

Introduction of Molecular Spacers Between the Crosslinks of a Cellulose-Based Superabsorbent Hydrogel: Effects on the Equilibrium Sorption Properties

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Received 29 October 2002; accepted 14 January 2003

ABSTRACT: The possibility to modulate cellulose-based hydrogel sorption properties through the insertion of molecular spacers between the crosslinks was investigated. Starting polymers were the sodium salt of carboxymethyl cellulose, a polyelectrolyte cellulose derivative, and hydroxyethyl cellulose, a nonpolyelectrolyte derivative. Poly(ethylene glycol) with various molecular weights was linked by its free ends at two divinyl sulfone (DVS) crosslinker molecules, to increase the average distance between two crosslinking sites and thus to act as a spacer. Both the effect of the concentration and the molecular weight of the spacer on the hydrogel final sorption properties in water and water

solutions were investigated. The presence of the spacer allowed us also to perform hydrogel synthesis with higher concentrations of cellulose in the reactive mixture, and the effect of the polymer concentration in the batch was analyzed. Hydrogels obtained in the presence of spacers displayed significantly higher equilibrium sorption properties than those of the ones obtained without spacers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 168–174, 2003

Key words: hydrogels; polyelectrolytes; crosslinking; swelling

INTRODUCTION

Chemical hydrogels are a particular class of macromolecular gels, obtained by chemical stabilization of hydrophilic polymers in a tridimensional network, in which the dispersed phase is water present in a substantial quantity. They are involved in many industrial applications, such as the controlled release of drugs,^{1,2} modern soft contact lenses, or superabsorbents for personal hygiene products,^{3–6} such as baby diapers or female hygiene absorbents. Other advanced applications, such as fast-response artificial muscles,⁷ scaffolds for cellular growth in tissue engineering, or body water-elimination systems,⁸ constitute the frontier in biomaterials research.

Superabsorbents for hygiene products represent, however, 80% of the hydrogel production nowadays, with more than 8000 tons of demand in 1999 in the European market alone. This attractive business has pushed multinational groups toward the development of new technologies both in the chemistry definition^{9,10} and the production processes^{11,12} of these materials. An important focus of the research in this field

is the material's biodegradability. Modern superabsorbents are acrylamide-based products and, thus, are nonbiodegradable. The renewed attention of institutions and public opinion toward environmental-protection issues sensitized some producers to the development of biodegradable superabsorbents.¹³

A potential biodegradable cellulose-based superabsorbent, with sorption properties similar to those displayed by acrylate-based products,¹⁴ was recently patented.⁶ This material was obtained by chemical crosslinking of cellulose polyelectrolyte derivatives using small difunctional molecules as crosslinkers, which covalently bound different polymer molecules in a tridimensional hydrophilic network. Once in contact with water or water solutions, network expansion is prevented by the crosslinking junction, providing an elastic (entropic in nature) response, which highly influences hydrogel swelling properties.¹⁵ Hence, two important parameters for the evaluation of the material swelling capacity are the length and the flexibility of the crosslinking molecules.

The aim of this work was to increase the equilibrium sorption capacity of a cellulose-based superabsorbent hydrogel by introducing difunctional molecules capable of producing chain extension of the crosslinking molecules. These molecules, acting as molecular spacers, increase the length and flexibility of the crosslinking junctions, thus allowing the macromolecular network to further expand. The final

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Contract grant sponsor: SCA Monlycke, AB.

properties of the hydrogels were analyzed in terms of the swelling capacity, monitored as a function of the degree of crosslinking in the presence of spacer molecules and at different polymer concentrations in the reactive mass. The action of spacers was demonstrated to be particularly effective when high polymer concentrations were investigated, preventing a constraining action to the material's swelling due to higher polymer molecular packing.

