Water and Synthetic Urine Sorption Capacity of Cellulose-Based Hydrogels under a Compressive Stress Field

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ABSTRACT: A new apparatus was developed and used to investigate the swelling behavior of crosslinked hydrophilic polymers under an applied load as a function of the absorbed weight in both water and water solutions. A model able to predict the material water uptake as a function of the isotropic compressive stress was also studied. Centrifugation tests were performed to measure the material retention capacity under load, in both water and synthetic urine. The polymers studied in the tests were from a particular class of superabsorbent hydrogels based on cellulose derivatives chemically crosslinked with divinyl sulfone. The hydrogels showed high sorption and retention capacity in both water and water solutions, both in the free state and under load, and significant variations were observed during the modulation of the dry sample porosity. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3791–3796, 2004

Key words: hydrogels; crosslinking; swelling; compression

INTRODUCTION

The study of the absorption properties of superabsorbent hydrogels was pushed in the second half of the 21st century by a rapidly increasing demand for their applications in the market of personal care absorbent products.[1,2] At first, their sorption capacity in the free state was widely studied and improved; subsequently, it was understood that a parameter closer to the effective end use of such materials was their absorbency under load (AUL), and many efforts were made to improve this parameter. However, AUL is strongly related to the degree of crosslinking of the polymer network, and increasing the degree of crosslinking reduces the hydrogel swelling capacity in the free state. Thus, looking at the trend of the last 2 decades, we can see an increase in AUL and a decrease in the absorbency in the free state for most of the superabsorbents on the market.[3]
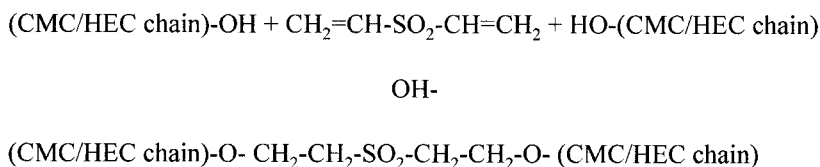
Hydrogel swelling properties under load are important for a number of industrial applications, such as baby diapers and female personal care absorbent products, water release systems in agriculture, and water protection systems in communication cables, in which the material is supposed to absorb in a confined environment exerting an external force opposite to the swelling process. A test closer to the actual end use of the material in such applications is water absorption under a compressive stress field.

Several devices have been developed to measure the swelling behavior under stress,[4–10] and most of them measure the material swelling and swelling pressure as a function of time. The problem with these techniques is that they cannot measure the swelling of polymer microparticles or disks under load. Bell and Peppas[11] set up a technique to test polymer gel microparticles under a preapplied load, which can be applied to the testing of AUL of superabsorbent polymers. However, an isotropic compressive stress field cannot be simulated with these techniques, and this is important for our understanding of the swelling forces generated during the swelling process and for the development of a model able to predict the polymer swelling capacity as a function of the applied stress.

In this work, experimental efforts were devoted to developing equipment able to reproduce an isotropic compressive stress field on a hydrogel during sorption and to developing a model able to predict the material water uptake as a function of isotropic compressive stress. In this article, we report the model development in detail, along with its efficiency in describing experimental results, with reference to a cellulose-based hydrogel that displays a connected porosity in the dry form. This study was completed with water and synthetic urine retention tests after centrifugation on both porous and nonporous samples. The synthetic urine was considered with the aim of reproducing the actual end-use environment of hydrogels in their principal applications as absorbent cores in personal care products.

(CMC/HEC chain)-OH + CH$_2$=CH-SO$_2$-CH=CH$_2$ + HO-(CMC/HEC chain)

OH-

(CMC/HEC chain)-O- CH$_2$-CH$_2$-SO$_2$-CH$_2$-CH$_2$-O- (CMC/HEC chain)

Figure 1 Scheme of the crosslinking reaction between cellulose derivatives and DVS.

