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Investigation of Water Uptake Behavior and Mechanical Properties of Superporous Hydrogels

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The present study describes the water uptake behavior and mechanical properties of superporous hydrogels prepared through rapid copolymerization of acrylamide and acrylic acid in the presence of $NaHCO_3$ used as porogen. The formation of pores has been confirmed by SEM analysis. The increase in concentration of porogen from 23.8×10^{-2} mM to 71.4×10^{-2} mM caused enhancement in the equilibrium water uptake from 1068 ± 48 to 8087 ± 112 percent. Likewise, the variation in crosslinker content from 64.8×10^{-3} mM to 194.5×10^{-3} mM caused the percent water uptake to decrease from 9237 ± 123 to 2758 ± 61 in distilled water. For 9.71 mM of acrylic acid the equilibrium water uptake was found to be maximum (i.e., 10733 ± 168) and it decreased above and below this optimum value. The gelation time varied appreciably with crosslinker and monomer acid concentrations in the gelation mixture. The water uptake of superporous gel decreased sharply when an equilibrated sample was put in $NiCl_2$ solutions of different concentrations. However, NaCl was not found to be effective in reducing the water uptake. The gels, prepared with different amounts of crosslinker, showed different percent water retention capacity under varying loads. Surprisingly, gels prepared by adding 40 and 60 mg of $NaHCO_3$ (porogen) showed nearly the same retention capacity. The gels swollen in gastric fluid of pH1.2 showed higher values of ultimate compressive strength. However, the gels, swollen in distilled water, had poor mechanical strength. Finally, the porosity, and pore volume were also determined for various samples and their buoyancy test was also performed.

Keywords superporous, ultimate compressive strength, water retention, gelation time, porogen

Introduction

For two decades, hydrogels have been extensively used as an invaluable tool in the field of controlled drug delivery (1) due to their special property of slow swelling in physiological fluids. This results from the diffusion of water into the glassy polymer causing disentanglement of polymer chains with subsequent swelling (2). Although, slow swelling of hydrogels is useful in a number of applications, there are also other applications where buoyant porous hydrogels with fast swelling and deswelling are required. These are

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usually called superabsorbents. These materials, firstly originated in the United States as water retention agents in agriculture, were developed in Japan in the mid 1970s in the field of personal care and sanitary goods (e.g. disposable diapers, feminine napkins(3). In addition, they are also used in soil conditioning as artificial soils for hydroponics, as controlled release agents for agrochemicals or pharmaceuticals, as artificial snow for skiing (4), for metal extraction and separation applications (5, 6). Finally, porous hydrogels also find applications as biocompatible implants in tissues, such as in the central nervous system (7), or in cellular and tissue engineering (8, 9), and as gastroretentive devices (10–12).

Porosity is usually achieved by the use of one of the following basic methods: Crosslinking polymerization in the presence of substances that are solvents for the monomers but precipitants for the formed hydrogel; crosslinking polymerization in the presence of soluble substances (sugars, salts) that are washed out from the hydrogel after polymerization (13); crosslinking polymerization in the presence of substances liberating gases which remain in the resulting hydrogel (14); and frost sublimation of hydrogel swollen in water (15).

Using any of these procedures, hydrogels with communicating or non-communicating pores can be synthesized.

In the present work, we report the preparation of fast swelling superporous absorbents based on acrylic acid and acrylamide through highly concentrated (50 wt%) solution polymerization at room temperature under normal atmospheric conditions. The potassium persulphate/tetraethylmethylenediamine (TEMED) redox pair was used as initiator and $NaHCO_3$ as gas forming agent. A detailed investigation of dynamic swelling behavior of these superporous absorbent has been reported. Their water-retention capacity and buoyancy behavior has also been studied. The gelation time has been used as a major factor in explanations offered for various experimental findings.