Approach to the evaluation of spacer effect on hydrogel equilibrium sorption capacity

The hydrogel equilibrium swelling capacity depends on both internal parameters, proper to the macromolecular network, and external, proper to the environment contacting the material. In particular, for a polyelectrolyte network, characterized by fixed charges on the macromolecular backbone, there are four polymer properties affecting polymer swelling: (1) the polymer chain hydrophilicity, which promotes polymer-solvent mixing and thus promotes material swelling when in contact with water and water solutions; (2) the presence of fixed ionic charges, which induces a "Donnan-type" effect, an osmotic effect associated with the concentration of ionic charges in the hydrogel, which induces more water to penetrate the hydrogel to dilute this higher charges concentration; (3) the electrostatic repulsion between the charges of the same sign present on the polymer backbone, which tends to expand the macromolecular network and thus promotes polymer swelling; and (4) the elastic response, entropic in nature, of the crosslinks which stabilize the polymer chains in the hydrogel network and counteracts polymer swelling.

The second and third properties mentioned above, promoting polymer swelling, are strictly related to the use of a polyelectrolyte cellulose-based system, in particular, a mixture of carboxymethyl cellulose sodium salt (CMCNa), which is a polyelectrolyte, and hydroxyethyl cellulose (HEC), which is a nonpolyelectrolyte. These contributions are not affected by the presence of spacer molecules in the range of low concentrations. The fourth property, limiting polymer swelling (i.e., the elastic response of the crosslinks), depends on an effective degree of crosslinking of the polymer network. The degree of crosslinking can be evaluated as a function of the average molecular weight between two adjacent crosslinks. In the case of a *perfect* network with no dangling ends, loops, and entanglements, which could be obtained by joining pairs of segments of linear chains through chemical crosslinks, the concentration of *elastically effective* chain elements, $\rho_x = \nu_e/V$, corresponds to the concentration of all chemically crosslinked polymer segments (ν/V):

$$\rho_x = \frac{\nu_e}{V} = \frac{\nu}{V} = \frac{1}{\bar{\nu}\bar{M}_c} \quad (1)$$

where \bar{V} is the specific volume of the polymer; \bar{M}_c , the average molecular weight between crosslinks; and ν_e/V , the moles of *elastically effective* chains per unit volume of the network. According to the definition given above, ρ_x and $\rho_x/2$ represent, respectively, the moles of polymer segments engaged by crosslinks and the moles of crosslinks per unit volume of the network.

Clearly, the higher the length of the crosslinker, the higher the average distance between two adjacent joined sites. Thus, the spacer plays the multiple role of (a) increasing the macromolecular network expanding properties; (b) increasing the average distance between two adjacent crosslinking sites, thus reducing the effective crosslinking density of the polymer network; and (c) decreasing the number of crosslinker molecules active for the crosslinking reaction, starting from the same initial crosslinker concentration.

As already mentioned, the industrial field of interest in which these materials find wider application is represented by personal-care products. Thus, a set of sorption measurements was carried out in synthetic urine, in which the high ionic strength of the solution negatively affected the hydrogel sorption properties. The effect of the external parameters, affecting the hydrogel swelling capacity, pH, and ionic strength of the external solution bathing the gel, were not further analyzed. Further studies are in progress for the evaluation of the influence of these parameters in the presence of molecular spacers.

Hydrogel preparation

The materials investigated in this work were obtained by the chemical crosslinking of CMCNa and HEC chains stabilized in a tridimensional network. The synthesis procedure for low polymer concentrations and without molecular spacers, together with the analysis of the degree of crosslinking of the polymer network, was already reported elsewhere.^{14,16} According to this procedure, the reaction is performed in an aqueous solution at a 2% polymer concentration by weight; divinyl sulfone (DVS) is added to the solution as a crosslinking agent, in a concentration which can be modulated as a function of the degree of crosslinking to be induced in the network. After complete mixing, KOH is added to the solution as a catalyst, up to a 0.02M concentration. At this stage, the crosslinking reaction takes place and solution viscosity rapidly increases.

