ELSEVIER

Concurrent effect of microporosity and chemical structure on the equilibrium sorption properties of cellulose-based hydrogels

A. Sannino[a,*], L. Nicolais[b]

[a]*Department of Engineering for Innovation, University of Lecce, via per Monteroni, 73100 Lecce, Italy*
[b]*Department of Materials and Production Engineering, University of Naples 'Federico II', Piazzale Tecchio, 80-80125 Naples, Italy*

Abstract

Polyelectrolite hydrogels are crosslinked polymers which display high sorption capacity in water and water solutions. They are widely used in the marked of personal hygiene products, as well as in other biomedical and industrial applications. In the most industrial application they are not biodegradable and prepared starting from acrylamide.

In this work, the chemical–physical analysis of a novel class of natural polymers-based microporous superabsorbent hydrogels has been presented. The main focus is the definition of the relationship between material's chemical–physical structure and its equilibrium sorption properties.

The effect of the variation of the degree of crosslinking, the polyelectrolyte nature of the backbone and the hydrogel microporosity on its swelling properties has been analysed, and a good agreement with the theoretical statements has been displayed.

The effect of the ionic strength and the pH of the external solution in contact with the hydrogel on its equilibrium sorption properties has also been assessed, and an high sensitivity to these variations was detected for all the tested chemical compositions and physical structures.

This work have to be considered part of the efforts towards the reduction of the environmental impact of the large scale consumption industrial polymer based products.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Hydrogel; Swelling; Ionic strength

1. Introduction

In the last 50 years the research in the field of superabsorbent products was drawn by the rapidly increasing demand for their application in the market of personal care absorbent products [1,2].

The production of superabsorbents for personal care products covers almost the 80% of the overall hydrogel production nowadays, and this attractive business pushes multinational groups toward the development of new technologies both in the material chemistry definition [3,4] and production processes [5,6]. However, they are widely used also in other fields, such as drug delivery [7–9], biosensing [10], soft actuators/valves [11], and catalysis

[12]. The characteristic which makes these materials very interesting from both theoretical and practical point of view is the possibility to modulating their water retaining capabilities, and therefore their volume, by external stimuli (e.g. pH, ionic strength, temperature).

Properties of chemically crosslinked hydrophilic polyelectrolytes in aqueous solution are determined by several chemical and morphological factors. Hydrophilic nature of polymer backbone, degree of crosslinking, density and type of fixed charges, degree of ionization of ionic complexes, all play an important role. The relative importance of these factors depends upon the properties of aqueous solution in contact with the network: pH, ionic strength, presence of other solvents. Absorbed amounts of water solution in the hydrogel result by the addition of different mechanisms: polymer/solvent mixing, entropic elastic response of the network, Donnan type equilibrium and electrostatic interactions among fixed charges [13–15]. Dry hydrogel microporosity represents a futher positive contribution to the material swelling capacity.

* Corresponding author. Tel.: +39 832 297321; fax: +39 832 297525.
E-mail address: alessandro.sannino@unile.it (A. Sannino).

In fact, porous hydrogels significantly increase their equilibrium sorption properties due to capillary effects, which increase water retention in the free state. Moreover, the presence of an open porosity in the hydrogel increases the surface area to volume ratio and therefore enhances the diffusion rate of the solvent within the material. The use of lyotropic surfactant phases [16,17] leads to a rich variety of morphologies such as layer like architectures, 'cauliflower' structures, and gel sheets or platelets with a pore size spanning from hundreds of nanometers to the micrometers, depending on the types of monomers and surfactants. Ikada and colleagues [18] introduced a controlled open porosity in a bulk hydrogel by means of a freeze-drying technique. Other techniques are based on the segregation of the solvent from the polymer network during the polymerization process [19]. Park [20–22] developed a bubbling technique to induce an open porosity within polymer gels based on the entrapment of CO_2 bubbles within the polymer network during the crosslinking reaction. Porous hydrogel presented higher swelling capacity and faster swelling kinetics when compared to bulky hydrogels.

Research in the field of superabsorbents focuses also on material's biodegradability. Modern superabsorbents for personal care industry are acrylamide based products and, thus, non-biodegradable. The renewed attention of institutions and public opinion towards environmental protection issues awakened producers in the development of biodegradable superabsorbents [23].

A cellulose based superabsorbent, with sorption properties similar to those displayed by acrylate based products, to be used as a substitute of the traditional acrylamide based products, has been recently patented [24, 25]. Novelty of these products is related not only to their physical microstructure, which displays a porosity able to significantly increase hydrogel sorption capacity, but also in the possibility to modulating the physical structure and chemical (amount of polyelectrolyte and not polyelectrolyte polymers constituting the network) composition to modulating their sensitivity to external solution variations. Here we present the study of the relationship between the hydrogel microstructure and its sorption properties; in particular, the complex phenomenon of coupling the thermodynamic of sorption and physical–chemical network parameters has been investigated. This has been carried out changing both the properties of the absorbing medium (pH, ionic strength) and the hydrogel network structure (e.g. the degree of crosslinking and the weight ratio of the cellulose derivatives of the backbone).

Moreover, materials with a different degree of porosity have been prepared, acting on the desiccation process. Samples desiccated by phase inversion in acetone, a non solvent for the polymer, display an higher degree of porosity when compared with the ones obtained by freeze drying or desiccated in air atmosphere at room conditions. Equilibrium sorption properties of the micro-porous samples have been studied in different water solutions, and results have been compared with those obtained for the non porous ones.

