

Novel Superabsorbent Cellulose-Based Hydrogels Crosslinked with Citric Acid

Christian Demitri,¹ Roberta Del Sole,¹ Francesca Scalera,¹ Alessandro Sannino,¹ Giuseppe Vasapollo,¹ Alfonso Maffezzoli,¹ Luigi Ambrosio,² Luigi Nicolais²

¹Innovation for Engineering Department, University of Salento, via per Monteroni, km 1,73100, Lecce, Italy

²Department of Materials and Production Engineering, University of Naples "Federico II", Piazzale Tecchio, 80 (80125) Naples, Italy

Received 18 September 2007; accepted 9 March 2008

DOI 10.1002/app.28660

Published online 20 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This work is focused on the preparation of new environmentally friendly hydrogels derived from cellulose and hence originating from renewable resources and characterized by biodegradable properties. Two cellulose derivatives, sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC), were used for superabsorbent hydrogel preparation. Citric acid (CA), a crosslinking agent able to overcome toxicity and costs associated with other crosslinking reagents, was selected in a heat activated reaction. Differential scanning calorimeter (DSC),

fourier transform infrared spectroscopy (FTIR), and swelling measurements were performed during the reaction progress to investigate the CA reactivity with each of the polymers. Also, CMCNa/HEC polymer mixtures (3/1 w/w) crosslinked with CA were investigated and compared with previous results. Finally, a possible reaction mechanism was proposed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2453–2460, 2008

Key words: cellulose; crosslinking; hydrogels; FTIR

INTRODUCTION

Superabsorbent hydrogels are crosslinked hydrophilic polymers insoluble in water, but capable to absorb large amounts of water through a swelling process. Swollen hydrogels swell to a volume much larger than their original size with a weight 10–1000 times higher than their initial one. For this characteristic, hydrogels have been widely used in many fields such as diapers and napkins for personal care, drug delivery systems in pharmaceutical area, in catalysis, and in biosensing.^{1–8} Recently, their application has been extended also in agriculture, since could represent a suitable solution for water storage and controlled release.^{9–13}

The swelling capacity of hydrogels has been studied by different authors. It is well known that the presence of fixed charges, typical of polyelectrolyte gels, determines a significant swelling of the polymer in water. This behavior is due to a Donnan equilibrium established between gel and the external solution, whose ionic strength strongly affects the swelling degree.¹⁴

A considerable drawback for traditional hydrogels, which are usually crosslinked sodium polyacrylates, is given by their environmental impact. Because envi-

ronmentally friendly products and processes are nowadays of great importance especially in industrial research, we focused our attention on the synthesis of novel cellulose-based hydrogels. In fact, cellulose is a natural polymer which can be employed as renewable-based polymeric material with biodegradable properties.

In this work, two cellulose derivatives, sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC), were used for hydrogels preparation.

It is well known that the effective swelling of cellulose-based hydrogels require a chemically crosslinked network that can be obtained by following different paths.^{15,16} Esterification path is one of them, which can be achieved among others either by using formaldehyde-based compounds, which are toxic, either by using alternative not dangerous esterification reagents.¹⁷ In the previous works,^{15,18} cellulose-based superabsorbent hydrogels, with sorption properties similar to those displayed by traditional acrylate-based products were synthesized and characterized by reacting in water mixtures of CMCNa and HEC crosslinked with divinylsulphone (DVS) or with a carbodiimide crosslinking agent.

In this study citric acid (CA), a new crosslinking agent able to overcome toxicity and costs compared with the former reagents was selected. As no complete data are available in the literature, CMCNa, HEC, and CA hydrogels were synthesized and characterized through differential scanning calorimeter (DSC) and fourier transform infrared spectroscopy (FTIR) techniques.

Correspondence to: C. Demitri (christian.demitri@unile.it).

Contract grant sponsor: Italian Minister for University and Research (MIUR), COLGEL project; contract grant number: L297/9400.

Cellulose crosslinking reaction

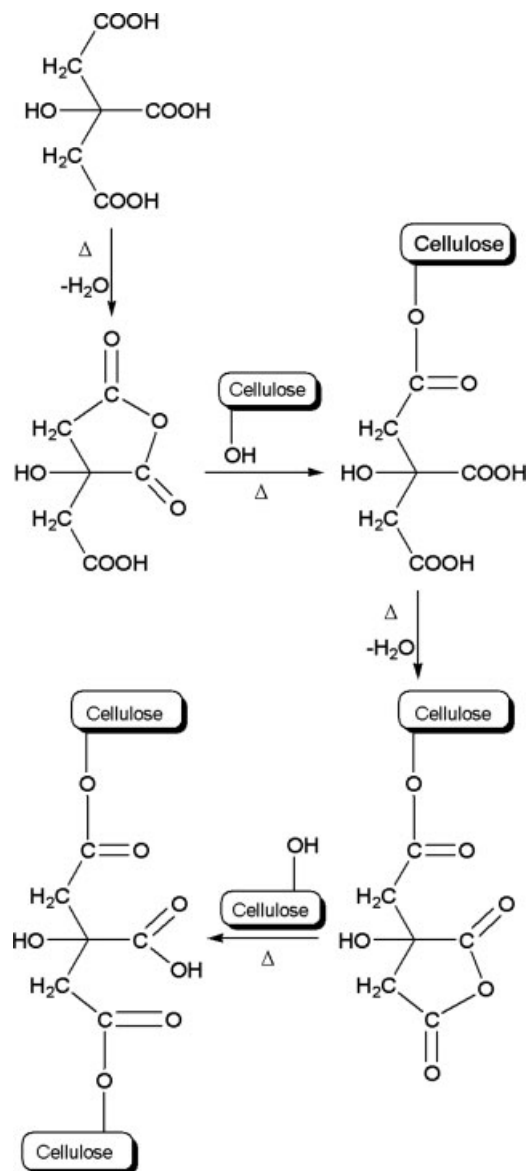
CA, widely used in food and drug industry, is an excellent crosslinking agent. CA, extensively widespread in nature (lemon juice contains $\sim 5\%$ of CA), is prepared commercially by fungal fermentation of glucose. CA and its salts, with a good affinity for metal ions, are used in a wide variety of applications: in soft drinks and effervescent salts, as an antioxidant in food, as a sequestering agent for metal ions, as a cleaning, and polishing agent for metals, as a mordant in dyeing. Moreover, CA and its salts have fundamental biological functions. For example, CA is involved as intermediate in the "Krebs cycle" in all living cells, also known as "citric acid cycle," for the production of usable energy.¹⁹