Experimental

Monomers acrylamide (AAm), acrylic acid (AAc) and foam stabilizer pluronic F127 (PF) were purchased from Hi Media Lab, Mumbai, India. The crosslinker N,N′-methylene bisacrylamide (MB) and initiator potassium persulphate were received from the Research Lab, Mumbai, India and used as received. The catalyst TEMED and remaining chemicals were purchased from Merck, Mumbai, India. The monomer acrylamide was recrystallized in methanol to remove the inhibitor, while AAc was used as received. The double distilled water was used throughout the investigation.

Synthesis of Superporous Poly(AAm-co-AAc) Hydrogels

Superporous hydrogels were synthesized by carrying out free-radical aqueous polymerization of AAm and AAc in the presence of CO_2 gas bubbles, generated during the polymerization process due to reaction between citric acid and sodium bi-carbonate.

Typically, the following components were added sequentially to the test tube (outer diameter 22 mm, inner diameter of 19 mm and height of 175 mm):1000 μL of 50% AAm; 1000 μL of 50% AAc; 0.123 mM of crosslinker MB, 0.119 mM of citric acid; 0.074 mM of initiator KPS; 0.012 mM of pluronic F127. The solvent used was de-ionized distilled water unless specified otherwise. The test tube was shaken to mix the solution after each ingredient was added. Now, 200 μL of TEMED was added and the test tube was shaken again. Finally, 0.119 mM of $NaHCO_3$ was added and the mixture was immediately stirred vigorously using a spatula for 10 sec. The polymerization is accelerated after adding $NaHCO_3$ and is complete in a few minutes. The superporous hydrogel, so produced was cured for 30 min, then retrieved from the test tube, cut into discs of 5.0 ± 0.2 mm thick, and dried in a vacuum chamber at 30°C till they attained constant weight. The above sample shall be called 'control sample'.

We prepared a number of samples with different concentrations of monomers, cross-linker and sodium bicarbonate and stored them in the dried state for further investigations.

Swelling Studies

A completely dry, pre-weighed disc-shaped superporous hydorgel was placed in double distilled water at room temperature. The weight of the hydrating sample was measured at different time-intervals after removing the excess water by gentle blotting. The percent water uptake was given as:

$$Q = W_s - W_d/W_d \times 100$$

Where W_s is the weight of the superporous sample at time t and W_d is the weight of the dried hydrogel. When the gel attained constant weight, the W_s was replaced by W_∞ in the above expression to give equilibrium water uptake value. The study was carried out with five samples and the average values have been reported in the data points displayed in various figures.

Measurement of Gelation Kinetics

When the polymerization reaction proceeded, the viscosity of the reaction medium continuously increased until the complete network was formed. The gelation time was defined as the duration time for the gel formation after the addition of initiator KPS. To measure this, the reaction mixture was taken in a long cylindrical glass tube, tilted slightly downwards. The gelation time was determined by the measurement of time when the reaction mixture was no longer descending in the tilted tube as its movement was stopped as the mixture had become extremely viscous and converted into gel (16). The experiment was repeated five times to obtain an average gelation time for a particular composition of gel.

Determination of Foam Height

In order to determine the height of the foam produced during the course of polymerization, the reaction mixture was placed in the long cylindrical graduated tube. Finally, $NaHCO_3$ was added and the upward movement of foam was monitored by putting marks on the cylindrical tube at regular time intervals of 5 sec until the foam height became constant. The experiment was repeated five times and average data was produced in the figures.

Scanning Electron Micrograph

A porous structure of hydrogels was examined using a scanning electron microscope. Dried superporous hydrogels were cut to expose their inner structure, coated with a thin layer of palladium gold alloy in a Hummer I Sputter Coater, and imaged in a SEM (JSM-840, JEOL).

Measurement of Mechanical Strength

Superporous hydrogel sample was equilibrated in water and then the fully swollen gel was placed on the bench comparator (Ames, Waltham, MA). Different loads in increasing order were applied on the top of the sample. The ultimate compressive strength (UCS) was determined as the compressive force at breakage (17) divided by the cross sectional area of sample in contact with the load.