2. Experimental section

2.1. Materials

Cellulose based hydrogels have been synthesized crosslinking water mixtures of carboxymethylecellulose sodium salt (CMCNa) and hydroxyethylcellulose (HEC), using divinylsulphone (DVS) as crosslinking agent. CMCNa and HEC are both cellulose ethers, where substituting groups are methylcarboxylic groups and oxyethylene chains, respectively (Fig. 1). The degree of substitution and the relative distribution of substituents in C-2, C-3 and C-6 position may strongly affects the equilibrium sorption properties of these polymers.

CMCNa (cod. 41,933-8), HEC (cod. 30,683-3) and DVS (cod. V370-0) were purchased from Aldrich Chimica s.r.l. Milano and used as received.

The NaCl for tests at different ionic strength was purchased from Aldrich; the buffer solutions for the tests at different pH from Fluka. All the products were used without any further purification.

2.2. Samples preparation

Crosslinking reaction has been performed according to procedures reported in the literature [23,24,26]. First, liquid DVS has been added to the distilled water, stirring gently at room temperature till complete dissolution (approx. 5 min). Batches with different DVS concentrations (0.04, 0.066, 0.1 and 0.133 M) were prepared in order to obtain samples with various degrees of crosslinking. A mixture of CMCNa and HEC has been added to the DVS water solution till a concentration of 2% by weight. Four different CMCNa/HEC weight ratios have been investigated (0, 1/3, 1/1 and 3/1). CMCNa dissolution is slow at the concentration adopted. Thus, first the HEC has been added to the DVS water solution till a clear solution was obtained, after about 5 min, with a slight increase of the viscosity. Then, the CMCNa has been added to the obtained solution, and the mixing has been carried out overnight, till a clear solution was obtained, with a significant increase of the viscosity (viscosity data are not reported). After the mixing stage, an aqueous solution of KOH was added as catalyst to the polymer solution until a pH = 12.5 was reached. Hydrogel formation occurred in about 15 h in air atmosphere at room conditions.

The obtained partially swollen hydrogel was cut in small disks with a volume of about 1 cm^3 each. In order to remove the unreacted DVS, the KOH and other impurities, hydrogel disks were soaked in distilled water ('washing' stage) till the equilibrium swelling was reached under continuous stirring. Water during this stage, used in large excess, has been changed with fresh water several times.

NaCMC   R = -H, -CH2COONa

HEC   R = -H, -CH2CH2OH,

           -CH2CH2OCH2CH2OH,
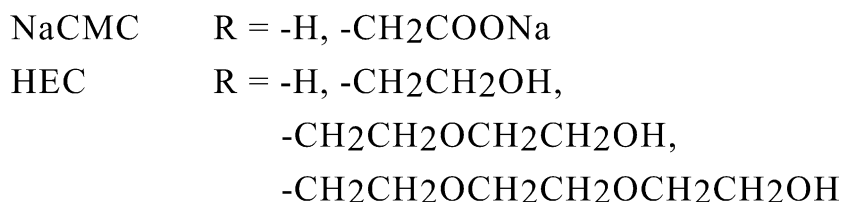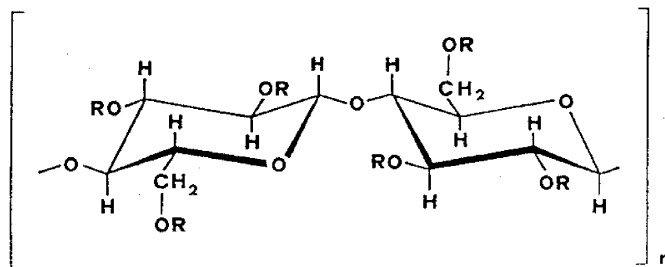
           -CH2CH2OCH2CH2OCH2CH2OH

Fig. 1. Scheme of the CMCNa and HEC unit.

Three different desiccation techniques have been adopted in order to get a dry xerogel sample: desiccation at atmospheric conditions, desiccation under vacuum and desiccation by phase inversion in acetone. The first consisted in keeping the sample in air atmosphere at room conditions, in a clean environment, till complete desiccation was achieved (i.e. sample weight did not change with time). Desiccation under vacuum has been performed keeping the hydrogel under vacuum (10^{-4} bar) at room temperature for 24 h. Desiccation by phase inversion in acetone has been carried out immersing the swollen sample in a liquid acetone bath (97% pure acetone). Liquid acetone has been periodically changed with fresh acetone, to remove water expelled from the hydrogel during the shrinking process, till a white glassy xerogel sample precipitation; thus, the precipitated sample has been collected from the bath and further dried in oven in air atmosphere at 35 °C for 5 h, to remove the excess of acetone on the sample surface.

For the sake of comparison, HEC crosslinked samples were also prepared.

The presence of HEC is necessary to promote inter-molecular rather than intramolecular crosslinking. In fact, poor crosslinking efficiency is reported [23] if only CMCNa is used, due both to the electrostatic repulsion between polyelectrolyte chains and to the high degree of substitution of hydroxyl groups at C6 most reactive position.

2.3. Methods

The equilibrium swelling was measured by weighting samples after their immersion in water solutions for about 24 h. During this period of time, hydrogel samples have been removed from water solution, weighed and then immersed again in the solution. The water solution has been periodically changed with fresh solution during this period of time, in order to remove impurities expelled from the hydrogel during the swelling. Any weight change was

observed after 24 h, thus assuming that equilibrium swelling was achieved. Only equilibrium swelling data are reported in this work. The effect of ion concentration on hydrogel equilibrium swelling capacity was evaluated by equilibrating desiccated gel samples in solutions at different NaCl concentrations (0.01; 0.05; 0.15; 0.5 and 1 mol/l). Samples were then weighted again after 24 h, when equilibrium swelling was reached (i.e. their weight remained constant).