EXPERIMENTAL

Materials

The hydrogels used in this investigation were obtained from mixtures of carboxymethylcellulose sodium salt (NaCMC) and hydroxyethylcellulose (HEC). The macromolecular hydrogel network was chemically stabilized with divinyl sulfone (DVS), which was used as a crosslinker. According to procedures reported in the literature,[12] the crosslinking reaction was performed in an alkaline water solution (0.02M potassium hydroxide). NaCMC was completely dissociated in water, and the resulting hydrogel was a polyelectrolyte, displaying fixed charges on the macromolecular backbone. This significantly increased its water sorption capacity because of the Donnan effect associated with the difference in the charge concentration between the hydrogel and the external solution.[13] DVS was a difunctional molecule able to bond the free hydroxyl groups of the unsubstituted carbon atoms of the polysaccharide ring, following the mechanism reported in Figure 1. The sample preparation procedure can be schematized as follows: a crosslinking reaction (step 1), the soaking of the crosslinked sample in water to equilibrium (step 2), and a desiccation stage (step 3). Three different desiccation procedures were adopted: desiccation under room conditions in an air atmosphere, desiccation *in vacuo*, and desiccation by phase inversion in acetone (a nonsolvent for the polymer). The sample microstructure was demonstrated[12] to be different, depending on the desiccation procedure adopted. In particular, samples desiccated by phase inversion in acetone displayed a connected microporosity, whereas those desiccated in an air atmosphere had a compact structure; an intermediate porosity between these two limits was displayed by samples desiccated *in vacuo*.

Two different sets of samples were prepared for the test under isotropic compression and for the centrifugation test. For the isotropic compression measurements, hydrogels were prepared from mixtures of 2 wt % polymer in distilled water, with an NaCMC/HEC ratio of 3/1 (w/w) and a DVS concentration of 0.04 mol/L. The samples were crosslinked in spherical molds of five different diameters (0.5, 1, 1.5, 2, 2.5, and 3 cm) in a partially swollen state in the form of spheres; they were soaked in distilled water and desiccated in acetone.

Different types of samples were prepared to investigate the effect of desiccation procedures (air atmosphere, *in vacuo*, and phase inversion in acetone) on the final water retention and synthetic urine retention after centrifugation. For all the samples, the DVS concentration was 0.04 mol/L, and the NaCMC/HEC ratio was 3/1 (w/w). The starting water solutions had, in all cases, an overall polymer concentration of 2% b.w.

All the reagents were supplied by Aldrich s.p.a. (Milan, Italy) and used as received.

Modeling

Because of the high porosity of the dry gel structure, the material has been envisioned as a cellular solid. A schematic representation is given in Figure 2. In the case of unconstrained sorption, both capillary retention and bulk sorption play roles in determining the total amount of absorbed water (the theoretical aspects involved in bulk sorption are extensively reported in the literature[13]). When constrained sorption (swelling under compressive stress) is considered, a reduction in the sorption capacity is to be expected in comparison with free swelling. This effect can, in principle, be ascribed to both a reduction of the microporous volume (and, therefore, of capillary retention) promoted by compression and a reduction of the bulk sorption capability related to the presence of the compressive field. As a first approximation, the effect of the pressure on the intrinsic absorption capacity of the matrix has been neglected, and the dependence of the sorption capacity on the compressive stress has been attributed only to the volume reduction of the foamlike structure. This approach is expected to be reasonably close to the actual behavior for relatively low compressive stress fields, as is the case for the practical applications of the material.

The strain (ϵ) associated with the compressive stress (σ) can be defined as follows:

$$\varepsilon = (\Delta SR/SR_0) \quad (0 < \varepsilon < 1) \tag{1}$$

where ΔSR is equal to $SR_0 - SR$, SR_0 is the unconstrained swelling ratio, and SR is the actual swelling ratio. In fact, ΔSR is a measure of the volume change due to compressive loading.
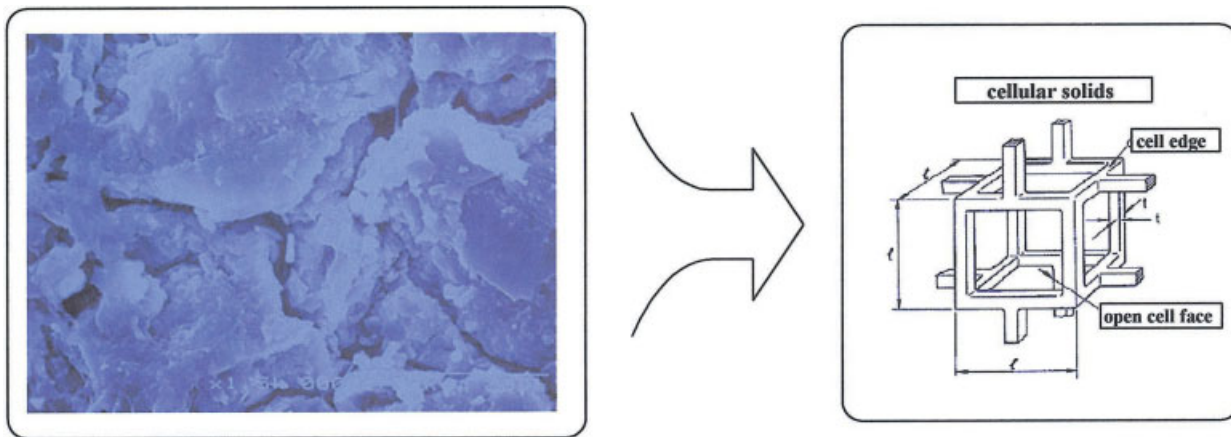
Figure 2 Schematic representation of the material envisioned as a cellular solid.