Synthesis products are partially swollen gels; thus, a purification and desiccation procedure is required to remove from the hydrogel the KOH, the unreacted

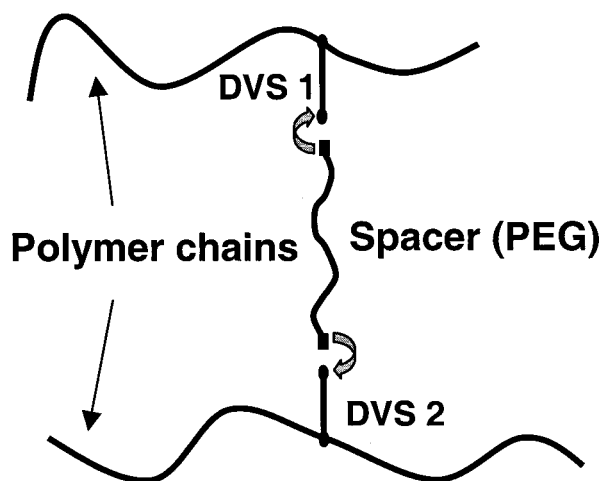


Figure 1 Scheme of the crosslinking bridge in the polymer network in presence of spacers.

DVS, and all the other eventual impurities. Purification is carried out by swelling the material several times in distilled water, until the equilibrium sorption capacity is reached (i.e., the sample weight remains constant). The last step is the desiccation. Two techniques were adopted: The first was a phase inversion in a nonsolvent for the polymer, such as acetone; the second was a simple water elimination by evaporation in an air atmosphere at ambient conditions. It was demonstrated that the desiccation by phase inversion in acetone induces a connected microporosity in the dry hydrogel, which increases its sorption capacity for capillary retention effects.

In this work, poly(ethylene glycol) (PEG) molecular spacers between the crosslinks were also added. PEG molecules of various molecular weight were mixed in the reactive mass. The terminal OH group present on the PEG chain is supposed to be attached by one of the two unsaturated groups of the DVS molecule by a nucleophilic addition, with the same mechanism involved for the addition to the OH present on the cellulose derivative chain. Since PEG is not able to join to any group present on the cellulose backbone, a chain-extension procedure on DVS is obtained, leading to a DVS-PEG-DVS crosslinking agent. This molecule is responsible for the crosslinks between the cellulose chains due to the free unsaturated terminal group of the DVS, as presented in the scheme in Figure 1. The resulting crosslinking bridge is thus longer and more flexible than is the single-molecule DVS bridge, thus allowing higher network expansion (i.e., hydrogel swelling capacity). Hence, an analysis of the effect of the spacer insertion between crosslinks on the hydrogel equilibrium sorption properties was carried out, keeping both the spacer length (i.e., PEG average molecular weight) and the concentration constant and varying the DVS concentration or fixing the DVS concentration and varying the PEG length and

concentration. In particular, PEG molecules with a molecular weight ranging from 400 to 10,000 were used.

Another modification to the standard synthesis procedure involves the polymer concentration in the reactive batch. In particular, higher polymer (CMC + HEC) concentrations, ranging from 10 to 20% by weight, were also tested, using vigorous mixing due to the high solution viscosity. At higher polymer concentrations, the average distance between the reactive sites of the cellulose backbone was reduced, and this allowed us to reduce significantly the crosslinker concentration. Hydrogels were obtained with a crosslinker concentration less than 0.001M, starting from polymer concentrations in the reactive mix of 10%.

RESULTS AND DISCUSSION

The polyelectrolyte nature of the CMC portion of the hydrogel makes possible the development of a Donnan equilibrium between the gel and the external solution, strongly increasing the polymer swelling capacity.^{17,18} High-field NMR techniques¹⁹ revealed a 0.66 ± 0.03 degree of substitution for the carboxylic group on the CMC backbone. On the other hand, HEC is a highly hydrophilic cellulose derivative, but it is not a polyelectrolyte.

An analysis of the sorption properties was carried out on the materials obtained with different DVS and polymer concentrations in the reactive mix. Hydrogel swelling measurements were performed on materials desiccated following the procedures described above.

First, a measurement of the effect of the crosslinking degree on material's sorption capacity was performed on hydrogel synthesized starting from 2% by weight polymer solutions with a CMC/HEC weight ratio of 3/1 and two different DVS concentrations (0.04 and 0.02 mol/L) using 15% by weight of PEG of an average molecular weight of 4600 as a spacer. Two sets of samples were prepared for each DVS concentration; one set was desiccated by phase inversion with acetone, and a second set, by water evaporation at atmospheric pressure.