Recently, CA was used as crosslinking agent in various cellulose derivative systems^{19–23} and different mechanisms have been proposed in the literature to explain the crosslinking reaction of cellulose polymers with CA. Xie et al.²² for example, studied the optimum conditions for corn starch and CA reaction to produce resistant starch and studied the thermal stability of citrate starch products. The authors reported that when CA is heated, it will dehydrate to yield the cyclic anhydride that reacts with starch; successively another cyclic anhydride function can be achieved into CA structure through the other two nonreacted carboxylic groups allowing the attachment of another hydroxylic starch group (Scheme 1). Coma et al.²¹ carried out the crosslinking of hydroxypropyl-methyl cellulose with CA simply heating the reagents and determining the rate of crosslinking. According to Zhou et al.¹⁷ the two main stages of the reaction of polyfunctional carboxylic acids with cellulose are due to the attachment of the polyfunctional carboxylic acids via esterification with a cellulosic hydroxyl group and its further reaction—via esterification—with another cellulosic hydroxyl group producing a crosslink between cellulose chains. This mechanism is based on an anhydride intermediate formation. Attachment of the carboxylic acid moiety to celluloses hydroxyl group via esterification reaction of the first cyclic anhydride would expose a new carboxylic acid unit in CA, which has the proper chemical connectivity to form a new intramolecular anhydride moiety with the adjacent carboxylic acid unit. Further reaction with a cellulose hydroxyl of another chain can then lead to crosslinking.

EXPERIMENTAL

Materials

CMCNa (MW 700 kDa, DS 0.9 viscosity 3400 cm/s, food grade) and HEC (MW 250 kDa MS 2, viscosity 80–125 cm/s, food grade) were purchased from



Scheme 1 Possible crosslinking reaction mechanism of citric acid with cellulose.

Eigenmann e Veronelli S.p.A. Milano (Milano, Italy) and CA was supplied by Dal Cin S.p.A. Sesto San Giovanni Milano (Milano, Italy) and used as received.

Hydrogels synthesis

Hydrogel samples were obtained reacting, in water, CMCNa and HEC with CA as a crosslinking agent according the following procedure. First, a total polymer concentration of 2% by weight of water, using a mixture of CMCNa and HEC, with weight ratio equal to 3/1 was dissolved in distilled water by stirring gently at room temperature until a clear solution was obtained. The presence of HEC is necessary to promote intermolecular rather than

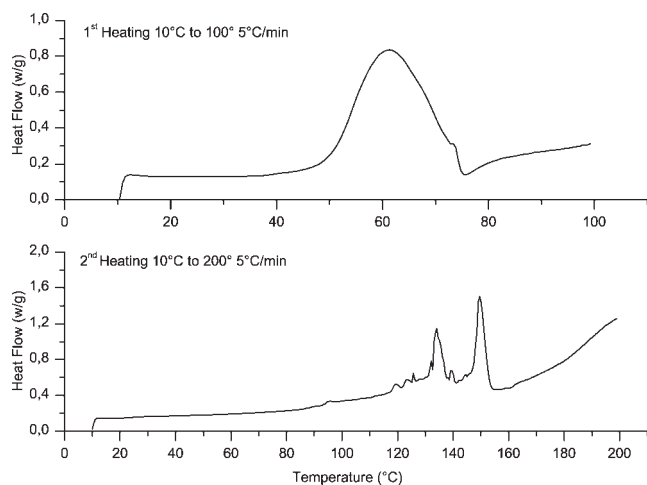


Figure 1 DSC curing thermogram of citric acid.

intramolecular crosslinking. In fact, poor crosslinking efficiency is reported if only CMCNa is used, due to the electrostatic repulsion between polyelectrolyte chains and to the high degree of substitution of hydroxyl groups at C6 most reactive position.¹⁵ CMCNa dissolution is slow at the concentration adopted; thus, first HEC was added to water till, after 5 min, a clear solution was obtained with a slight increase of viscosity; then, CMCNa was added, and the stirring was kept on till a clear solution was obtained (24 h), with a significant increase of viscosity. Finally, CA was added at different concentrations (1.75%, 2.75%, 3.75%, 10% and 20% w/w polymer) to obtain samples with various crosslinking degrees. This final solution was used to mold 10-mm thick samples. All samples were first pre-dried at 30°C for 24 h to remove absorbed water and then kept at 80°C for the crosslinking reaction (24 h with intermediate control).