The same procedure was adopted for the analysis of the swelling capacity at different pH ($2 \div 10$). Buffer solutions at different pH were used, adding to the solution a proper amount of salt in order to obtain the same ionic strength for all the buffer solutions. All the measurements were performed in air atmosphere at room conditions. Samples were weighed with a 'Mettler' balance (10^{-5} sensitivity).

For the sake of comparison, equilibrium swelling test were performed for all the samples in distilled water.

Hydrogel microstructure of cryogenic fracture of dry samples desiccated by the three different techniques mentioned above has been analysed by means of scanning electron microscope (SEM), model JEOL 6400.

3. Results and discussion

A hydrolized gel can change its volume varying the composition of the solution in which it is immersed. Charged groups of the polyelectrolyte structure play an essential rule in this phenomenon [13]. In order to evaluating the influence of the characteristics of the external solution on hydrogel equilibrium sorption capacity, swelling experiments have been performed in solution differing both for ionic strength and pH.

3.1. Influence of the ionic strength of the external solution on hydrogel equilibrium swelling capacity and morphological analysis

A first set of samples has been prepared for swelling measurements solutions at different ionic strength. The value of the pH was 7 for all the solutions tested. Samples have been prepared starting from different CMCNa/HEC weight ratio (0, 1/3, 1/1, 3/1) and different crosslinking agent (DVS) concentration: 0.04, 0.066, 0.1 mol/l. Samples have been desiccated with different techniques: desiccation in air atmosphere at room conditions, desiccation under vacuum and desiccation by extraction with acetone.

Figs. 2–4 refer to samples obtained keeping fixed the amount of crosslinking agent (DVS) at a concentration of 0.04 mol/l, and varying the NaCMC weight ratio (3/1, 1/1, 1/3, 0). A monotonic decrease of the swelling ratio has been observed increasing the ionic strength of the external solution for all the samples tested, independently from the chemical composition and the desiccation procedure adopted. This behaviour has been related to the polyelectrolyte nature of the polymer chains. In fact, fixed charges on the polymer backbone play an essential role in swelling mechanism. This is related both for to the electrostatic repulsion between charges of the same sign, which contributes to expand the polymer structure, and to the 'Donnan type' absorption contribution to water sorption, which promotes an osmotic pressure, π_I, favouring the water to enter the hydrogel. Both these contributions to the hydrogel swelling depend to the difference in ion concentration between the internal of the gel (c) and the external

solution (c^*), as reported in literature [13,27]:

$$\pi_I = RT\left[\frac{ic_2}{z_- - n(c^* - c)}\right] \qquad (1)$$

where c_2 is the concentration of fixed ionic charges on the network, i is their dissociation degree, z_- their charge and n the number of ions generated by the dissociation of one salt molecule.

In particular, increasing the number of fixed charges on the polymer network increases the hydrogel swelling capacity, which, instead, decreases increasing the ionic strength of the external solution. This is due to a neutralization of the fixed charges by the free charges present in the solution bathing the gel, thus reducing both the repulsion effect between polymer chains and the osmotic contribution to the swelling due to the Donnan contribution. This last effect can be seen also as a reduction of the chemical potential of water in the external solution, with a consequent reduction of its ability to penetrate the gel.

We can also observe that samples desiccated by extraction with acetone (Fig. 2) show the higher equilibrium swelling capability, if compared with those desiccated by other procedures (Figs. 3 and 4). This has been attributed to a different microstructure induced in the hydrogel during desiccation. In fact, as shown in the SEM pictures (Fig. 5), samples desiccated by extraction with acetone seem to display a porosity, induced by the fast water extraction procedure, higher than those desiccated under vacuum and in air atmosphere, respectively.

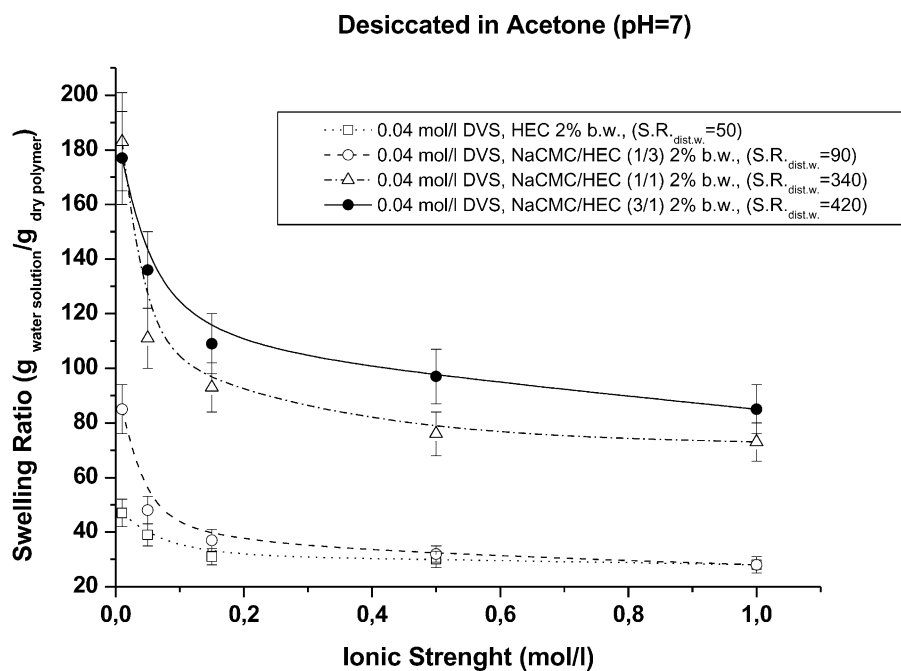The swelling ratio also decreases decreasing the NaCMC/HEC weight ratio, for all the desiccation