σ is related to ϵ through the compressive bulk modulus (K) according to the following expression:

$$\sigma = K\varepsilon \qquad (2)$$

K is expected to be a function of the amount of absorbed water. In particular, it is assumed that K spans between K_d for $\epsilon \geq 1$ and K_0 for $\epsilon \geq 0$, where K_d is the compressive bulk modulus of the swollen polymer matrix and K_0 is the compressive bulk modulus of the foamlike water-containing structure ($K_d > K_0$). In fact, for $\epsilon \geq 0$, the response of the material to compressive stress is essentially due to K_0, whereas for $\epsilon \geq 1$, the response of the material to compressive stress can be attributed only to the matrix because no more voids are supposed to be present.

It can be demonstrated that K_0 is related to the bending modulus (E_b) of the swollen polymer matrix and pore volume fraction (ϕ) through the following relationship:

$$K_0 = C_1 E_b (1 - \phi)^2 \qquad (3)$$

E_b accounts for hydrogel bulk properties (e.g., chemical composition and crosslinking degree) and equilibrium swelling conditions (e.g., ionic strength and pH), that is, all the parameters expected to affect the matrix sorption capacity.

As a first approximation, it has been assumed that K depends on ϵ through a sigmoidal function bound between the two limits reported previously, as represented schematically in Figure 3. According to this assumption, the following expression can be proposed for K:

$$K = M_1 + M_2 \left\{ 1 - \exp \left[-\left(\frac{\varepsilon}{M_3} \right)^{M_4} \right] \right\} \qquad (4)$$

As a result, the dependence of the swelling pressure (p) on ϵ takes the following form:

$$p = \left\langle M_1 + M_2 \left\{ 1 - \exp \left[-\left(\frac{\varepsilon}{M_3} \right)^{M_4} \right] \right\} \right\rangle \varepsilon \qquad (5)$$

This expression has been used to fit the experimental results.

Equipment and methods

To prove the validity of the proposed model for the isotropic compression study, we designed and built a proper apparatus. In particular, we needed to apply isotropic deformation to samples and measure the relative compressive stress. For this purpose, we built a porous spherical mold and connected it to a loading cell. A scheme and photograph of the apparatus are given in Figures 4 and 5, respectively. Molds with spherical cavities of several diameters were used.

The samples used for the tests were synthesized in spherical shapes of different diameters with a properly designed Teflon mold. Spheres were desiccated by extraction with acetone according to procedures
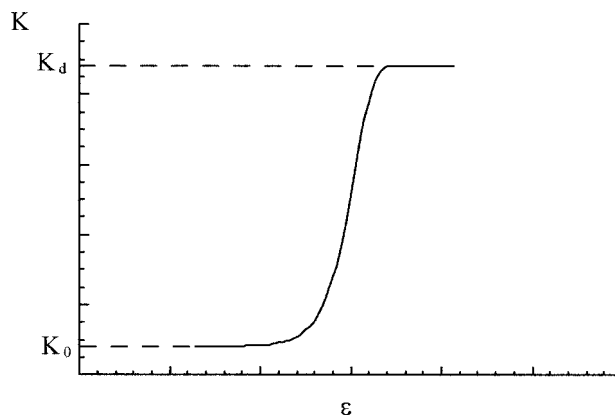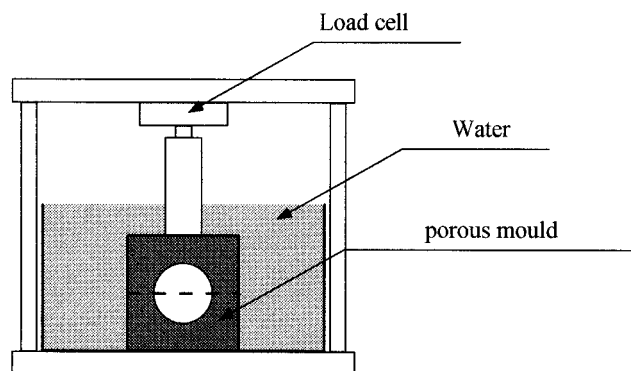

