Water Sorption in Cellulose-Based Hydrogels

F. ESPOSITO,[1] M. A. DEL NOBILE,[2] G. MENSITIERI,[1] and L. NICOLAIS[1,*]

[1]Department of Materials and Production Engineering, University of Naples "Federico II," Piazzale Tecchio 80, 80125 Naples, Italy, and [2]Institute of Composite Materials Technology, National Research Council, Piazzale Tecchio 80, 80125 Naples, Italy

SYNOPSIS

Sorption of distilled water in a cellulose-based hydrogel is presented. The examined system is based on a mixture of sodium salt of carboxymethylcellulose and hydroxyethylcellulose, crosslinked with divinilsulphone. The effect of chemical composition, manufacturing procedures, as well as desiccation protocols on equilibrium water uptake was investigated. Experimental results were interpreted in terms of crosslinking density, presence of ionic groups on the backbone, as well as macroscopic sample morphology detected by electron scanning microscopy. The reported results evidence the possibility to bias the process parameters in order to obtain hydrogels characterized by the desired water sorption levels. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Usually, polymer-based superabsorbent materials are made of synthetic polyelectrolytes such as cross-linked poly(sodium acrylate). Due to environmental issues, growing efforts have been put forward in developing natural polymer-based superabsorbent materials that guarantee biodegradability. Applications of superabsorbent materials span from personal hygienic products to water reservoir systems for agriculture, as well as innovative absorbent systems for a wearable artificial kidney.[1,2]

As reported in the literature,[3,4] a high degree of swelling in water can be achieved using polyelectrolyte gels. In fact, the presence of fixed charges on macromolecular chains determines a large swelling of the polymer due to a Donnan equilibrium established between gel and the external solution, whose ionic strength strongly affects the swelling degree.[5–7] In addition, hydrophilicity of backbone brings a considerable contribution to the swelling capacity because of the high affinity between polymer chains and water.

The basic idea developed in this work is the utilization of a linear biodegradable water-soluble material which, properly crosslinked, turns into a bio-degradable hydrogel. Carboxymethylcellulose (CMC), which is a biodegradable polymer easily available on the market, could be thought of as a possible candidate. However, CMC cannot be used as itself because, as reported in the literature,[8] it tends to form intramolecular rather than intermolecular crosslinks. For this reason a mixture of CMC, in its sodium salt form (CMCNa), with hydroxyethylcellulose (HEC) was crosslinked using divinylsulphone (DVS). The introduction of HEC avoids the formation of intramolecular crosslinks. Several factors are expected to affect the final hydrogel swelling properties in distilled water, such as chemical composition and type of manufacturing procedures. For this reason water swelling properties of various samples differing for the CMCNa/HEC ratio and DVS content as well as for the adopted manufacturing protocols were evaluated.

MATERIALS AND METHODS

Hydrogels used in this investigation were obtained by crosslinking mixtures of CMCNa and HEC with DVS as a crosslinking agent. CMCNa, HEC, and DVS were purchased from Aldrich Chimica, and were used as received.

According to procedures reported in the literature,[8] the crosslinking reaction was performed in alkaline water solution (0.02 M potassium hydrox-

ide). The sample preparation procedure can be schematized as follows: step 1 is the crosslinking reaction; step 2, if present, consists of soaking the crosslinked sample in water to equilibrium; step 3, if present, consists of soaking the crosslinked sample in methanol to equilibrium; and finally, step 4, which is the desiccation stage. In the following, step 2 and 3 together will be referred to as the "manufacturing" procedure.

A first group of samples were prepared with the aim of investigating only the effect of manufacturing protocol on the final water-swelling properties. In fact, each sample of this group is characterized by the same chemical composition and the same desiccation procedure. In Figure 1 the adopted manufacturing protocols are reported with corresponding sample labels. For all these samples the desiccation step, where present, was performed at room conditions (1 atm and 25°C). The starting water solution had in all cases an overall polymer (HEC + CMCNa) concentration equal to 2% by weight, while the adopted composition for the reacting system consisted in a DVS concentration equal to 0.04 mol/L and a CMCNa/HEC weight ratio equal to 3 : 1. The calculated crosslinking density, defined as the ratio between the theoretical number of reacted sites and the total number of reactive sites on the cellulose derivatives backbone, is equal to 0.4.