Fig. 2. Plot of the equilibrium swelling ratio vs ionic strength of the external solution bathing the hydrogel. Samples have been obtained all with the same DVS crosslinker concentration (0.04 mol/l) and with a different CMCNa/HEC weigh ratio; all the samples have been desiccated in acetone.
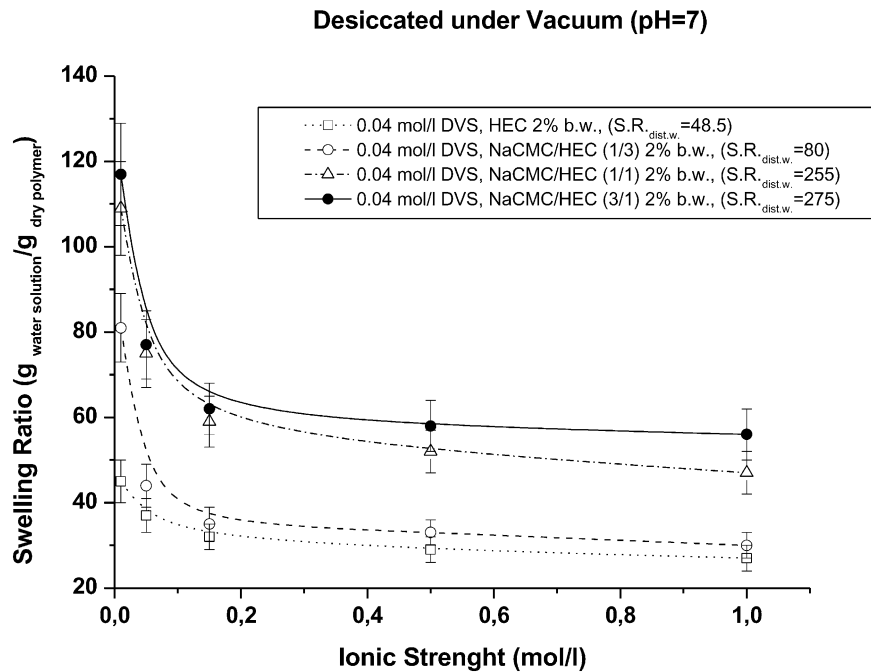
Desiccated under Vacuum (pH=7)

Fig. 3. Plot of the equilibrium swelling ratio vs ionic strength of the external solution bathing the hydrogel. Samples have been obtained all with the same DVS crosslinker concentration (0.04 mol/l) and with a different CMCNa/HEC weigh ratio; all the samples have been desiccated under vacuum.

procedures investigated (Figs. 2–4). This has been attributed to the polyelectrolyte nature of the NaCMC, which is responsible for the Donnan contribution to hydrogel swelling. Thus, increasing the HEC content in the starting polymer mixture, decreases the ionic contribution to the water absorption. Both in Figs. 2 and 4 there is an intersection between the curves related to NaCMC/HEC weight ratios of 3/1 and 1/1; this was attributed to an higher sensitivity to changes in ionic strength of the external solution of the samples with an higher amount of the polyelectrolite component (NaCMC), which decreases its equilibrium swelling capacity as the ionic strength of the

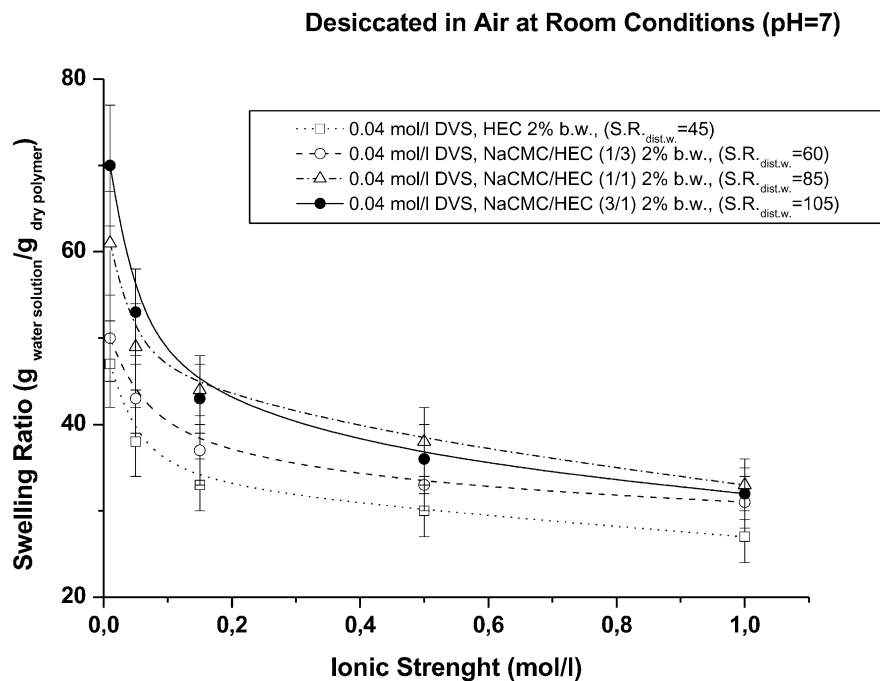**Desiccated in Air at Room Conditions (pH=7)**