Figure 3 Sigmoidal function bound between the two limits of K as a function of ϵ.
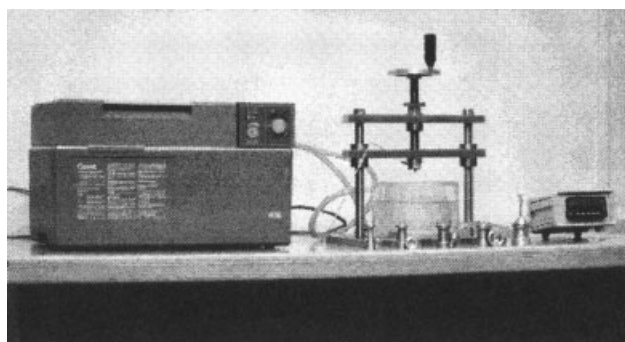
Figure 4 Layout of the equipment for the isotropic compression measurements of the cellulose-based spherical hydrogel samples.

Figure 6 Hydrogel swelling under isotropic compression: the swelling pressure versus ϵ (deformation).
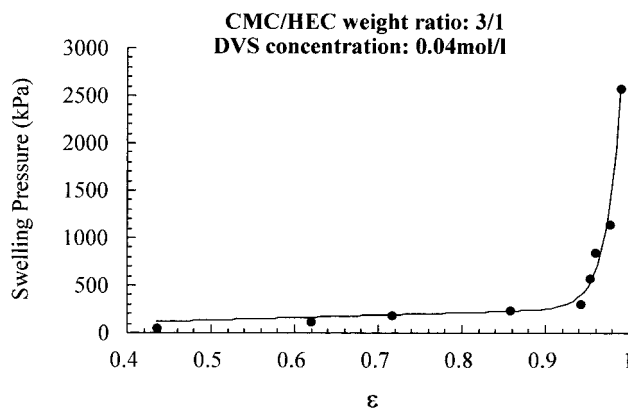
described previously. Desiccated samples were inserted into the porous mold, and the loading cell sensor was put into close contact with the top of the mold; this exerted a negligible stress on it to prevent any movement. At this stage, distilled water was poured into the space surrounding the mold (the temperature of the water was carefully controlled with a water jacket connected to a temperature controller). As the water penetrated the mold, the sample started to absorb water, and its dimensions increased up to the mold volume. After this stage, no more swelling was allowed, and the loading cell started to detect an increase in the load corresponding to the development of compressive stress. Finally, the load reached a steady value, from which the equilibrium swelling compressive isotropic stress (i.e., swelling pressure) was evaluated:

$$\sigma = p = F/\pi R^2 \qquad (6)$$

where R is the radius of the mold. The deformation associated with this stress was easily evaluated from the measurement of the sample weight right after the experiment and after free swelling in water. Different

Figure 5 Equipment for the isotropic compression measurements of the cellulose-based spherical hydrogel samples.

deformations were imposed with molds of five different inner diameters and from samples of different dimensions.

The centrifuge apparatus consisted of a rotor with four tubes 100 mm long and 44 mm in diameter. A polyester mesh (59 μm) was used to contain the swollen hydrogel samples. The procedure was as follows. The polyester mesh was cut into 7-cm$\times$ 12-cm sheets and then folded to form tea-bag-shaped containers, which were weighed before and after the hydrogel dry sample insertion. The bags were then immersed into distilled water or synthetic urine for about 24 h, when the hydrogel equilibrium swelling was reached (i.e., the bag weight remained constant). Then, the bags were suspended in an air atmosphere to allow excess water to drip away. At this stage, the samples were weighed and positioned in the centrifuge tubes, to which a plastic filler was added to make the total weight 150 g per tube. Centrifugation took place for 10 min at 1500 rpm. After centrifugation, the samples were extracted from the tubes and reweighed. All the tests were repeated five times.

Equilibrium swelling measurements in distilled water and synthetic urine and measurements after centrifugation were carried out for all the samples with a Mettler AE 100 electronic microbalance with an accuracy of $\pm 10^{-4}$ g. For each type of sample, the synthesis was repeated four times, and from each round of synthesis, three samples were obtained.