The water retention test was also performed by putting various loads on the swollen gel and measuring the water retained within the hydrogel. The amount of water retained was calculated by the following formula:

$$\%\ \text{water retention} = \frac{\begin{matrix}(\text{percent equilibrium water uptake} - \text{percent}\\ \text{water uptake after Putting load})\end{matrix}}{\text{percent equilibrium water uptake}} \times 100$$

Five measurements were performed at room temperature and the average values have been reported in the data points displayed in figures.

Porosity and Buoyancy of SPHs

The superporous hydrogels were characterized with respect to their porosity and pore volume in the dry state.

The apparent density (d_a) and true density (d_T) were calculated using the following equation:

$$d_a = \text{mass of superporous disc/volume of the disc} \quad (1)$$

$$d_T = \text{mass of superporousdisc/volume of the polymer} \quad (2)$$

According to Equations (1) and (2), a material is homogenous if its apparent density is equal to its true density. The lower the apparent density, the higher the porosity of the material. The density measurements were carried out using n-heptane as described elsewhere (18).

The total porosity was evaluated by Equation (3):

$$\begin{aligned} P &= \text{volume of pores/volume of the disc} \quad \text{or}\\ \%\ P &= \text{volume of pores/volume of the disc} \times 100 \end{aligned} \quad (3)$$

The total pore volume was evaluated by Equation (4):

$$V_p = \text{volume of the pores/mass of the disc} \quad (4)$$

The total porosity and the total pore volume were calculated from the density measurements using the following equations:

$$P = 1 - d_0/d_2 \text{ and } V_p = 1/d_0 - 1/d_2$$

To test the buoyancy of superporous hydrogels specific gravity of the test solution (distilled water, simulating gastric fluid of pH 1.2) were measured using a standarad pyknometer. The superporous samples ($n = 5$) were steeped in 100 mL of each test solution and the buoyancy (sink or float) was observed visually. The hydrogel samples were considered to have buoyancy in the test solution only when all the samples floated in it (19).

Results and Discussion

Gelation Kinetics

The most salient property of a superporous hydrogel is its fast swelling ability, which is due to the presence of large and uniform pores within the polymer structure. These are produced due to the formation of foam at the time of polymerization. In order to produce large and uniform pores, the blowing agent must be introduced when the reactant system has appropriate viscosity. Bubbles cannot maintain their shape for a long time if a gas blowing agent is added too early, or if gelation time is relatively longer. On the other hand, bubbles cannot even be formed if porogen is introduced too late or the gelation time is extremely short because, in this case, the reaction system becomes viscous in such a short period that the porogen added cannot produce bubbles. Therefore, the gelation process and foam formation are of significant importance for making SPHs. The gelation kinetics can provide valuable information to determine the proper time to introduce a gas blowing agent into the reaction mixture.

Figure 1 depicts the variation in gelation time (as determined by the tilting method) with varying concentrations of crosslinking agent in the feed mixture ranging from 32.43×10^{-3} mM to 259.44×10^{-3} mM. It is very obvious that the gelation time decreases with the increase in MB content. The gel synthesized with 259.44×10^{-3} mM of MB in the feed mixture took nearly 8 ± 2 sec, while the gelation time for the gel formed with $32.\ 43 \times 10^{-3}$ mM of crosslinker was 35 ± 4 sec. This can be attributed to the fact that with the increase in MB concentration, the crosslinking process becomes fast and the reaction mixture takes less time to transform into the state when gelation has occurred. However, for all the concentrations of the crosslinker, gelation time was not more than 35 sec, thus indicating a fast gelation process. This was also attributed to the fact that in the present study the monomer concentrations was as high as 50 wt%. From this relationship between the gelation time and crosslinker content, it was decided to introduce the gas blowing agent as soon as possible after the addition of the initiator.