A second group of samples was prepared to investigate the effect of both chemical composition (CMCNa/HEC ratio and DVS content) and desiccation procedures on the final water-swelling properties. For these samples manufacturing procedure is the same as for sample C. Seven different chemical compositions were adopted and are re-

ported in Table I along with the calculated crosslinking densities. Also, in this case, starting water solutions had in all cases an overall polymer concentration equal to 2% by weight. For each of these samples three different drying methods have been adopted, giving a total number of 21 types of samples. The three desiccation procedure were: desiccation at atmospheric pressure, desiccation under vacuum, and desiccation by extraction with acetone.

Equilibrium swelling measurements in distilled water were carried out for all the samples using an electronic microbalance (Mettler AE 100) with an accuracy of $\pm$ 10^{-4} g. Reported values of equilibrium water uptakes are averaged over 12 measurements. In fact, for each type of sample, synthesis was replicated four times, and from each batch of synthesis three samples where obtained.

Wide-angle x-ray diffraction patterns were obtained with nickel-filtered CuKα radiation with an automatic Philips powder diffractometer.

Electron scanning micrographs were obtained using an Hitachi scanning electron microscope S-2300.

RESULTS AND DISCUSSION

Liquid water sorption tests have been performed on a total of 25 types of samples to assess the effect of chemical composition (CMCNa/HEC ratio and DVS content), manufacturing protocol, and drying procedures on water-swelling properties of these cellulose-based materials. Remarkable differences in water sorption capabilities were detected for the various samples. The following analysis is divided
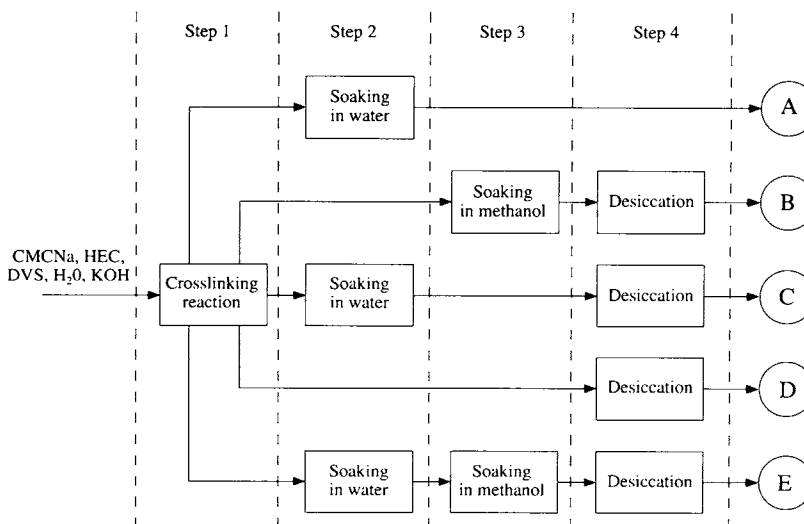
Figure 1   Scheme of manufacturing procedures for the first group of samples.

Table I   Scheme of Adopted Chemical Compositions Denoted by "X"

DVS/ CMCNa/HEC	0.04	0.066	0.1	0.13
0	X (0.27)	—	—	—
1/3	X (0.31)	—	—	—
1/1	X (0.35)	—	—	—
3/1	X (0.4)	X (0.66)	X (1)	X (1.3)

The DVS content is expressed in mol/l. In parentheses are reported the values of calculated crosslinking density.

in two parts concerning, respectively, the first and second group of samples introduced in the Materials and Methods section.

As a first step we focused our attention on samples differing for manufacturing procedures (step 2 and 3) but characterized by the same chemical composition as well as desiccation procedure. The degree of swelling in distilled water for samples A through E is reported in Figure 2. Equilibrium water uptakes were measured after desiccation in the case of samples B, C, D, and E, while the value reported for sample A was measured right after step 2.