RESULTS AND DISCUSSION

The results of the absorption tests under isotropic compression are reported in Figure 6, in which the swelling pressure is reported as a function of ϵ, which is a measure of material deformation or, in different terms, the ratio between its sorption capacity under isotropic compression and the swelling capacity in the free state. Increasing the external pressure on the hy-

CMC/HEC weight ratio: 3/1
DVS concentration: 0.04mol/l
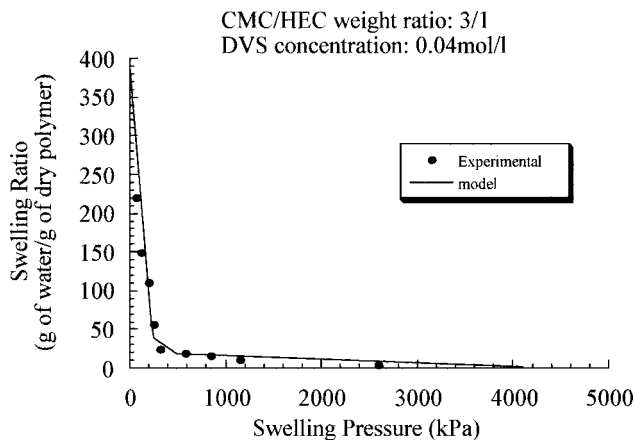
Figure 7 Hydrogel swelling under isotropic compression: (●) the swelling ratio versus the swelling pressure and (—) interpolation model predictions.
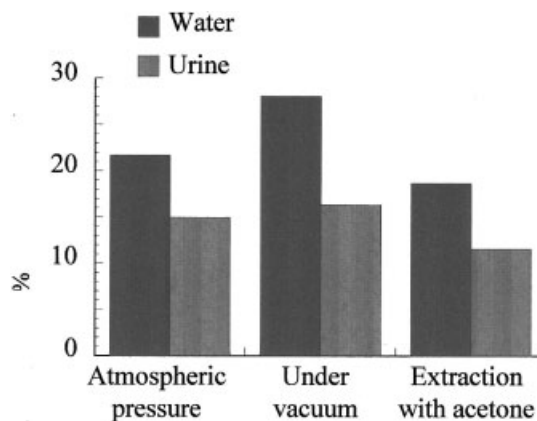
Figure 8 Comparison of the sorption properties in distilled water and synthetic urine: the percentage of liquid released after centrifugation.

drogel increased the value of ϵ and, therefore, the amount of absorbed water. Different compression ratios were modulated by the proper choice of the dimensions of the hydrogel sphere and porous mold.

A re-elaboration of these data is presented in Figure 7, in which the experimental water uptake is reported as a function of the swelling pressure. In the same figure are presented model predictions evaluated with
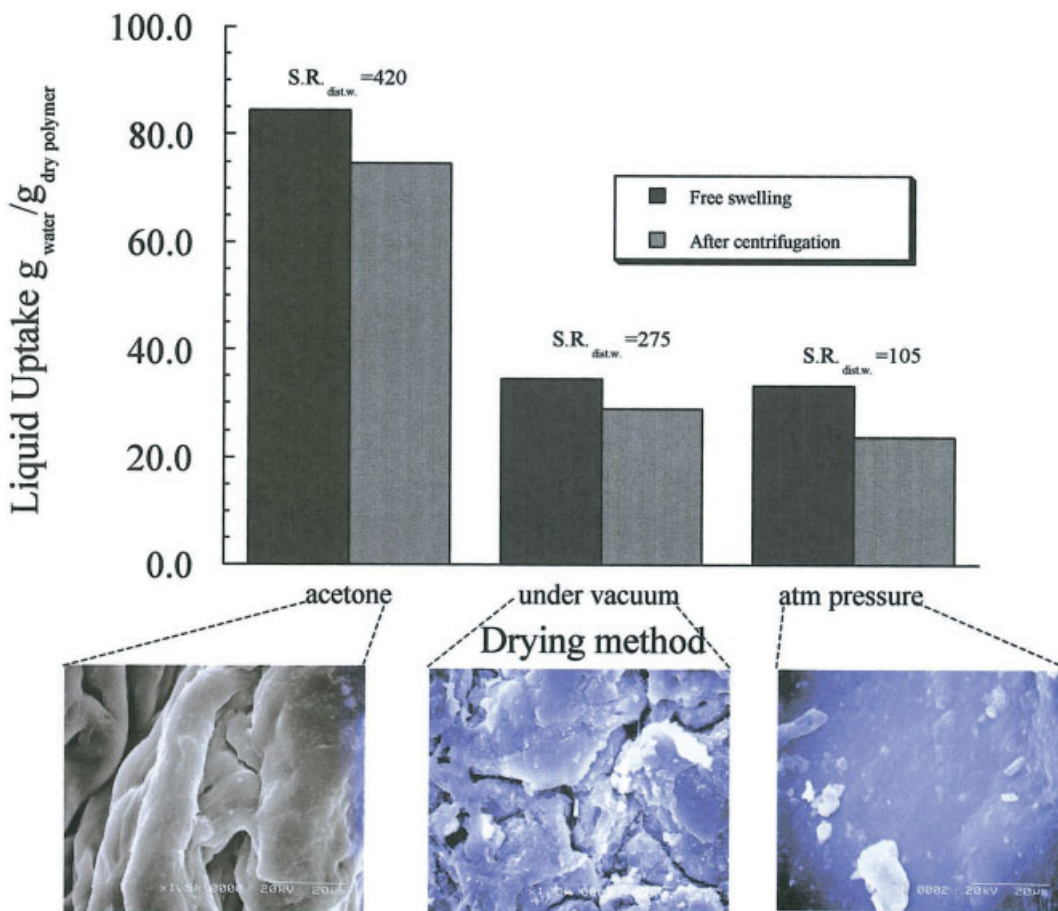
Figure 9 Swelling in synthetic urine: free swelling and swelling after centrifugation for different desiccation procedures. The results for free swelling in distilled water are indicated in terms of the swelling ratio $SR_{dist.w.}$ (g of the swollen sample/g of the dry sample). SEM micrographs are also given for each desiccation procedure.