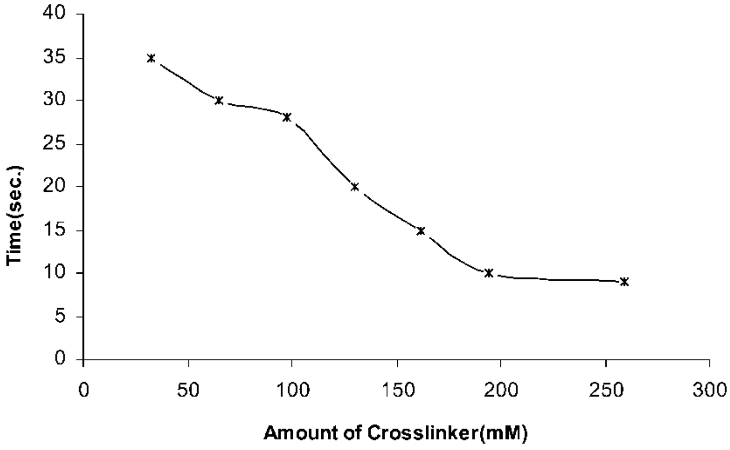


Figure 1. Effect of variation in amount of crosslinking agent on the gelation time.

We also determined the gelation times for hydrogels prepared with varying amounts of acrylic acid, ranging from 1.38 mM to 11.10 mM, keeping the total number of moles and other factors the same (data not displayed). The gelation time was found to be in the range of 10 ± 2 to 91 ± 4 sec for corresponding acrylic acid contents ranging from 1.38 to 11.10 mM. Therefore, it was decided to introduce a blowing agent 20 sec before the completion of the gelation for hydrogels with a higher AAc content, while for gels with a lower AAc content, the blowing agent was added as soon as possible after adding an initiator.

The swelling behavior of a porous hydrogel depends upon the number of pores generated within the network at the time of gelation, which in turn depends upon gas bubbles produced within the gelation network. The height of the foam at the time of gelation is an important parameter. If the foam height is small, it indicates that either the gelation was so fast that pores could not be generated or the gelation was so slow that most of the air bubbles might have escaped off the reaction mixture. So, we also studied the dynamic increase of foam height. Figure 2 depicts the foam height obtained during the synthesis of various superporous samples with varying crosslinker. It is clear from Figure 2 that as the concentration of crosslinker in the gelation medium increases, the foam height decreases. Initially, when the crosslinker content is quite low, the gelation process is slow or gelation time is large, and so the foam has sufficient time to acquire maximum height. (Although there is a possibility that the bubbles formed may escape off the reaction mixture if gelation time is sufficiently large, but this was not found in the present case). With the increase in crosslinker content, the gelation time decreases (as shown in Figure 1) and the gelling medium becomes highly viscous in such a short period that the gas bubbles cannot develop to their full shape due to enhanced viscosity of the reaction mixture and, fail to form foam with the maximum height. In this way, with the increase in crosslinker, foam height continues to decrease.

Swelling Behavior of Superporous Hydrogels

The SPHs absorb a large amount of water in a very short period of time due to the presence of interconnected microscopic pores (20). Because of the porous structure, they also possess hundreds of times more surface area and shorter diffusion distance than conventional hydrogels. These features allow dried SPHs to swell very fast to a very large size upon contact of water (Figure 3). Therefore, the presence of interconnected pores

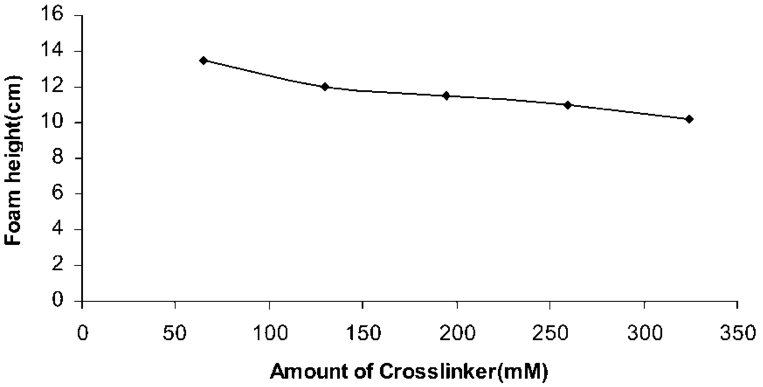


Figure 2. Variation in height of foam with amount of crosslinker.