In the case of sample A, remarkably high amounts of absorbed water were detected, which were about fivefold the quantity measured in the case of the samples C and D. The strongly different behavior between samples A and C could be related to a difference in the actual crosslinking density. In fact, the calculated crosslinking density might be not attained in the case of sample A because of the swollen structure of the reacting system (step 1 in Fig. 1), which avoid complete reaction among reacting groups. Swelling occurring in step 2 obviously keeps crosslinking sites further apart and does not promote an increase of crosslinking density. Conversely, in the case of sample C, the desiccation stage (step 4), promoting a strong reduction of average distance among crosslinking sites, causes a substantial increment of the actual crosslinking density and, in turn, a dramatic reduction of water uptake. A further increase in crosslinking density and decrease of water uptake is expected if the desiccation stage is not preceded by soaking in water, as in the case of sample D. In fact, soaking in water should promote a depletion of KOH in the system and, consequently, a reduction of the extent of reaction during the desiccation step.

To confirm the hypothesis that crosslinking reaction is not completed during step 1 and still takes place during the desiccation step, analysis was performed on samples B and E. If the reaction is not effectively completed during step 1, contacting the

system after step 1 with a substance capable of reaction with DVS (such as methanol) should affect the degree of crosslinking. In fact, sample B, which, differently from sample C, is obtained by soaking in methanol rather than water, is characterized by a water-swelling degree slightly higher than sample C. This is likely due to a slightly lower level of crosslinking density related to competition for reaction with DVS between methanol and the functional sites still present on the macromolecules.

If soaking in methanol is preceded by a water-soaking step, as in the case of sample E, an increase of water uptake compared to sample B is detected. In the case of sample E, the reaction of methanol with DVS, which occurs during step 3, is more favored than in the case of sample B. In fact the water-soaking step (step 2) actually increases the distance between macromolecules and lowers KOH concentration if compared to the case of sample B. Water sorption uptake for sample E is comparable to that of sample A, suggesting that methanol actually has neutralized all the unreacted DVS.

The effects of chemical composition and desiccation procedures were assessed studying the swelling properties of the second group of samples. In Figure 3, the equilibrium water uptakes as a function of the HEC weight fraction in the case of samples obtained starting from the same DVS concentration (0.04 mol/l) and differing for desiccation procedures are reported. Very high water uptakes (up to 400 g of water per gram of dry polymer) were measured. The water uptake increases as the amount of CMCNa increases, due to the presence of ionic groups on CMCNa. Nevertheless, as mentioned, maximization of water uptake cannot be obtained utilizing 100% CMCNa because over a critical CMCNa concentration intramolecular crosslinking sets in and gelation is not attained. Desiccation procedures remarkably affect the swelling degree, and the highest water uptake is detected for the gel dried
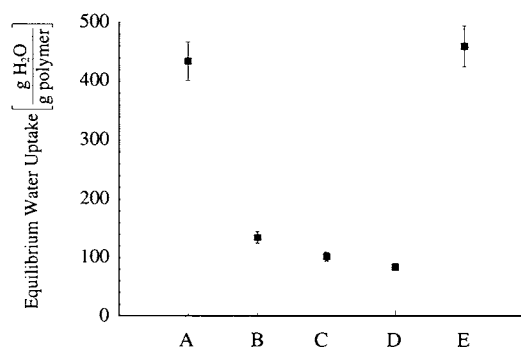
**Figure 2**   Swelling degree of samples A through E in distilled water.
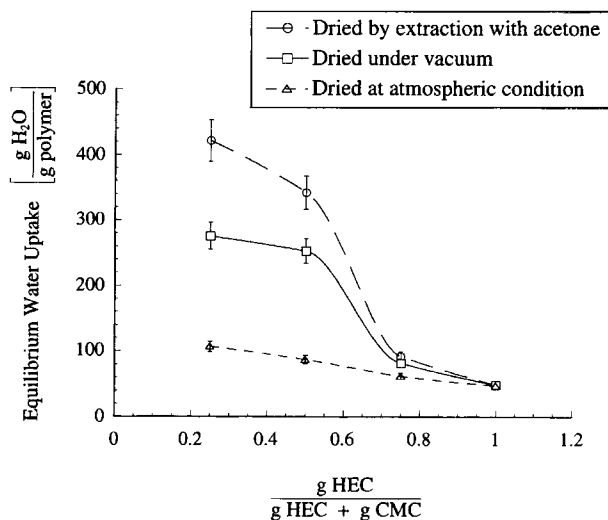
Figure 3 Equilibrium water uptake as a function of HEC weight fraction for a sample obtained starting from equal DVS concentration (0.04 mol/L) but differing for desiccation procedures.

using extraction with acetone, while the lowest is for the gel desiccated at room conditions. This effect is related to the different sample morphologies obtained, as will be discussed further in the following.

