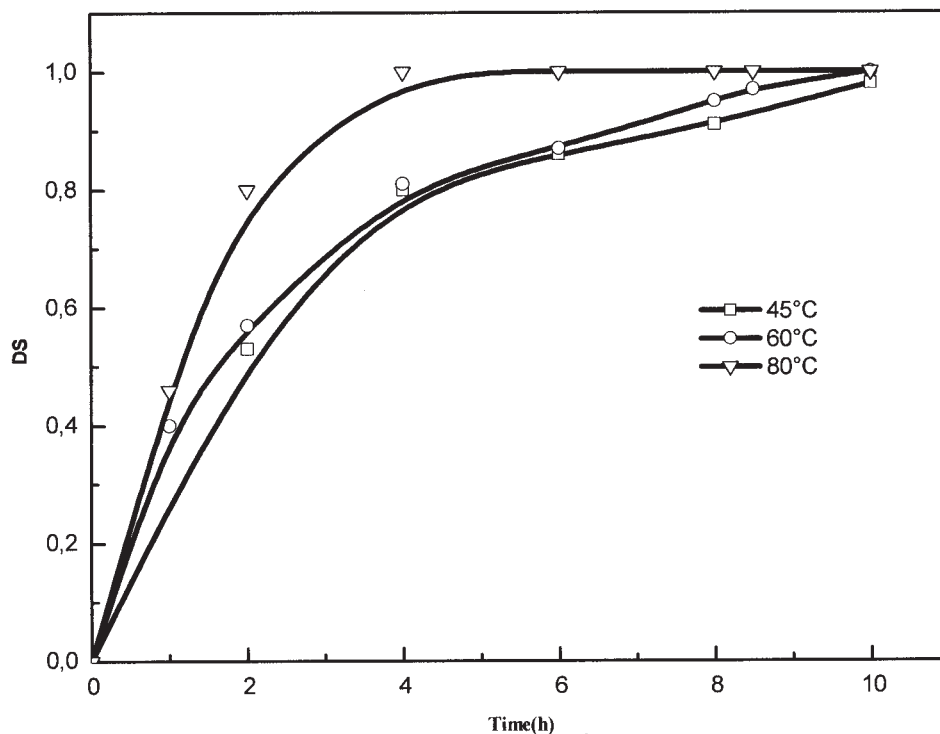| Source	Origin of cellulose	T (°C)	NaOH (%)	Cellulose/MAC	t (min)
Zanata et al.[17]	Cotton	55	40	1/0.60	120
Barai et al.[18]	Water hyacinth	75	10	1/0.92	360
This work	*Posidonia*	45	40	1/0.59	240

Figure 8 The effect of the temperature on the carboxymethylation rate of *Posidonia oceanica* cellulose as a function of time in *n*-butanol.

function of the NaOH concentration can explained by the existence of two competitive reactions. The first reaction, which is the Williamson's ether synthesis,[28]

involves two steps. The first step is an equilibrium reaction between NaOH and the hydroxyl groups of cellulose [eq. (1)], and the second step is the fixation of
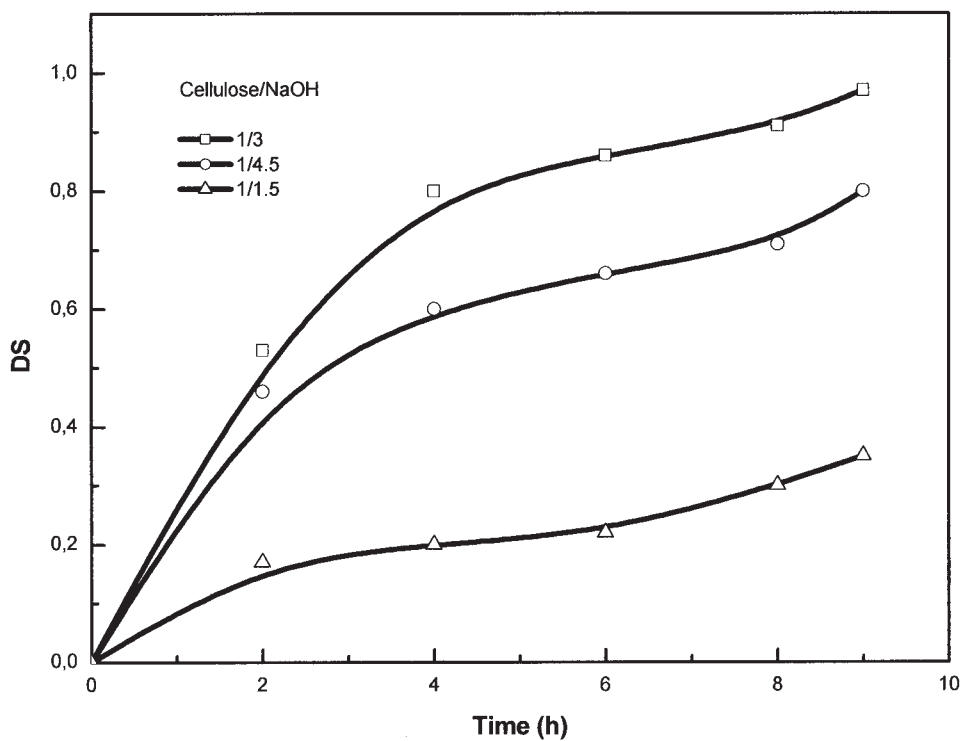