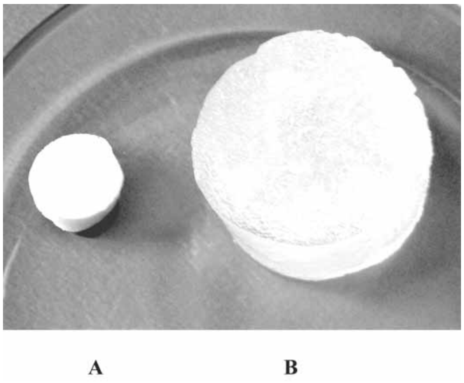


Figure 3. Photograph showing a superporous hydrogel sample in (a) dry state and, (b) fully swollen state in distilled water.

within the polymer network contributes to fast swelling of superporous gels, due to capillary action, as well as a larger surface area exposed to water. This indicates that the amount of gas generating agent (in this study, $NaHCO_3$, which is responsible for the formation of pores), content of crosslinker in the feed mixture, composition of superporous gels,etc. can play a significant role in governing the swelling behavior of the superporous hydrogel systems. In the present work, we have investigated the effect of these parameters on the dynamic swelling behavior of SPHs.

Firstly, we varied the amount of blowing agent in the 11.9×10^{-2} mM range to 71×10^{-2} mM and studied the water uptake kinetics of the resulting hydrogels. The results, as depicted in Figure 4 clearly indicate that as the amount of $NaHCO_3$ in the feed mixture increases, the water absorbency of resulting hydrogels also increases. This may simply be attributed to the fact that with the increase in sodium bicarbonate content, the amount of CO_2 generated also increases, thus producing more and more

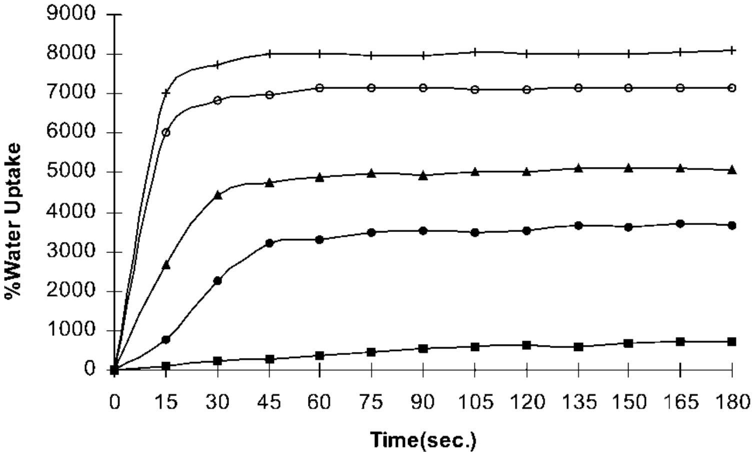


Figure 4. Effect of variation in the amount of porogen $NaHCO_3$ on the swelling behavior of superporous hydrogels in distilled water at 30°C. (–■–) 23.8×10^{-2} mM; (-●-) 35.7×10^{-2} mM; (–▲–) 47.6×10^{-2} mM; (–O–) 59.5×10^{-2} mM and (+) 71.4×10^{-2} mM.

bubbles within the gelling medium. Therefore, the number of pores within the polymer network increases, thus resulting in a higher water uptake with enhancement in uptake rates also.