The swelling ratios (grams of absorbed water per gram of dry polymer), obtained with and without a spacer, are reported in Figure 2. It can be observed that increasing the DVS concentration in the reactive mix decreases the material swelling capacity. This is a consequence of an increase of the crosslinking density, associated with an improved elastic response of the polymer network counteracting the material swelling.¹⁵ Hydrogels obtained by phase inversion with acetone display a higher swelling capacity if compared to those desiccated in an ambient atmosphere, due to a high retention capacity for capillary effects

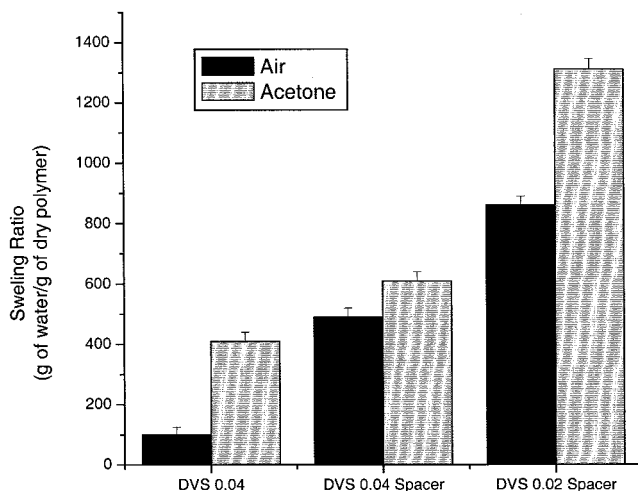


Figure 2 Hydrogel swelling ratio in distilled water versus type and concentration of the crosslinker in the reactive mix. Spacer is PEG with a molecular weight of 4600.

due to the porosity induced in the material in the first case.¹⁴

It can be observed that the presence of PEG spacers greatly increases the polymer swelling capacity. Samples with a DVS concentration of 0.04 mol/L, crosslinked with spacers and desiccated in acetone, display swelling ratios of about 600 in distilled water, while the gels without a spacer are characterized by values of about 400. A further increase of the swelling ratio, up to 1300, was observed when decreasing the DVS concentration in the reactive mixture to a value of 0.02 mol/L, in the presence of spacers.

The sorption capacity of the samples, desiccated in an ambient atmosphere, is characterized by swelling ratios more than eight times higher than for the ones without spacers. On the other hand, little difference in the sorption capacity, as a function of the desiccation procedure, is observed for samples with a DVS concentration of 0.04 mol/L crosslinked with a spacer. This result is particularly interesting for industrial aspects, where the substitution of the procedure of phase inversion in acetone by desiccation by evaporation in the atmosphere would mean an easier, cost-effective, and more environmentally friendly process.

A second set of samples was processed in the mixer, increasing the polymer concentration and decreasing the crosslinker concentration. This would lead to a double advantage when crosslinking is scaled-up to a production process: First, increasing the polymer concentration in the reactive mix implies a reduction of the amount of water to remove in the drying stage; second, decreasing the DVS concentration, to have a negligible amount of an unreacted crosslinker, would avoid the soaking procedure, onerous in terms of industrial costs.

A graph of the swelling ratio as a function of polymer concentration in the reactive mix is presented in

Figure 3. The DVS concentration was 0.0016 mol/L for all the samples. PEG of molecular weight 4600 was used as a spacer in a fixed concentration (0.77% by weight of the total reactive mass).

The swelling ratios are much lower than are the ones observed for materials obtained with low polymer concentrations, and this was attributed to a higher polymer chain interpenetration during the crosslinking reaction, with a consequent higher effective degree of crosslinking and, thus, a higher elastic response counteracting the hydrogel swelling. However, increasing the polymer concentration increases process feasibility, as mentioned above.