Moreover, samples containing neat HEC or neat CMCNa samples crosslinked with CA were also prepared following exactly the same experimental conditions used for HEC/CMCNa mixtures.

All samples were analyzed by FTIR measurements. Anhydride formation was detected by monitoring its characteristic stretching band in the carbonyl region at 1738 cm^{-1} .²⁴

Swelling ratio

Equilibrium swelling measurements for all the samples were carried out in distilled water using a Sartorius microbalance (10^{-5} sensitivity). The swelling ratio (SR) was measured by weighing samples before and after their immersion in distilled water for about 24 h. The SR is defined as following:

$$SR = (W_s - W_d)/W_d$$

where W_s is the weight of the swollen hydrogel, and W_d is the weight of the dried sample.²⁵

Differential scanning calorimeter

A differential scanning calorimeter (DSC, Mettler-Toledo 822^e Mettler DSC) was used for thermal analysis. The scanning temperature range and the heating rate were 10–200°C and 5°C/min, respectively.

The adopted thermal cycle was: (1) heating 10–100°C; (2) isotherm at 100°C for 3 min; (3) cooling from 100°C to 10°C; (4) heating from 10°C to 200°C; (5) isotherm at 200°C; and (6) cooling until room temperature. An empty pan was used as a reference.

Fourier transformed infrared spectroscopy

All FTIR spectra were recorded on a JASCO FTIR 660 plus spectrometer equipped with an attenuated total reflectance (ATR) crystal sampler. Film samples were used directly on a ATR crystal sampler at a resolution of 4 cm^{-1} , by 300 scans, at absorbance range from 4000 cm^{-1} to 600 cm^{-1} .

RESULTS AND DISCUSSION

A DSC thermogram of neat CA is reported in Figure 1. A peak at about 60°C, attributed to a water loss process associated with the dehydration leading to an anhydride is evident. A complete degradation, starting at about 160°C, is observed in the 2nd scan.

DSC analysis of neat CMCNa and HEC powders are reported in Figure 2. The peak in the first scan indicates that some water is still absorbed in the polymers. Above 100°C, a possible degradation peak of CMCNa is detected. Both CMCNa and HEC show a thermal stability below 100°C.

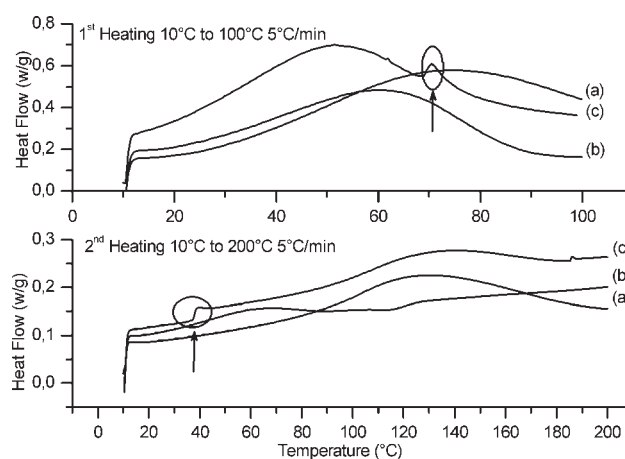


Figure 2 DSC curing thermograms of CMCNa (a); HEC (b); and CMCNa/HEC (3/1) hydrogel (3.75% of CA) (c).

TABLE I
Samples Composition Used for Each Crosslinking
Reaction Performed at 80°C

Reaction name	Initial polymer	Citric acid concentration (% w/w polymer)
A10	CMCNa	10
A20	CMCNa	20
B10	HEC	10
B20	HEC	20
C10	CMCNa/HEC (3/1)	10
C20	CMCNa/HEC (3/1)	20

Then, a film of hydrogel obtained using a 3 : 1 ratio of CMCNa/HEC and 3.75% by weight of polymer of CA was analyzed by DSC (Fig. 2) after drying the sample at 30°C for 24 h and then reduced in powder. A large endothermic peak associated to the evaporation of the water produced by the anhydrication process is evident in Figure 2(c). A small exothermic peak, attributed to esterification is superimposed on the first one. In the second heating cycle the glass transition ($T_g = 38^\circ\text{C}$) of the crosslinked cellulose mixture is observed.

After this preliminary DSC study, different hydrogel samples were prepared according the following procedures. After mixing reagents in water, the reaction vessel was kept at 30°C for 24 h in dry conditions to remove water. Then temperature was raised above 60°C, according to the results of DSC analysis of Figure 1, to obtain the CA anhydride. Above this limiting temperature citric anhydride is available for the crosslinking reaction with cellulose OH groups. Different reaction conditions were attempted to optimize the synthetic procedure such as temperature and CA concentration as summarized in Table I. Two different reaction temperatures for the crosslinking process, 80°C and 120°C, were attempted. However, either to prevent degradation risks or to limit the reaction rate a temperature of 80°C was chosen. Moreover, very high concentration (10 and 20% by weight) of CA were initially used to amplify the FTIR signals associated to each chemical reaction step. First, neat CMCNa and HEC were crosslinked with CA to investigate its reactivity with each of the polymers.