SPHs with a varying amount of crosslinker in the 64.86×10^{-3} mM to 194.50×10^{-3} mM range were synthesized and the kinetics of water uptake in distilled water was investigated. The results, as depicted in the Figure 5, indicate that as the amount of crosslinker increases, water absorbency of resulting hydrogels decrease. Here, the increase in degree of crosslinking in the network results in a decrease in flexibility of macromolecular chains. This restricts the chain relaxation process, thus causing a decrease in the water uptake values. There may be one more reason for decrease in water uptake with crosslinker content. When we increase the amount of crosslinker, the gelation time decreases, thus suggesting a fast gelation process. So, for higher concentrations of crosslinking agent, the gelation time is so short or the gelation process is so fast that bubbles formation do not occur in the proper manner, due to increased viscosity of the gelation medium. This will decrease the extent of porosity in the resulting hydrogels, thus finally lowering their water uptake. On the other hand, the feed mixture with 64.86×10^{-3} mM of crosslinker required nearly 25 sec for gelation (see Figure 1). In the course of this time-duration the bubble formation must have taken place in the proper way and $NaHCO_3$ had sufficient time to produce CO_2 gas and form a good number of properly shaped bubbles, thus making a porous network with almost interconnected pores. As a result, the gel demonstrated higher water uptake. Contrary to this, K. Kabiri and co-workers (21) synthesized partially neutralized and non-neutralized polyacrylic acid superporous gels and reported an increase in their water uptake with crosslinker content. However, we did not observe any such behavior.

Finally, we determined the equilibrium water uptake for the hydrogel samples prepared with a varying content of monomer acrylic acid in their feed mixture ranging from 1.38 mM to 11.04 mM. The results, as depicted in Figure 6, clearly indicate that equilibrium water uptake changes significantly with polymer composition. As shown, it does not change monotonically with monomer acid concentrations. Initially, the water

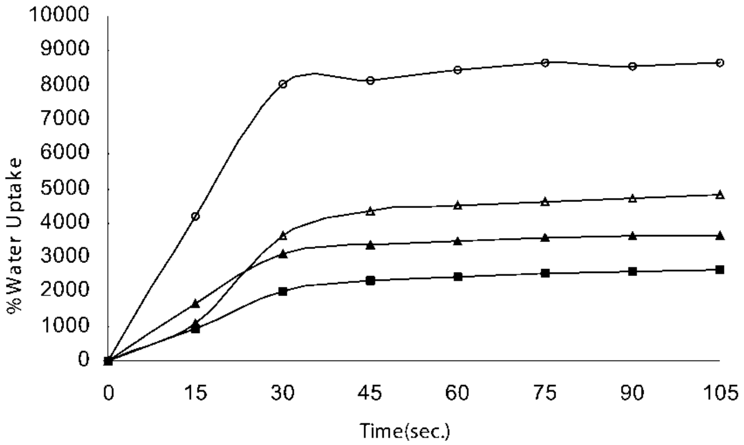


Figure 5. Effect of variation in amount of crosslinking agent on the swelling behavior of SPHs I distilled water at 30°C (–■–) 194.5×10^{-3} mM; (–▲–) 162.1×10^{-3} mM; (–△–) 129.6×10^{-3} mM and (–○–) 64.8×10^{-3} mM.

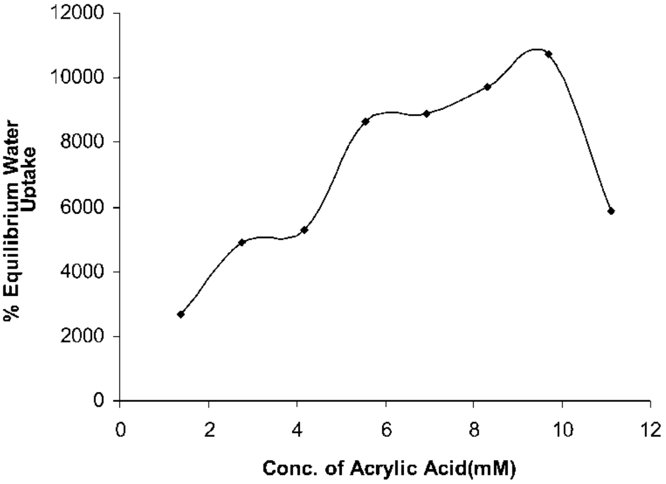


Figure 6. Effect of variation in concentrations of monomer acid on the equilibrium water uptake of superporous hydrogels in distilled water at 30°C.