To increase polymer swelling properties for material synthesized at high polymer concentrations, a significant reduction of DVS in the reaction mix was tested. The hydrogel swelling capacity, as a function of the crosslinker concentration in the mixer, is reported in Figure 4. The polymer concentration was 10% by weight for all the samples, and a PEG spacer of 4600 molecular weight was used in the same concentration as for the former set of samples. A decrease in the swelling capacity was observed to increase the DVS concentration, which is related to the development of a looser network. The decrease of the DVS concentration, however, is limited by a value at which gel formation is prevented, leading to a poorly crosslinked network dissolving in water during the swelling experiments.

The effect of the spacer length and concentration was investigated by synthesizing samples characterized by the same value of the DVS concentration and different PEG molecular weights and concentrations. In particular, the DVS concentration was 0.04M and the polymer concentration in the reactive mix was 2% by weight. PEG of molecular weights of 400, 4600, and 10,000 was used. All the samples were desiccated by phase inversion in acetone. The swelling ratio of the different samples is plotted, as a function of the ratio between PEG and DVS molar concentrations, in Figure 5.

As was expected, the presence of a spacer increases the hydrogel sorption capacity, which passes from a value of around 400 for the gel containing only DVS to a value of around 600 for the gel containing PEG with a molecular weight of 4600. However, a maximum in the hydrogel swelling capacity was observed to increase the PEG concentration for all the PEG molecular weights tested. Two concurrent effects were considered to be responsible for this behavior: The increase in the PEG concentration increases the positive contribution to network expansion and thus increases the swelling ratio. Increasing the PEG concentration, however, decreases the weight ratio of CMC and HEC in the reactive mixture, thus decreasing their contribution to hydrogel swelling. In particular, the ionic contribution to polymer swelling, due to the presence

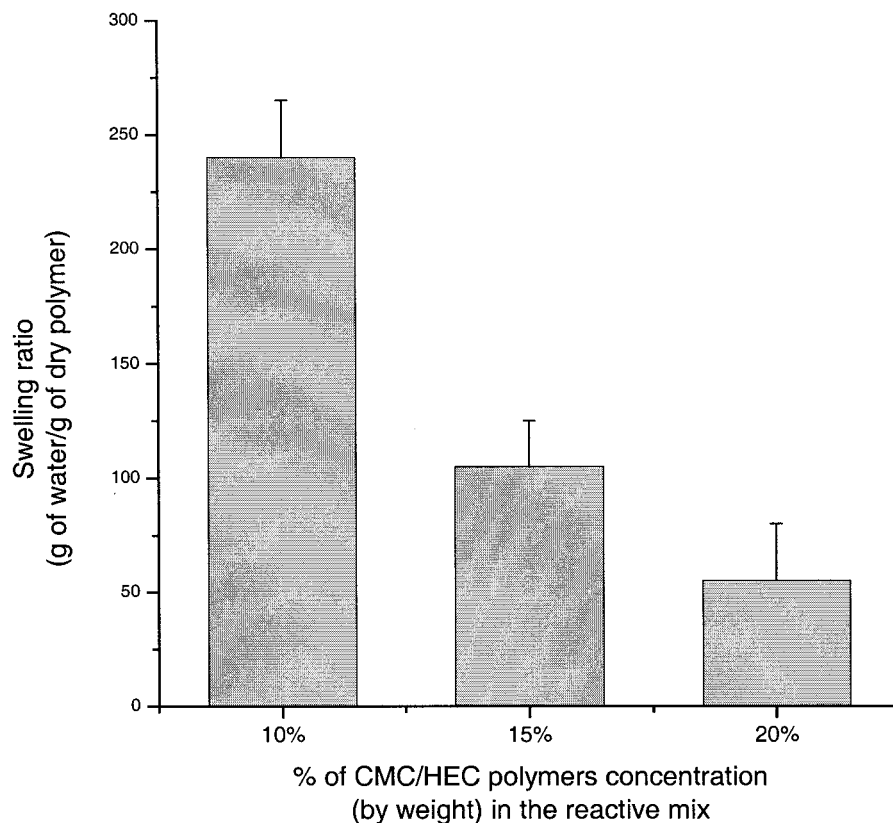


Figure 3 Hydrogel swelling ratio in distilled water versus CMC/HEC polymer concentration in the reactive mix, in presence of PEG, molecular weight 4600, spacer.