Figure 9 The effect of the NaOH concentration on the carboxymethylation rate of *Posidonia oceanica* cellulose with the operating conditions in Table II.
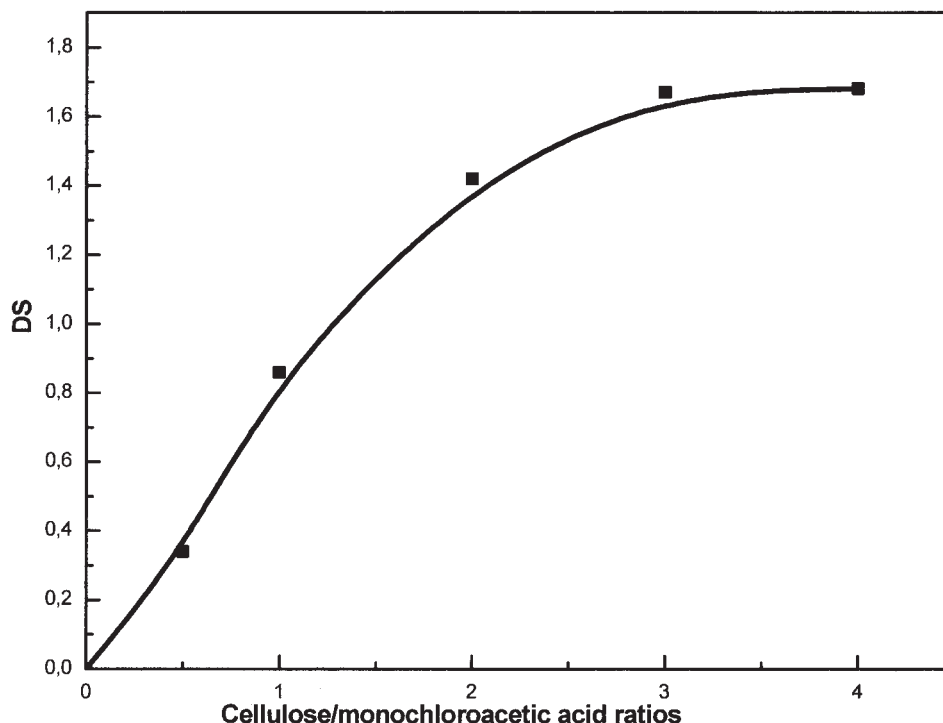
Figure 10 The effect of the chloroacetic acid concentration on the degree of substitution in the carboxymethylation of cellulose from *Posidonia oceanica*.

the carboxymethyl group by the substitution on the sodium monochloroacetate [eq. (2)]. The second reaction [eq. (3)] is the substitution of Cl^- by OH^- in MAC to form sodium glycolate.[18]

The first reaction seems to prevail above the second one up to a sodium hydroxide ratio of 1/3. When this ratio increases, the undesired side reaction [eq. (3)] predominates with the formation of large amounts of glycolate, which limits the DS.

Influence of MAC concentration

With *n*-butanol as the organic medium and a 3/1 NaOH/cellulose ratio, Figure 10 demonstrates that, when the concentration of MAC increases, the DS value increases as well. The rate of this increase of the DS becomes lower and lower when the MAC/cellulose ratio increases. When the MAC/cellulose ratio becomes equal to or greater than 3, the DS then reaches a constant value of about 1.68. Similar results have been reported in the carboxymethylation of sugar beet pulp cellulose.[19]

Influence of repetitive carboxymethylation

To improve the obtained DS in our case (maximum of about 1.68), the procedure described by Mahmud[24] and Claudia et al.,[5] which is called stepwise modification, is applied. The procedure consists of repeating the carboxymethylation reaction several times, and each reaction is done on the product of the precedent (Fig. 11). The reaction conditions and the DS obtained in our work in the three reaction steps are illustrated in Table IV. As a conclusion, in terms of the DS, it is advantageous to perform the carboxymethylation in a stepwise manner. According to these conditions, the DS increases from 0.53 to 2.75 in the third carboxymethylation.

CONCLUSION

This work shows that the *P. oceanica* collected on the Tunisian coast can be used as a raw material for the production of cellulose and its derivatives. The cellulose extracted from *P. oceanica* was used to produce

Figure 11 A schema of the stepwise modification.