uptake value increases with monomer acid content and attains maximum water uptake of nearby 10733 ± 168 when concentration of acrylic acid becomes 9.61 mM in the feed mixture. However, with a further increase in acrylic acid concentration there occurs a sharp decrease in the equilibrium water uptake. This unexpected behavior, can be explained as follows. Initially, the reaction mixture contains a low concentration of acrylic acid (and a high concentration of other monomer acrylamide). Because of greater reactivity of the latter, the gelation process takes place at a faster rate and the reaction mixture becomes highly viscous very quickly. Therefore, the gas bubbles are not produced in sufficient number. This results in the formation of a less porous network which exhibits low water absorbency. However, with the increase in acid concentration, the gelation time also increases and the large sized inter-connected pores begin to form within the network. At the same time, increase in ionic content also enhances the chain relaxation process within the swelling network due to repulsion among similarly charged –COO– groups along the macromolecular chains. These two factors ultimately cause an increase in the equilibrium water uptake. However, when the monomer acid content exceeds beyond 9.61 mM, there occurs a sharp decrease in the water uptake. This may probably be due to the fact that for higher acid content, the gelation process becomes slow or gelation time becomes so long (nearly 61s for gel with 9.61 mM of monomer acid) that majority of carbon dioxide gas produced must have escaped off the gelation mixture. This ultimately resulted in a less porous structure, which exhibited lower equilibrium water uptake.

Salt Effect

The concentration and nature of metal ions in the swelling media demonstrate a well-known influence on swelling properties of a superabsorbent hydrogenl (22). To investigate this, a representative hydrogel sample with 97.20×10^{-3} mM of crosslinker MB was allowed to swell fully in distilled water and then transferred into salt solutions of NaCl and $NiCl_2$, with varying molar concentrations, namely 0.01 M, 0.05 M, and 0.10 M. The results, as depicted in Figure 7, reveal some interesting facts. With the increase in concentration of metal ions, the equilibrium water uptake decreases. Moreover, the superporous gel underwent a sharp volume phase transition in the case of $NiCl_2$ solutions, while the water uptake decreased gradually and slowly in solutions of NaCl with increasing concentrations. The observed findings may be explained as follows:

When swollen hydrogel is put in solutions of varying concentrations of NaCl, the presence of Na^+ ions in the outer solution causes a decrease in the osmotic swelling pressure which operates due to difference of counter ions in the gel phase and solution phase. With the increase in concentration of Na^+ ions in the swelling medium, the difference between the concentration of counter ions in the gel phase and solution phase decreases, thus causing a decrease in the equilibrium water uptake of hydrogel sample. However, in the case of solutions containing Ni^{2+} ions, the results obtained are rather interesting. For example, the equilibrium water uptake decreases from 8342 ± 113 to 3278 ± 76 as the swollen gel is transferred from distilled water into solution of Ni^{2+} ions with a 0.01 M concentration, while the percent water uptake decreases to 7772 ± 103 when the same swollen gel is transferred from distilled water into a 0.01 M NaCl solution. The sharp deswelling of the superporous swollen gel in solutions of Ni^{2+} ions may be attributed to fast ion-exchange process between Ni^{2+} ions of external solution and monovalent Na^+ and H^+ ions present within the gel phase. This ion-exchange process decreases the water uptake of gel in two ways. Firstly, when swollen gel is placed in a solution containing Ni^{2+} ions, these ions enter into the gel phase and for entry of each divalent ion, two monovalent ions diffuse out to the external solution. This results in a sharp decrease in the osmotic swelling pressure and so the gel deswells to a great extent. In addition, the Ni^{2+} ions may also bind to the charged COO^- groups of two different polymeric chains, thus functioning as additional crosslinks. Finally, the greater deswelling in the solution of Ni^{2+} ions (transition metal ions) may be attributed to the fact that transition metal ions have a strong complex forming tendency with polyanions as compared to alkali metal ions. These results are similar to our previous finding (6). This special property of superporous hydrogel can be used very well for the efficient and fast removal of toxic metal ions (e.g. Ni^{2+}, Cd^{2+}, Cu^{2+}etc.) from industrial effluents, as well as domestic water.