of fixed charges (carboxylic groups) available only on the CMC chain backbone, is reduced. It was already shown^{20–22} that the Donnan effect between the inside and the outside of the gel, due to the presence of fixed

charges, is one of the main contributions to the material's sorption capacity. For the same reason, there is an optimal average molecular weight of PEG to be employed as a spacer molecule, after which the

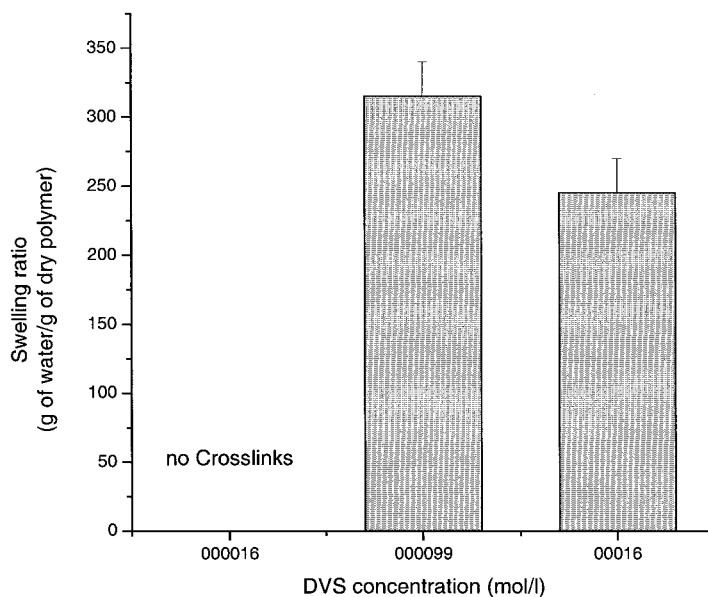


Figure 4 Hydrogel swelling ratio in distilled water versus DVS concentration in the reactive mix, in presence of PEG, molecular weight 4600, spacer.

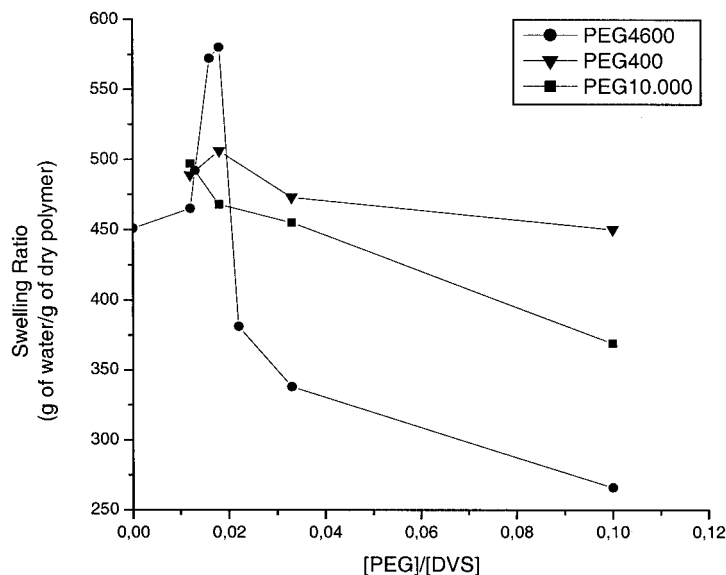


Figure 5 Hydrogel swelling ratio in distilled water versus PEG/DVS molar ratio. Total polymer concentration in the reactive mix 2% by weight; DVS concentration 0.04 mol/L; samples desiccated in acetone.

amount of PEG molecules in the network structure becomes too high and the material no longer behaves as a polyelectrolyte cellulose-based hydrogel, but as a cellulose-PEG-based polymer.