Fig. 4. Plot of the equilibrium swelling ratio vs ionic strength of the external solution bathing the hydrogel. Samples have been obtained all with the same DVS crosslinker concentration (0.04 mol/l) and with a different CMCNa/HEC weigh ratio; all the samples have been desiccated in air atmosphere at room conditions.
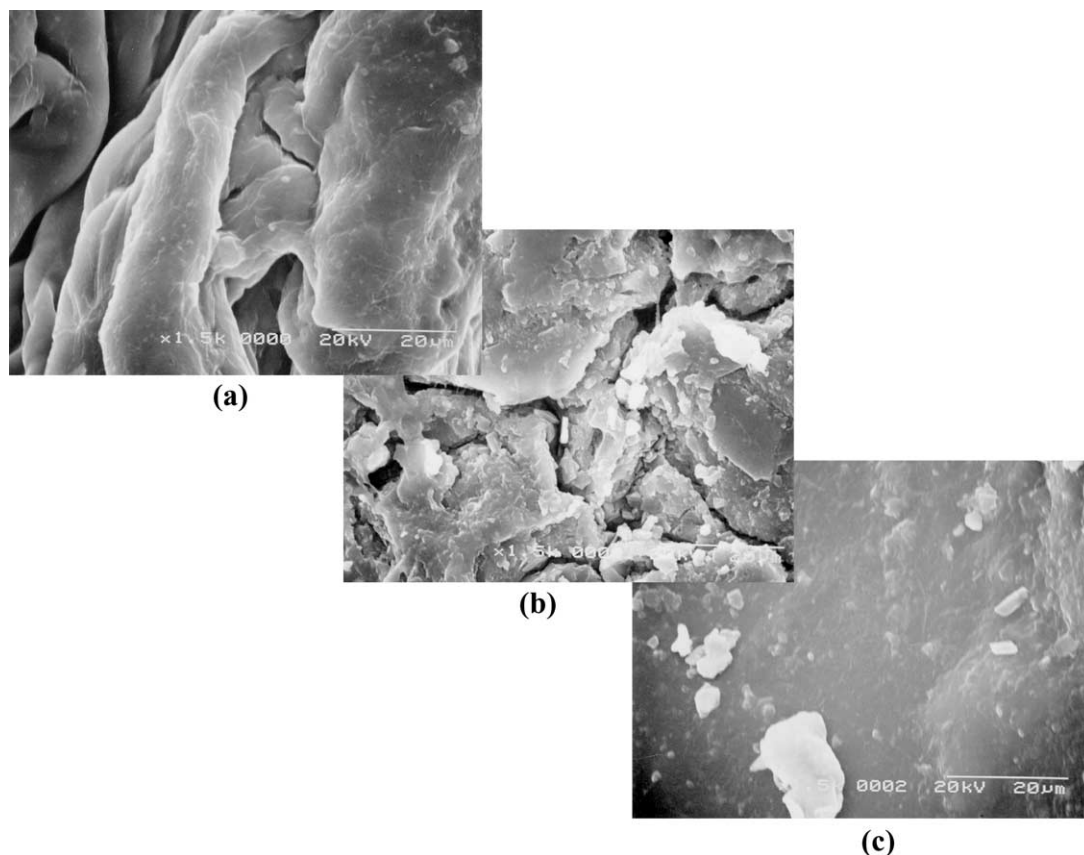
Fig. 5. SEM pictures of (a) samples desiccated in acetone; (b) under vacuum; (c) in air atmosphere at room conditions.

external solution is, even slightly, changed. This sensitivity to changes in ionic strength of the external solution is not displayed for samples constituted only by HEC (the non polyelectrolite component), which do not change their absorption capacity almost for all the values of ionic strength, independently by the desiccation procedure adopted. Moreover, values of swelling ratio for all the samples in Figs. 2–4 are lower than those obtained in distilled water.

Data of equilibrium swelling ratio as a function of the ionic strength of the external solution have been obtained on a second set of samples (Fig. 6), obtained keeping fixed the NaCMC/HEC weight ratio (3/1) and varying the crosslinking agent (DVS) concentration. All the samples were desiccated in acetone. As in the previous case, a monotonic reduction of the swelling capacity has been observed increasing the ionic strength of the external solution. We should also observe that, increasing the DVS concentration, decreases the absorption capacity. This has been explained with an increase of the degree of crosslinking of the gel network, as reported in literature [28,29], since the crosslinking agent is in stoichiometric defect. Thus, the higher the degree of crosslinking, the higher the elastic contribution (entropic in nature) opposite to the hydrogel swelling.

3.2. Influence of the pH of the external solution on hydrogel equilibrium sorption capacity

In this analysis, the ionic strength of the different buffer solutions was set at a value of 0.4 mol/l, while the pH was changed ranging from 2 to 10. Results are reported in Figs. 7–10. All the samples have been prepared starting from the same value of DVS concentration, differing for the value of the NaCMC/HEC weight ratio (3/1, 1/1, 1/3 and 0) and for the desiccation procedure. For all the samples, an increase of the swelling ratio has been observed increasing the pH of the external solution, with an exception for the sample constituted by only HEC (weight ratio NaCMC/HEC=0). Most samples displayed a maximum at a value of pH between 8 and 10.

This has been related to the dissociation of the carboxylic groups present on NaCMC chains, depending upon the pH of the surrounding environment. As the pH of the external solution decreases, decreases the number of the carboxylic groups dissociated on the polymer backbone. Thus, decreases the ionic contribution to the hydrogel equilibrium swelling capacity. On the other hand, increasing the pH of the external solution, increases the number of the dissociated carboxylic groups; thus, increases the 'Donnan type' contribution to water sorption due to the presence of fixed charges, increasing the swelling equilibrium capacity,