TABLE IV
Experimental Conditions Used in Three Reaction Steps and Performance of Carboxymethylation
of Cellulose from *Posidonia*

Carboxymethylation	Cellulose/NaOH (mol/mol)	Cellulose/MAC (w/w)	T (°C)	t (h)	ΔDS	DS_{th}	DS
First	1/3	1/0.583	45	2	1	1	0.53
Second	1/3	1/0.874	45	7	2.03	1.5	1.8
Third	1/3	1/0.757	45	24	3.1	1.3	2.75

DS_{th}, the degree of substitution in the step, which takes into account the amount of MAC in each reaction; DS, the global experimental degree of substitution; ΔDS, the sum of the DS values obtained in the previous step and the DS_{th}.

CMC after a reaction with MAC in a basic medium. The performance of this reaction was evaluated by the DS. The adequate solvent medium for the carboxymethylation reaction was *n*-butanol at an optimum temperature of about 80°C. The best concentration ratio of cellulose/NaOH and cellulose/MAC was 1/3. We established an experimental method allowing the improvement of the DS value reported in the literature and related to carboxymethylation of cellulose extracted from other raw materials such as cotton, wood, and water hyacinth.

References

1. Balser, K.; Hoppe, L.; Eicher, T.; Wendel, M.; Astheimer, A.-J. Ullmann's Encyclyclopedia of Industrial Chemistry, 5th ed.; 1986; Vol. A5, p 461.
2. Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Meufes, G. Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1985; Vol. 3, p 226.
3. Batdorf, J.; Soap, B. Chem Spec 1962, 38, 58.
4. Barber, E. J. TAPPI 1961, 44, 179.
5. Claudia, B.; Marguerite, R.; Xavier, F. Cellulose 2002, 9, 319.
6. Allen, B. F. Maryland Pharm 1961, 37, 612.
7. Brown, C. J.; Houghton, A. A. J Soc Chem Ind (Lond) 1941, 60, 254.
8. Nicholson, M. D.; Merrit, F. M. T. In Cellulose Chemistry—Its Application; Nevell, Th.; Zeronian, P.; Haig, S., Eds.; Horwood: Chichester, 1998; p 363.
9. Zhang, L.-M. Carbohydr Polym 2001, 45, 1.
10. Claudia, B.; Reguant, J.; Xavier, F.; Montané, D. J Wood Chem Technol 2000, 20, 85.
11. Maddern, K. N.; French, J. Appita 1995, 48, 191.
12. Gupta, M. K.; Jain, S. C. Ind Pulp Paper 1966, 20, 433.
13. Khundkar, M. H.; Rahman, M. K. Pakis J Sci Ind Res 1967, 10, 17.
14. Lowwell, J.; Nevins, M. J.; Reid, I.; Walter, K. L. (to N.L. Industries Inc.), U.S. Pat. 4,401,813 (1983).
15. Olaru, N.; Olaru, L. Macromol Chem Phys 2001, 202, 207.
16. Thomas, H.; Katy, P. Angew Makromol Chim 1999, 266, 37.
17. Zenata, N.; El-Sakhawy, M.; Samir, K. Int J Polym Mater 2001, 50, 163.
18. Barai, B. K.; Singhal, R. S.; Kulkarni, P. R. Carbohydr Polym 1997, 32, 229.
19. Togɾul, H.; Arslan, N. Carbohydr Polym 2003, 54, 73.
20. Wata Susumu, I.; Narui, T.; Takahashi, K.; Shoji, S. Carbohydr Res 1985, 145, 160.
21. Zhang, J.; Li, D.; Zhang, X.; Shi, Y. J Appl Polym Sci 1993, 49, 741.
22. Salmi, T.; Valtakari, D.; Paaterot, E. Ind Eng Chem Res 1994, 33, 1454.
23. Khundkar, M. H.; Bhattacharjee, A. K.; Mosihuzzaman, M. Pakis J Sci Ind Res 1965, 8, 89.
24. Mahamud, M. U. Acta Polym 1987, 38, 172.
25. Olaru, N.; Olaru, L.; Stoleriu, A.; Tîmpu, D. J Appl Polym Sci 1998, 67, 481.
26. Wilson, K. Sven Papperstidn 1960, 63, 714.
27. Capitani, D.; Porro, F.; Segre, A. L. Carbohydr Polym 2000, 42, 283.
28. Hunze, J.; Ebert, A.; Fink, H. P. Cellulose Chem Technol 2000, 34, 21.
29. Zhang, J.; Li, D.; Zhang, X.; Shi, Y.; J Appl Polym Sci 1993, 49, 741.
30. Lin, X.; Qu, T.; Qi, S. Acta Polym 1990, 41, 220.