parameter values obtained from the fitting of the experimental data of the swelling pressure versus ϵ. The proposed model seems to properly describe the material behavior. Actually, the number of adopted fitting parameters is quite high. However, two other experiments could be devised to obtain two other independent relationships, thereby reducing the effective number of fitting parameters to two. In particular, this could be performed by the evaluation of K of the swollen dense polymer matrix (samples desiccated at atmospheric pressure) and K of the swollen porous samples for very low values of ϵ.

The results of the centrifugation tests are reported in Figure 8, in which the amount of water and synthetic urine released is indicated for each desiccation procedure adopted. The samples desiccated in acetone, which had a higher sorption capacity, also displayed a higher retention capacity, with a lower amount of released water and urine. In Figure 9, data are reported for urine sorption before and after centrifugation of samples obtained with different desiccation procedures. Water sorption data for each sample are also indicated. Samples desiccated in acetone, which displayed a higher porosity, maintained the higher sorption capacity before and after centrifugation. This was related to the strong capillary effect of the connected microporous structures, which increased the percentage of free liquid water solution absorbed and guaranteed strong capillary retention.

For the confirmation of the correlation between the sample porosity and water solution sorption and retention capacity, scanning electron microscopy (SEM) images of each sample are given in Figure 9. The hydrogel desiccated *in vacuo*, which displayed a pore size and distribution intermediate between those of the bulky sample desiccated in an air atmosphere and the porous sample desiccated in acetone, had an intermediate water sorption and retention capacity between those of the same samples.

The urine equilibrium sorption capacity of the sample desiccated in acetone (80 g/g of dry polymer) was significantly higher than the average value of commercially available acrylamide-based superabsorbents (ca. 50 g).

CONCLUSIONS

Sorption measurements and water solution retention capacities under stress of cellulose-based superabsor-

bents were analyzed in both distilled water and synthetic urine. An isotropic compression stress field was reproduced on hydrogel samples with a self-assembled apparatus consisting of a porous mold immersed in distilled water at a controlled temperature under a compression load cell. Hydrogel samples were synthesized in the form of spheres of different diameters and were inserted into the mold. The swelling pressure was monitored as a function of the sample deformation, which was related to the degree of hydrogel sorption. A model was derived for the description of the hydrogel sorption behavior under isotropic compression, and agreement was obtained between the model predictions and experimental data. Further independent experiments will be performed for the evaluation of K of a swollen dense polymer matrix and K of swollen porous samples for very low values of ϵ; this will reduce the fitting parameters from four to two.

Sorption tests were performed on swollen hydrogel samples under centrifugation, and the amount of distilled water and synthetic urine released after centrifugation was detected. Samples with higher porosity displayed a higher sorption capacity both in water and in synthetic urine before and after centrifugation.

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