Figure 3 shows the FTIR spectrum of CA (Curve a), of A10 reaction mixture before heating (Curve b) and of A10 reaction mixture after 5 h of heating (Curve c). In CA spectrum (Fig. 3, Curve a) it is possible to observe a strong C=O band centered at 1715 cm^{-1} due to carboxylic acid. The FTIR spectrum of sample A10 shows a strong absorption band at 1590 cm^{-1} , characteristic of cellulose.²⁶ When CMCNa is mixed with CA the 1590 cm^{-1} peak can cover the 1715 cm^{-1} peak of CA, present in a lower amount. After heating, (Fig. 3, Curve c) the absorbance band

at about 1590 cm^{-1} is still observed and additionally a new band at 1738 cm^{-1} appears. Anhydrides display two stretching bands in the carbonyl region around 1758 and 1828 cm^{-1} . The higher frequency band is the more intense in acyclic anhydrides, whereas cyclic anhydrides show the lower frequency C=O stretching band stronger than the stretching band at higher frequency.²⁴ The new peak observed at 1738 cm^{-1} can be attributed to the characteristic stretching band of carbonyl group at lower frequency related to anhydride formation, an intermediate reaction necessary for CA reaction with cellulose hydroxyl groups. In contrast, the carbonyl peak expected at higher frequency is not detectable probably due to its weak intensity.

FTIR spectra of CA (Curve a), B10 reaction mixture before heating (Curve d) and B10 reaction mixture after 6.5 h of heating (Curve e) are reported in Figure 3. The HEC spectrum shows the band at 1590 cm^{-1} as in Figure 5²⁶ before and after heating, (Fig. 3, Curves b and c) whereas the absorbance of the carbonyl group at 1738 cm^{-1} appears only after heating at 80°C as observed for the sample A10.

Although FTIR analysis is generally considered a qualitative technique, a study in literature carried out by Coma et al. demonstrated that infra-red spectroscopy could be used at first approximation for the determination of the crosslinking rate in crosslinked cellulosic derivatives.²¹ Starting from this consideration, the evolution of the different reactions finally

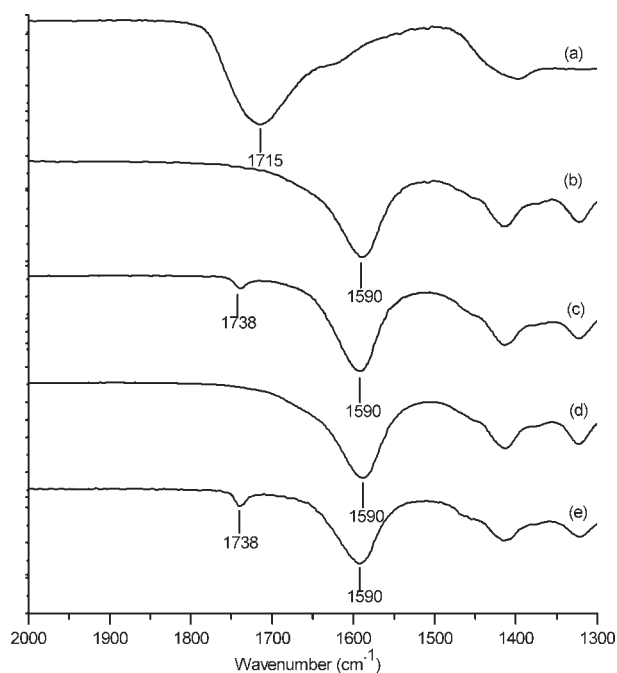


Figure 3 FTIR spectra of citric acid (CA) (a); A10 reaction mixture before heating (b); A10 reaction mixture after 5 h of heating (c); B10 reaction mixture before heating (d); and B10 reaction mixture after 6.5 h of heating (e).

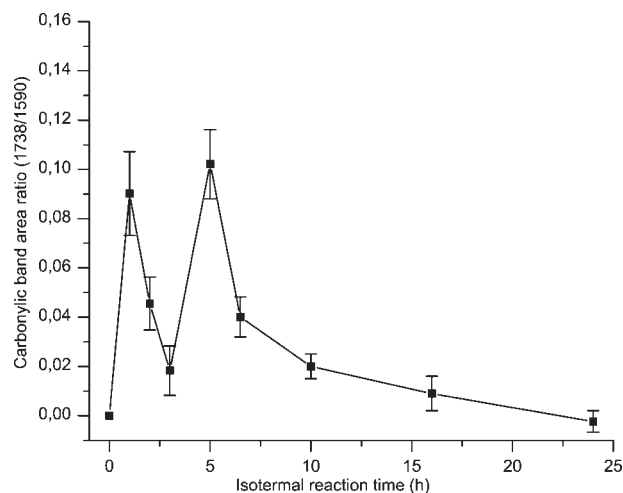


Figure 4 Carbonyl band area ratio ($1738\text{ cm}^{-1}/1590\text{ cm}^{-1}$) of reaction A20 at different reaction times.

leading to crosslinking at 80°C was monitored recording FTIR spectra at different reaction times.