Desiccated in Acetone (pH=7)
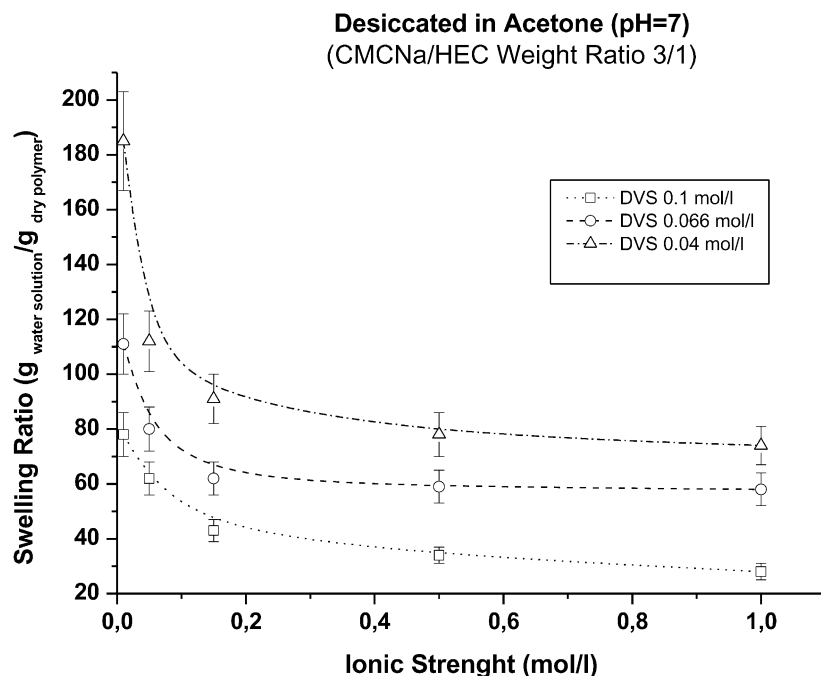(CMCNa/HEC Weight Ratio 3/1)

Fig. 6. Plot of the equilibrium swelling ratio vs ionic strength of the external solution bathing the hydrogel. Samples have been obtained all with the same CMCNa/HEC weight ratio (3/1) and with a different DVS concentration; all the samples have been desiccated in acetone.

as reported in Figs. 7–9. The supply of H+ ions from the dissociated groups on the backbone is, however, limited; at a certain value of the pH all the carboxylic groups will be dissociated, giving rise to a fully charged network. At this point, the hydrogel equilibrium swelling capacity displays a maximum, as observed in the plot in Figs. 7–9.

Also the hydrogel desiccation procedure influences the hydrogel absorption capacity, in terms of different capillary retention. Hydrogels desiccated in acetone display higher absorption capacity when compared to those desiccated under vacuum and at atmospheric pressure, respectively, for the same reasons discussed in the previous section.
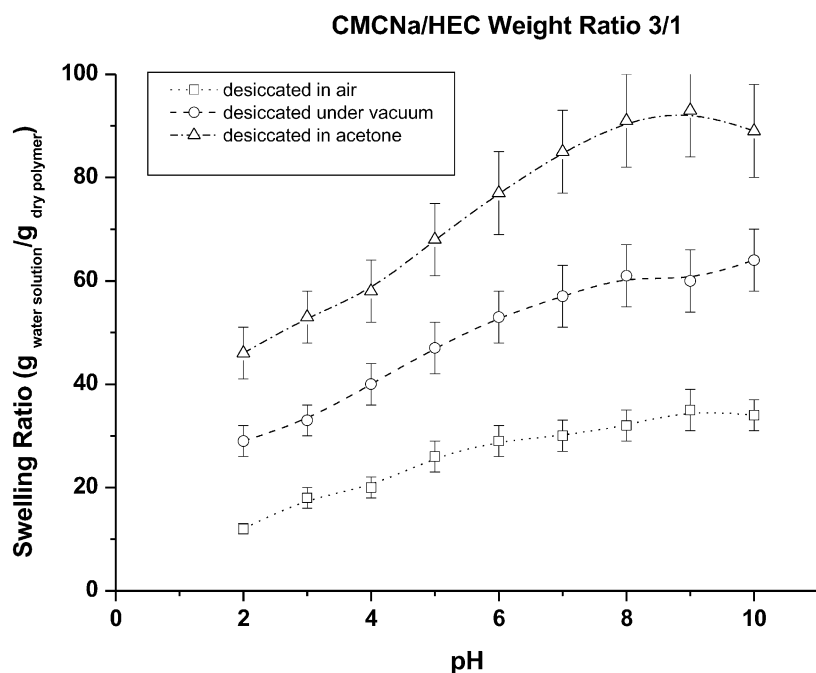
CMCNa/HEC Weight Ratio 3/1

Fig. 7. Plot of the equilibrium swelling ratio vs the pH of the external solution bathing the hydrogel. Samples have been obtained all with the same CMCNa/HEC weight ratio (3/1) and with a DVS concentration equal to 0.04 mol/l. Data are reported for samples desiccated in acetone, under vacuum and in air atmosphere at room conditions.