The swelling degree as a function of DVS concentration is reported in Figure 4 for samples obtained starting from the same CMCNa/HEC weight ratio (3 : 1) and differing for desiccation procedures. The equilibrium water content increases as the crosslinking agent concentration increases. This trend is related to the increase of the network elastic response to swelling, because at higher DVS concentrations the average molecular weight between two crosslinking points decreases. Also, in this case, different sorption amounts were detected as the desiccation procedure was changed according to the same trend followed for the samples obtained at constant DVS concentration.

To elucidate the effect of different desiccation procedures on water sorption behavior, x-ray diffraction tests as well as electron scanning microscope analysis were performed on samples of fixed composition (CMCNa/HEC weight ratio equal to 3 : 1, and DVS content equal to 0.04 mol/L). In Figure 5, x-ray diffractograms are reported, which do not evidence any substantial difference among the three samples examined. All the samples were found to be completely amorphous, indicating that the differences in sorption equilibrium uptake cannot be related to a different crystallinity level. On the other hand, the electron scanning micrographs of desiccated gel surfaces reported in Figure 6(a), (b), and (c) clearly evidence the morphological dif-
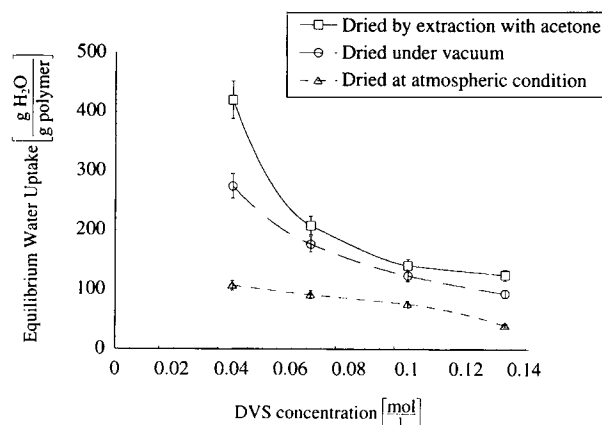

Figure 4 Swelling degree as a function of DVS concentration for samples obtained starting from equal CMCNa/HEC weight ratio (3 : 1) but differing for desiccation procedurres.

ferences. The gel desiccated at room conditions [Fig. 6(a)] is more dense and compact, while the acetone desiccated gel is characterized by a microporous structure [Fig. 6(c)]. In the case of gel desiccated under vacuum, an intermediate structure was observed [Fig. 6(b)]. Therefore, differences in sorption behavior can be explained in terms of the different macroscopic morphologies obtained. In fact, the structures characterized by a higher microvoids size show remarkably higher sorption uptakes, due to the fact that part of the water condensates in the microvoids whose dimension further increases after polymer swelling.

The presented experimental findings show different routes in obtaining cellulose-based superabsorbent materials characterized by a wide range of water sorption capabilities. Chemical composition, manufacturing procedures, and desiccation protocols can be biased to obtained a material suitable for a specific application.
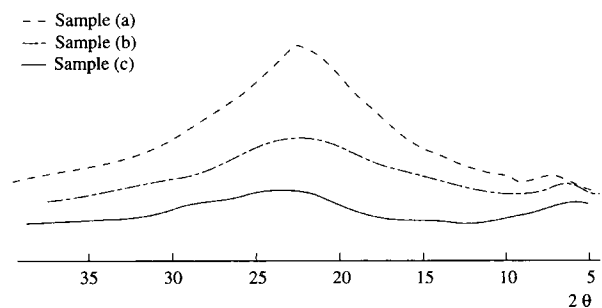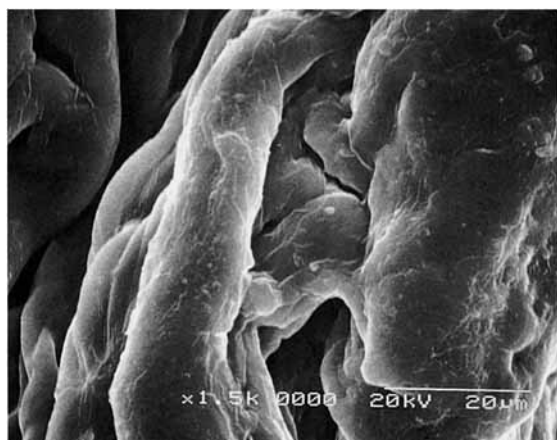