The area under the absorbance peak at 1738 cm^{-1} (A_1) representative of the carbonyl group was compared with the area under the reference absorbance peak at 1592 cm^{-1} (A_2) invariant in all spectra. The evolution of the anhydride was evaluated as the ratio of A_1/A_2 as a function of the reaction time. Figures 4 and 5 point up the behavior of CMCNa polymer when the reaction is performed at 80°C with 20% of CA (Fig. 4) or 10% of CA (Fig. 5). Both of them show a similar trend; the anhydride band, that is absent before heating, reaches a maximum almost immediately after the first hour, successively decreases to a minimum after 3 h, then increasing again reaching a second maximum after 5 h. Finally, a slower process reduces the band area to zero after 24 h. It is worth noting that in Figure 4 (20% of CA concentration) the second maximum matches a value ($A_1/A_2 = 0.10$) higher than those observed in Figure 5 ($A_1/A_2 = 0.04$).

It is assumed that the peak at around 1738 cm^{-1} is due to the anhydrification process involving free CA followed by the first condensation of this anhydride with cellulose OH leading to a fast disappearance of the anhydride C=O groups. Then the carboxylate groups now linked to the polymer are capable to form again an anhydride leading to an increase of the 1738 cm^{-1} peak. The second reaction of this anhydride, responsible of the crosslinking, results in a new anhydride group consumption and consequent 1738 cm^{-1} peak reduction (Scheme 1). This second reaction is slower because it involves groups linked to large macromolecules and hence more sterically hindered as also reported for other cellulose crosslinking processes.²⁷ This possible reaction mechanism is confirmed by the swelling measurements.

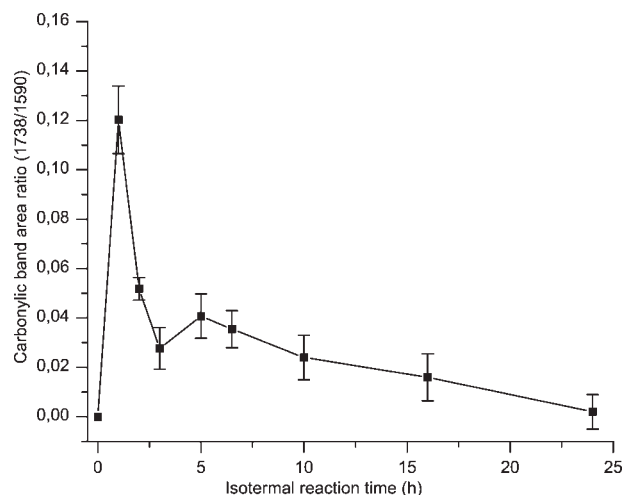


Figure 5 Carbonyl band area ratio ($1738\text{ cm}^{-1}/1590\text{ cm}^{-1}$) of reaction A10 at different reaction times.

Figure 6 shows peak area ratio A_1/A_2 of HEC polymer when the reaction is performed at 80°C with 20% of CA or 10% of CA. The anhydride band intensity increase from 0 to 0.098 when the reaction time increase from 0 h to 6.5 h, but drop to 0 when the reaction time reaches 24 h. The B20 reaction (Fig. 6, ■) follows exactly the same trend providing a maximum of 0.079 value at 5 h. Assuming that the crosslinking mechanism is the same described for CMCNa, the anhydrification and esterification reactions appear superimposed in this case. Therefore, HEC polymer shows a single peak in Figure 6. This latter result was in accordance with conclusion of Xie and Liu.²⁸ They studied the degree of substitution, as evaluation of crosslinking esterification, on starch thermally reacted with CA at different reaction time and found a maximum after few hours.

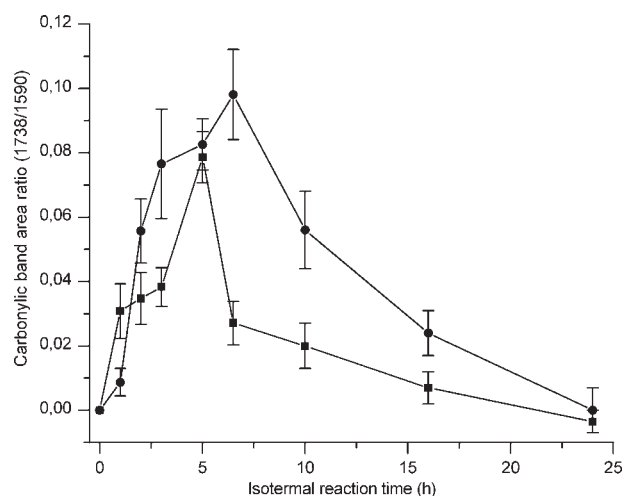


Figure 6 Carbonyl band area ratio ($1738\text{ cm}^{-1}/1590\text{ cm}^{-1}$) of reactions B10 (●) and B20 (■) at different reaction times.

To explain the data observed in all graphics after 24 h, (Figs. 4–6) we supposed that in all cases the polymer is unstable when kept in the oven for 24 h because of unidentified secondary reactions take place modifying polymer structure that involve also ester functions. Xie and Liu²⁸ work guessed that the degree of substitution reached a maximum and then decreased as dissociation of the substituents from starch occurred when the reaction time was longer than 7 h.