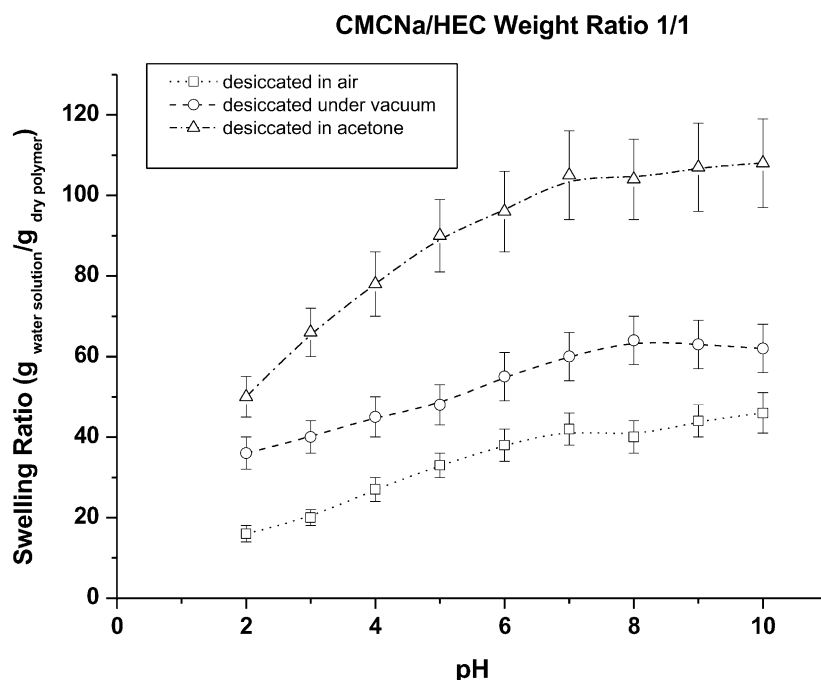**CMCNa/HEC Weight Ratio 1/1**

Fig. 8. Plot of the equilibrium swelling ratio vs the pH of the external solution bathing the hydrogel. Samples have been obtained all with the same CMCNa/HEC weight ratio (1/1) and with a DVS concentration equal to 0.04 mol/l. Data are reported for samples desiccated in acetone, under vacuum and in air atmosphere at room conditions.

Moreover, an increase of the NaCMC in the starting polymer mixture acts substantially in the same way observed for the ionic strength measurements, supplying a greater number of fixed charges on the polymer backbone, thus increasing the ionic contribution to hydrogel swelling capacity. We can also observe that, in the limit of very low pH values, almost all the carboxylic groups are in the undissociated form, and the material acts as a pure HEC based gel (not polyelectrolite), whatever the NaCMC content in the gel mixture. In Fig. 10, the swelling capacity
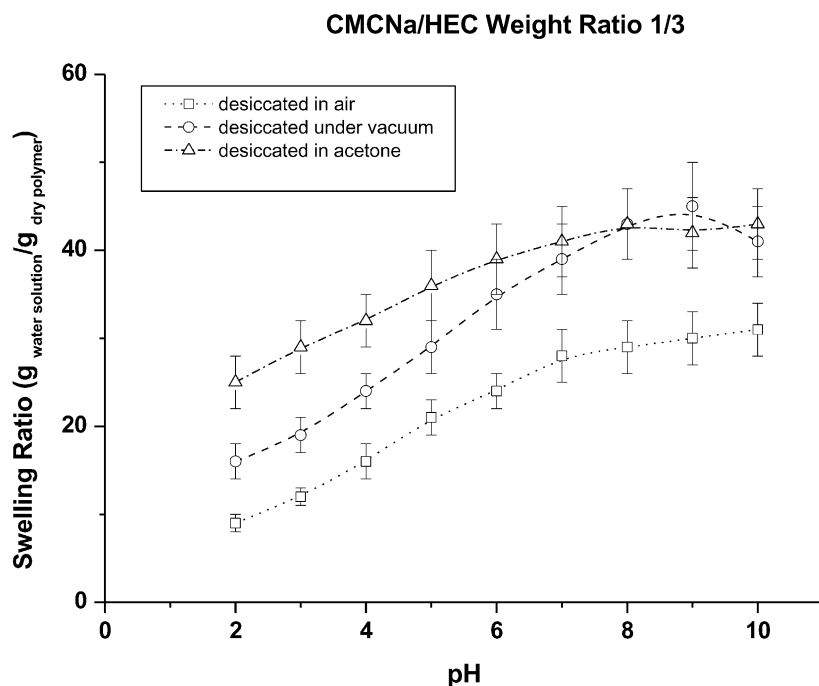
CMCNa/HEC Weight Ratio 1/3

Fig. 9. Plot of the equilibrium swelling ratio vs the pH of the external solution bathing the hydrogel. Samples have been obtained all with the same CMCNa/HEC weight ratio (1/3) and with a DVS concentration equal to 0.04 mol/l. Data are reported for samples desiccated in acetone, under vacuum and in air atmosphere at room conditions.
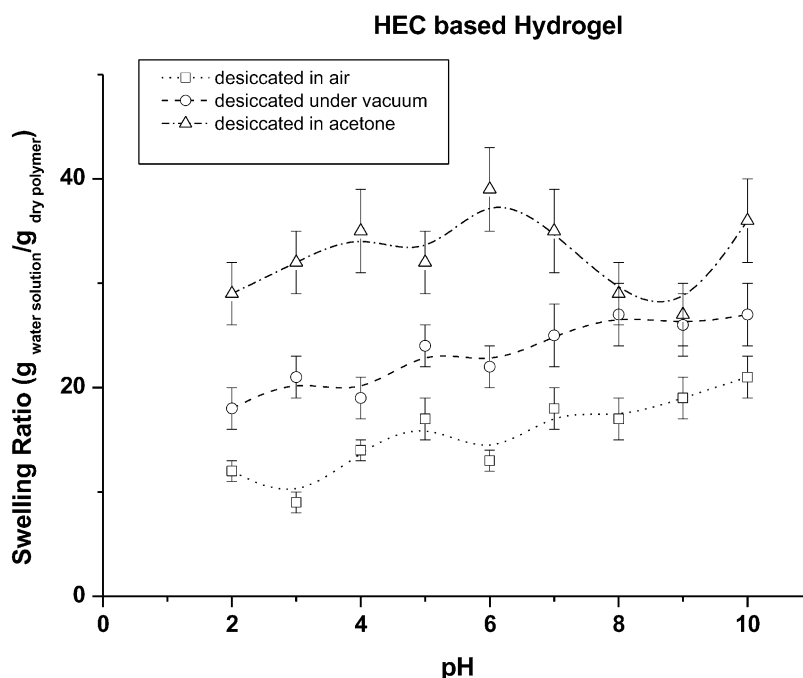
HEC based Hydrogel

Fig. 10. Plot of the equilibrium swelling ratio vs the pH of the external solution bathing the hydrogel. Samples have been obtained all with HEC and with a DVS concentration equal to 0.04 mol/l. Data are reported for samples desiccated in acetone, under vacuum and in air atmosphere at room conditions.

of samples constituted by only HEC is reported as a function of the pH and of the different desiccation procedures adopted. Any significant difference is detected for samples of the same type. The capillary retention effect, attributed to the different desiccation procedures, seems to be responsible for the difference between samples desiccated with acetone, under vacuum and at atmospheric pressure.