Finally, a set of samples was synthesized for swelling tests in synthetic urine, which was purchased from SCA Molnlycke AB (Goteborg, Sweden) and used as received. The ionic strength (I.S.) of the synthetic urine was 0.2 mol/L and the pH was 7. The materials were prepared starting from 2% by weight polymer solutions with a CMC/HEC weight ratio of 3/1 and two different DVS concentrations (0.04 and 0.02 mol/L). PEG of an average molecular weight of 4600 was used

as a spacer in a concentration equal to 15% of the polymer by weight. Two sets of samples were prepared for each DVS concentration; one set was desiccated by phase inversion with acetone, and a second set, by water evaporation in air at room temperature. The results shown in Figure 6, compared with those obtained in distilled water, indicate that the swelling capacity in this case is clearly reduced, due to an increase in the I.S. of the synthetic urine solution, which significantly affects the ionic contribution due to the Donnan effect and the electrostatic repulsion between charges of the same sign present on the CMC backbone. However, the swelling ratio is high if com-

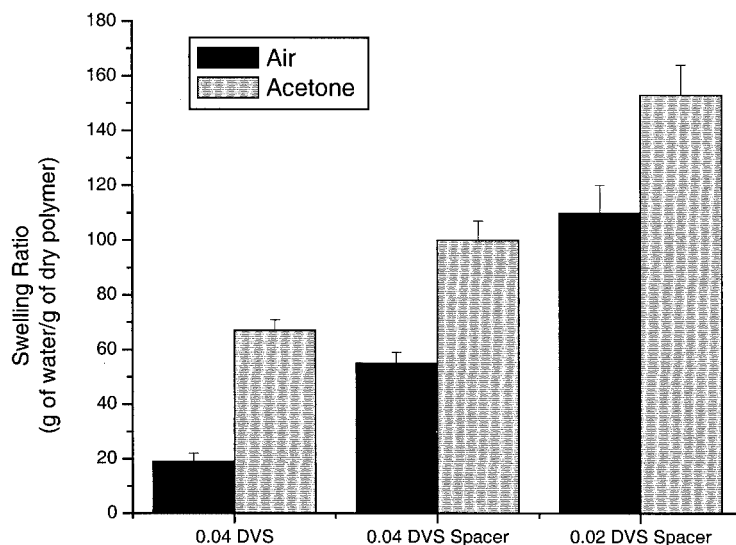


Figure 6 Hydrogel swelling ratio in synthetic urine versus type and concentration of crosslinker in the reactive mix. Samples obtained starting from 2% by weight polymer solutions with a CMC/HEC weight ratio of 3/1. Spacer is PEG of molecular weight 4600.

pared with the values obtained for the acrylate-based hydrogels, commercialized for the application of personal-care products, which are between 30 and 50.^{23,24}

CONCLUSIONS

In this work, the synthesis and properties of cellulose-based hydrogels obtained with two different crosslinkers were presented. In particular, a difunctional DVS molecule, with two reactive ends able to link the cellulose backbone and a longer crosslinking bridge constituted by two DVS molecules bounded with the other end to a PEG molecule, acting as a spacer, were used.

The effect of the degree of crosslinking was analyzed in terms of the hydrogel equilibrium swelling capacity in distilled water and synthetic urine. An increase in the degree of crosslinking resulted in a decrease in the swelling capacity for all the samples as a consequence of an increase of the elastic (entropic) response counteracting polymer swelling. The presence of PEG increases the hydrogel sorption capacity, with the average distance between polymer chains in the network and their mobility increased. This effect, particularly strong for materials desiccated in an ambient atmosphere, can lead to significant advantages in a material's synthesis process in terms of cost reduction, safety, and process scale-up simplification.

The effect of the polymer concentration in the reactive mixture was also evaluated for different crosslinker concentrations, indicating that the presence of spacers can be exploited to increase the polymer concentration in the solution during synthesis with a limited reduction of the polymer swelling capacity. An increase in the polymer concentration also allows a reduction of the DVS amount for gel formation and the elimination of the soaking procedure, with a further reduction of process cost and complexity.

The authors would like to acknowledge SCA Monlycke, AB, for financial support and useful discussions.

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