Finally, to complete this study, polymer mixtures of CMCNa and HEC were crosslinked. CMCNa has carboxylic groups in its structure that increase the volume variation process in solution. A preliminary attempt to follow the reaction pathway was failed. Probably the reaction systems considered are too complex having many different reaction centers. FTIR spectra of C10 reaction registered before (Curve a), after 8 h (Curve b), and after 13 h (Curve c) of heating are compared in Figure 7. Figure 7 (Curves d–f) shows similar spectra but referred to reaction sample C20. Moreover, it is worth noting that when polymer mixtures are used (C10 and C20) a broad signal appears at about 1715 cm^{-1} (see spectra 7a and 7d), especially when a higher CA concentration is used in the reaction. In fact, with 20% of

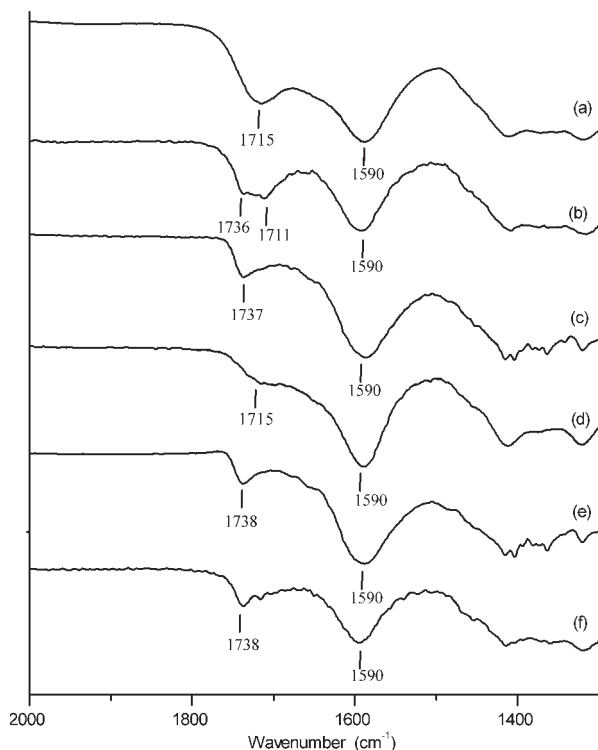


Figure 7 FTIR spectra of C10 reaction mixture before heating (a); C10 reaction mixture after 8 h of heating (b); C10 reaction mixture after 13 h of heating (c); C20 reaction mixture before heating (d); C20 reaction mixture after 8 h of heating (e) and C20 reaction mixture after 13 h of heating (f).

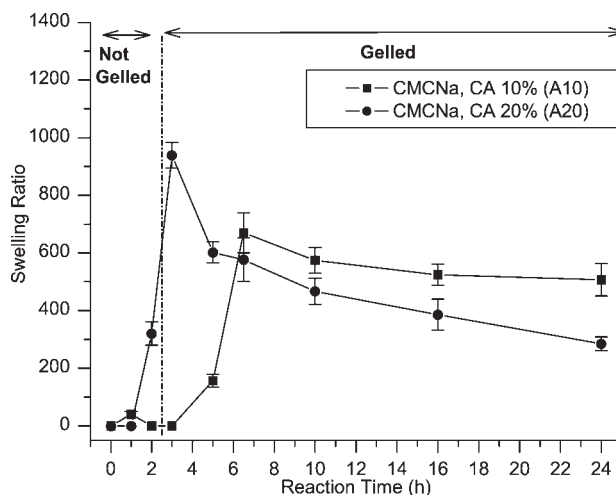


Figure 8 Equilibrium swelling ratio versus reaction time of CMCNa polymer with 10% w/w (■) or 20% w/w (●) of CA crosslinker concentration (both samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C).

CA, the signal of CA at 1715 cm^{-1} is very broad and overlapped to the polymer signal at 1590 cm^{-1} then a clear band is not detectable. C10 reaction mixture before heating (Fig. 7, Curve a) shows a band around 1715 cm^{-1} covering the absorbance region monitored previously for the other reactions (A10, A20, B10, B20); consequently, a clear assignment to the carbonyl group is difficult. However, the other two spectra indicate that this band moves to higher wavenumbers during the crosslinking reaction. In particular, after 8 h FTIR spectrum (Fig. 7, Curve b) shows a broad band in the range of $1711\text{--}1736\text{ cm}^{-1}$ and after 13 h (Fig. 7, Curve c) this band appears more clearly as a narrow absorbance band at 1737 cm^{-1} , which is typical of carbonyl groups. Spectra of C20 reaction (Fig. 7, Curves d–f) provide similar results. Although a quantitative analysis of carbonyl groups is not possible when C10 and C20 samples are crosslinked, an evolution of the carbonyl peak during crosslinking similar to those observed for the reaction of the neat polymers can be assumed.

The crosslinking kinetic was also monitored studying the swelling behavior during the reaction progress. SR was calculated as a function of the reaction time for: (a) CMCNa with 10% or 20% of CA concentration (Fig. 8); (b) HEC with 10% or 20% of CA concentration (Fig. 9); (c) the mixture of CMCNa and HEC (3/1) with 10% or 20% CA concentration (Fig. 10); and (d) the mixture of CMCNa and HEC (3/1) with 1.75%, 2.75% or 3.75% CA concentration (Fig. 11).