4. Conclusions

A novel class of cellulose based micro-porous super-absorbents has been developed and its equilibrium sorption properties in different media have been studied. Both the effect of the hydrogel chemical structure and its physical properties on the swelling behaviour have been investigated.

In terms of material's chemical parameters, it has been observed that, increasing the degree of crosslinking of the network, decreases its equilibrium sorption capacity, for all the different solutions tested, as well as an increase in the amount of fixed charges on the material's backbone increases its sorption capacity.

Physically, the presence of a microporosity, related to the hydrogel desiccation procedure, significantly increases its equilibrium sorption capacity, and this has been related to a capillary retention effect.

The effect of variation of the properties of the external solution in contact with the hydrogel on its equilibrium sorption capacity has been also investigated. In particular, swelling measurements have been carried out in solutions at different ionic strength and pH, and high sensitivity to the

external solution variations was displayed by all the different materials tested.

Sorption properties of micro-porous hydrogels, coupled to the possibility to modulating the swelling capacity acting on both chemical and physical parameters, makes these materials a suitable low environmental impact substitutes in most of the industrial applications of superabsorbents, and in particular in the field of personal care absorbent products.

References

[1] Gross JR. The evolution of absorbent materials. In: Brannon-Peppas L, Harland RS, editors. Absorbent polymer technology. Amsterdam: Elsevier; 1990.

[2] Masuda F. Superabsorbent polymers. Kyoritsu, Shuppann: Japan Polymer Society; 1987.

[3] Baker JP, Stephens DR, Blanch HW, Prausnitz JM. Macromolecules 1992;25:1955.

[4] Hooper HH, Baker DR, Blanch HW, Prausnitz JM. Macromolecules 1990;23:1096.

[5] Takeda H, Taniguchi Y. Patent US 4,525,527; 1985.

[6] Irie Y, Iwasaki K, Hatsuda T, Kimura K, Harada N, Ishizaki K, et al. Patent US 4,920,202; 1990.

[7] Park TG. Biomaterials 1999;20:517–21.

[8] Makino K, Hiyoshi J, Ohshima H. Colloids Surf B 2001;20:341–6.

[9] Ichikawa H, Fukumori Y. J Controlled Release 2000;63:107–19.

[10] Holtz JH, Asher SA. Nature 1997;389:829–32.

[11] Beebe DJ, Moore JS, Bauer JM, Yu Q, Liu RH, Devadoss C, et al. Nature 2000;404:588–90.

[12] Bergbreiter DE, Case BL, Liu Y-S, Caraway JW. Macromolecules 1998;31:6053–62.

[13] Flory JP. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.

[14] Harsh DC, Gehrke SH. Characterization of ionic water absorbent

polymers: determination of ionic content and effective crosslink density. In: Brannon-Peppas L, Harland RS, editors. Absorbent polymer technology. Amsterdam: Elsevier; 1990. p. 103–24.

[15] Brannon-Peppas L, Peppas NA. The equilibrium swelling behavior of porous and non-porous hydrogels. In: Brannon-Peppas L, Harland RS, editors. Absorbent polymer technology. Amsterdam: Elsevier; 1990. p. 67–102.

[16] Antonietti M, Caruso RA, Goltner CG, Weissenberger MC. Macromolecules 1999;32:1383.

[17] Antonietti M, Goltner C, Henyze H-P. Langmuir 1998;14:2670.

[18] Kang H-W, Tabata Y, Ikada Y. Fabrication of porous gelatin scaffolds for tissue engineering. Biomaterials 1999;20:1339–44.

[19] Monleon Pradas M, Gomez Ribelles JL, Serrano Aroca A, Gallego Ferrer G, Suay Anton J, Pissis P. Porous poly(2-hydroxyethyl acrylate) hydrogels. Polymer 2001;42:4667–74.

[20] Chen J, Park K. Synthesis and characterization of superporous hydrogel composites. J Controlled Release 2000;65:73–82.

[21] Chen J, Blevins WE, Park H, Park K. Gastric retention properties of superporous hydrogel composites. J Controlled Release 2000;64: 39–51.

[22] Chen J, Park K. Synthesis of fast-swelling, superporous sucrose hydrogels. Carbohydr Polym 2000;41:259–68.

[23] Anbergen U, Opperman W. Polymer 1990;31:1854.

[24] Del Nobile MA, Esposito F, Mensitieri G, Sannino A. Applicant: SCA Molnlycke AB, US Patent: 6,630,422; 2003.

[25] Mensitieri G, Porro F, Nicolais L, Sannino A. Applicant SCA Molnlycke AB, Int Pub No: WO 01/68713 A2; 2001.

[26] Esposito F, Del Nobile MA, Mensitieri G, Nicolais L. J Appl Polym Sci 1996;60:2403.

[27] Overbeek J. Prog Biophys Chem 1956;6:57.

[28] Sannino A, Lenzi F, Borriello A, Porro F, Capitani D, Mensitieri G. Polymer 2003;44:1577–88.

[29] Capitani D, Del Nobile MA, Mensitieri G, Sannino A, Segre AL. Macromolecules 2000;33:430–7.