Figure 5 X-ray diffraction patterns of samples with a CMCNa/HEC ratio equal to 3 : 1 and a DVS content of 0.04 mol/L desiccated: (a) at room condition, (b) under vacuum, (c) by extraction with acetone.
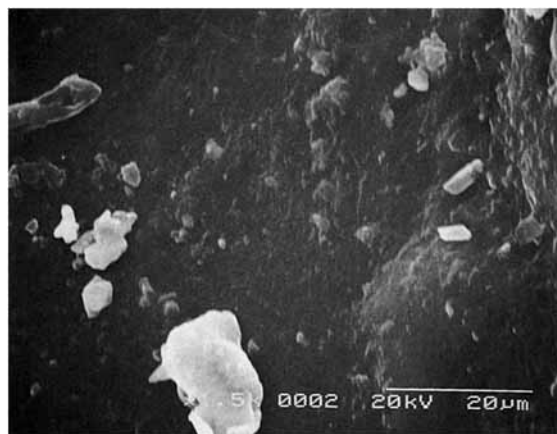
(a)
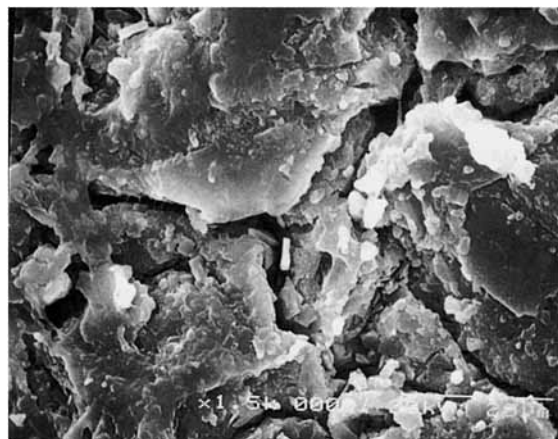
(b)

(c)

Figure 6 Electron micrograph of samples with a CMCNa/HEC ratio equal to 3 : 1 and a DVS content of 0.04 mol/L desiccated: (a) at room condition, (b) under vacuum, (c) by extraction with acetone.

The effects of ionic strength as well as of applied stresses on water sorption capability are also of primary importance and are currently being analyzed to assess material suitability for final use.

CONCLUSIONS

Water sorption behavior of a cellulose-based hydrogel has been presented. Water sorption uptakes as high as 400 g of water per gram of dry polymer were measured. Manufacture protocol prior to desiccation, desiccation procedures, and chemical composition all have been found to markedly affect water equilibrium uptake, obtaining a wide range of water swelling levels.

Manufacturing protocol, for a fixed chemical composition, remarkably influences the crosslinking density and, consequently, the equilibrium water uptake.

A decrease of crosslinking agent concentration or an increase of CMCNa/HEC ratio determine an increase of equilibrium water uptake due to a lower crosslink density and higher ionic group concentration.

Finally, drying procedures also affect water swelling due to the different macroscopic morphologies obtained.

REFERENCES

1. R. Esposito, M. Pluvio, P. Bello, E. Quarto, S. Savoia, and C. Giordano, *Abstr. XX Congr. Naz. Soc. Ital. Nefrologia*, 1979, p. 142.
2. E. Doelker, in *Absorbent Polymer Technology*, L. Brannon-Peppas and R. S. Harland, Eds., Elsevier, Amsterdam, 1990, p. 125.
3. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
4. D. Castel, A. Ricard, and R. Audebert, *J. Appl. Polym. Sci.*, **39**, 11 (1990).
5. L. Brannon-Peppas and N. A. Peppas, in *Absorbent Polymer Technology*, L. Brannon-Peppas and R. S. Harland, Eds., Elsevier, Amsterdam, 1990, p. 67.
6. S. Beltran, J. P. Baker, H. H. Hooper, H. W. Blanch, and J. M. Prausnitz, *Macromolecules*, **24**, 549 (1991).
7. J. Grignon and A. M. Scallan, *J. Appl. Polym. Sci.*, **25**, 2829 (1980).
8. U. Anbergen and W. Oppermann, *Polymer*, **31**, 1854, (1990).