According to the results of Figures 8 and 9 the swelling of CMCNa crosslinked with 10% of CA is higher than HEC with the same CA concentration after 24 h. When 20% of CA was added to the celluloses, the shape of the swelling curves is similar for

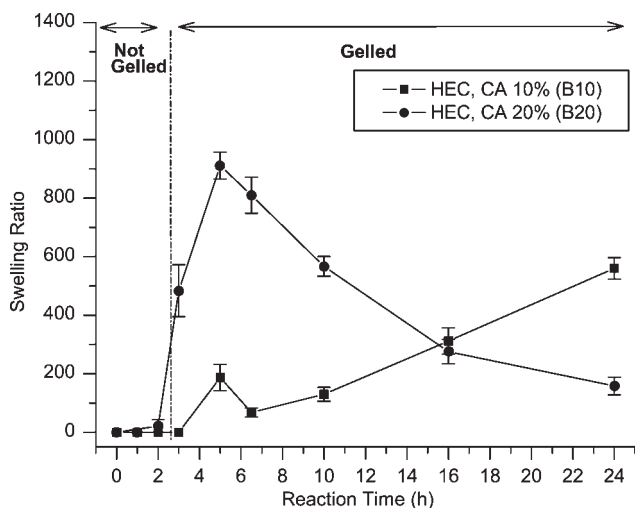


Figure 9 Equilibrium swelling ratio versus reaction time of HEC polymer with 10% w/w (■) or 20% w/w (●) of CA crosslinker concentration (both samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C).

HEC and CMCNa. In this case, as crosslinking proceeds the swelling of HEC-based samples decreases faster than CMCNa samples indicating that a higher rate of reaction between CA and HEC. This probably occurs because HEC is less sterically hindered than CMCNa and can react more quickly than CMCNa chains. In addition, in each repeating unit HEC has more OH groups than CMCNa (3 versus 2).

The maximum swelling of CMCNa/CA sample is observed at the gelation onset, after 3 h, when the second esterification reaction, those leading to crosslinking begins (Fig. 8). Then as the crosslinking process increases the corresponding equilibrium water

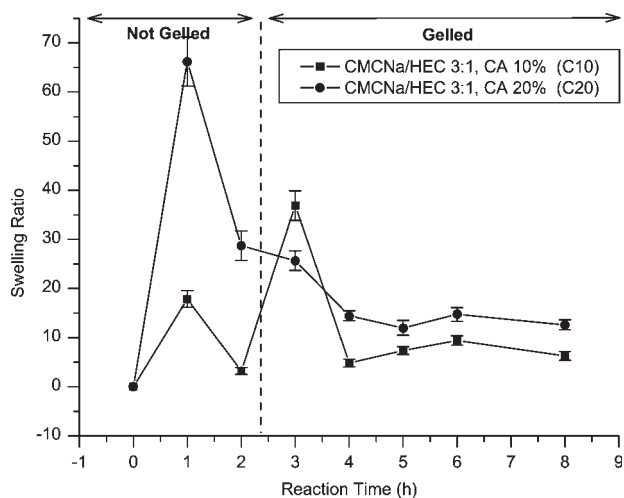


Figure 10 Equilibrium swelling ratio versus reaction time of CMCNa/HEC weight ratio 3/1 mixture with 10% w/w (■) or 20% w/w (●) of CA crosslinker concentration (both samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C).

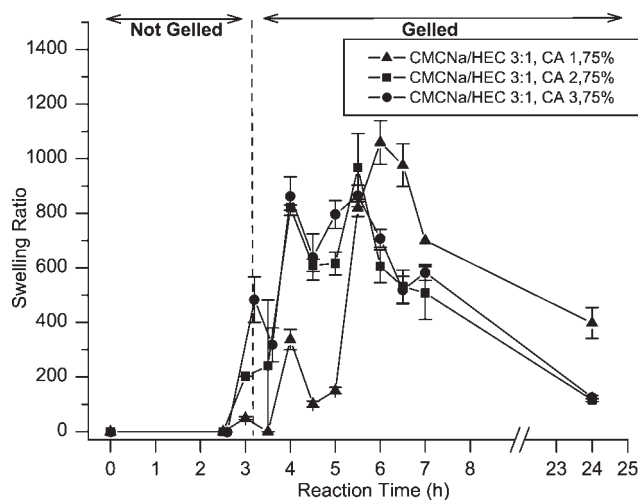


Figure 11 Equilibrium swelling ratio versus reaction time of CMCNa/HEC weight ratio 3/1 mixture with 1.75% w/w (▲), 2.75% w/w (■) or 3.75% w/w (●) of CA crosslinker concentration (all samples were dried under vacuum at 30°C for 24 h and then reacted at 80°C).

sorption decreases, confirming the results of FTIR analysis.

The same reaction mechanism can be assumed for neat HEC crosslinked with CA (Fig. 9). However in this case the overall behavior is slightly different as a consequence of the absence of carboxylic groups bonded to the polymer. The sample B10 in Figure 9 is characterized by a higher SR at the end of the reaction process as a consequence of a lower degree of crosslinking associated with a lower content of CA. The results of swelling experiments must be interpreted taking into account that the CA introduces the high hydrophilic carboxylic groups that are responsible of the formation of a polyelectrolyte network. Therefore the water sorption is significantly increased as carboxylic groups are linked first to the HEC chains and then to the gelled network. This effect cannot be appreciated in CMCNa hydrogels because a large amount of $-\text{COOH}$ groups, those linked to the CMCNa chains, is already bond to the network at gelation onset. Similar trend is observed for the mixtures of HEC and CMCNa in Figure 10.

Hydrogels of practical use presenting a high degree of swelling (Fig. 11) were obtained with a reduced concentration of CA (1.75%, 2.75%, 3.75% by weight of polymer). The lower SR reported in Figure 10 compared with Figure 11 for the same CMCNa/HEC mixture is attributed to a higher crosslinking and a faster kinetic when a higher CA concentration is used. Figure 11 shows that with a CA concentration of 3.75% the SR can reach 900. This hydrogel, after swelling, is characterized by adequate stiffness and it is capable to keep the same shape of the synthesis vat. Hydrogels formerly synthesized¹⁵ using divinyl sulfone, a toxic reagent, as

crosslinking agents and the same ratio between CMCNa and HEC were characterized by a maximum SR of 200. In this case, a higher SR is obtained using an environmental friendly crosslinking agents. At concentrations lower than 1.75% of CA a weak crosslinking associated with insufficient mechanical property is observed.

CONCLUSIONS

This work shows for the first time that CA can be successfully used as crosslinking agent of CMCNa/HEC mixtures. The mixture of two polysaccharides was addressed. An esterification mechanism based on an anhydride intermediate formation was proposed to explain the reaction of cellulose polymers with CA.

The crosslinking reaction for CMCNa/HEC system was observed either by DSC or by FTIR analysis. The evolution of the different crosslinking reactions was monitored by means of FTIR spectra collected at different reaction times using an excess of CA. The SR, monitored at different reaction times, confirmed the reaction path figured out from FTIR analysis. An optimal degree of swelling (900) for practical applications was achieved using low-CA concentrations. The hydrogel obtained through the method described in this article has the great advantage to reduce primary and production costs and avoid any toxic intermediate during its synthetic process.

Further studies can be specifically addressed to the application of superabsorbents in agriculture, wherein it is strategical to optimize water where water scarcity is a common problem.

References

- Buchholz, F. L. In *Superabsorbent Polymers: Science and Technology*, ACS Symposium Series 573, Buchholz, F. L.; Peppas, N. A., Eds.; American Chem Society: Washington, DC, 1994; p 27.
- Sakiyama, T.; Chu, C. H.; Fujii, T.; Yano, T. *J Appl Polym Sci* 1993, 2021, 50.
- Yoshida, M.; Asano, M.; Kumakura, M. *J. Eur Polym Mater* 1989, 25, 1197.
- Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. *J Appl Polym Sci* 1992, 44, 249.
- Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. *J Appl Polym Sci* 1993, 47, 113.
- Hogari, K.; Ashiya, F., Eds. *American Chem Society: Washington, DC, 1994; Vol. 1, p 12.*
- Ericksen, P. H.; Nguyen, H. V.; Oczkowski, B.; Olejnik, T. A. *Eur. Pat.* 40087 (1981)
- Kobayashi, T.; Kobunshi, T. *J Appl Polym Sci* 1987, 36, 612.
- Benhur, M.; Keren, R. *Soil Sci Soc Am J* 1997, 61, 565.
- Levin, J.; Benhur, M.; Levy, G. *J. Aust J Soil Res* 1997, 29, 455.
- Al-Harbi, A. R. *HortScience* 1999, 34, 223.
- Raju, K. M. *J Appl Polym Sci* 2001, 80, 2635.
- Marci, G.; Mele, G.; Palmisano, L.; Pulito, P.; Sannino, A. *Green Chem* 2006, 8, 439.
- Esposito, F.; Del Nobile, M. A.; Mensitieri, G.; Nicolais, L. *J Appl Polym Sci* 1996, 60, 2403.
- Sannino, A.; Nicolais, L. *Polymer* 2005, 46, 4676.
- Benke, N.; Takacs, E.; Wojnarovits, O. L.; Borsa, J. *Radiat Phys Chem* 2007, 76, 1335.
- Zhou, Y. J.; Luner, P.; Caluwe, P. *J Appl Polym Sci* 1995, 58, 1523.
- Sannino, A.; Madaghiele, M.; Lionetto, M. G.; Schettino, T.; Maffezzoli, A. *J Appl Polym Sci* 2006, 102, 1524.
- Glusker, J. P. *Acc Chem Res* 1980, 13, 345.
- Wang, C. C.; Chen, C. C. *Appl Catal A* 2005, 293, 171.
- Coma, V.; Sebti, I.; Pardon, P.; Pichavant, F. H.; Deschamps, A. *Carbohydr Polym* 2003, 51, 265.
- Xie, X. S.; Liu, Q.; Cui, S. W. *Food Res Int* 2006, 39, 332.
- Yang, C. Q.; Wang, X. J. *J Appl Polym Sci* 1998, 70, 2711.
- Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1991; pp 120–130.
- Peppas, N. A. *Hydrogels in Medicine and Pharmacy*; CRC Press: Boca Raton, Florida, 1987; p 29.
- Chen, C. C.; Wang, C. C. *J Sol–Gel Sci Technol* 2006, 40, 31.
- Lionetto, F.; Sannino, A.; Maffezzoli, A. *Polymer* 2005, 46, 1796.
- Xie, X. S.; Liu, Q. *Starch* 2004, 56, 364.