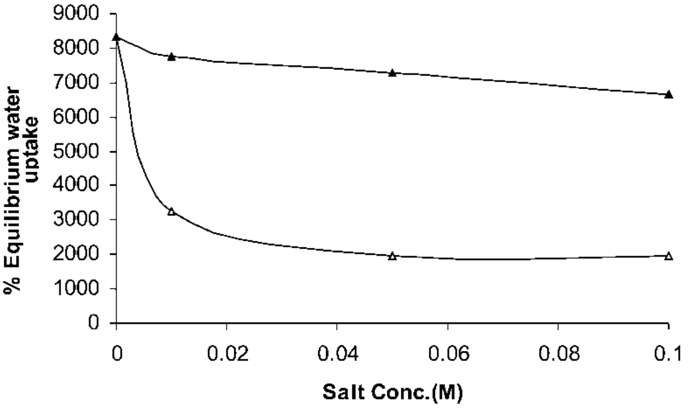


Figure 7. Equilibrium water uptake of superporous hydrogel samples in solutions of varying concentrations of NaCl (–▲–) and $NiCl_2$ (–△–) at 30°C.

In order to make quantitative interpretation of the above mentioned swelling behavior of SPHs in salt solutions, a dimension-less quantity α can be defined. It is expressed as ratio of equilibrium water uptake at a given salt concentration to that in salt-free water (23). We also measured the water absorbency of three superporous samples having varying amounts of crosslinker, namely 32.4×10^{-3} mM, 97.20×10^{-3} mM and 162.1×10^{-3} mM and determined the α values for them in NaCl and $NiCl_2$ solutions. (Table 1). It is clear that α values are smaller in $NiCl_2$ solutions, thus indicating that hydrogels demonstrate a greater sensitivity for Ni^{2+} ions as compared to the Na^+ ions for which α values obtained are higher.

Water Retention Test

In order to use superporous hydrogels as hygienic products (e.g. disposable diapers, sanitary napkins, surgical pads) it is very important that the hydrogels should have a high water retention capacity under a load that influences pad performance. For this purpose, retention capacity of these superporous hydrogels was determined under varying loads. Figure 8 depicts the % water retention of two superporous swollen hydrogel samples crosslinked with 64.8×10^{-3} and 162.1×10^{-3} mM of crosslinker under varying loads. It is clear that the sample with a higher concentration of crosslinker exhibits better water retention capacity as compared to the sample with a low degree of crosslinking. This can be explained on the basis of the fact that the macromolecular chains of the sample with higher crosslinker content are comparatively rigid or less flexible. Therefore, on putting loads of increasing order, they do not compress to a greater extent as compared to the other sample with a low degree of crosslinking and more flexible chains. Therefore, due to less compressibility, the pores are not deformed to a greater extent and hence, more water is retained within the network. On the other hand, the higher flexibility of network of loosely crosslinked gel causes the gel to compress to a greater extent with a subsequent greater loss of embedded solvent. In this way, we can conclude that the gels with a higher degree of crosslinking take up a less amount of water, but demonstrate a greater percent water retention capacity.

We also studied the retention behavior of hydrogel samples prepared with 47.61×10^{-2} and 71.4×10^{-2} mM of a blowing agent and studied their percent retention capacity under varying loads. The results, as shown in Figure 9, point to a very interesting fact. The two samples demonstrate nearly the same retention capacity.

Table 1

Dependency of the dimensionless swelling factor α, on the amount of crosslinker in the super porous hydrogels for swelling in salt solutions of NaCl and $NiCl_2$

Crosslinker concentration in hydrogels mM × 10^{-3}	Values of α in NaCl solutions of different concentrations			Values of α in $NiCl_2$ Solutions of different concentrations		
	0.01 M	0.05 M	0.10 M	0.01 M	0.05 M	0.10 M
32.40	0.98	0.93	0.91	0.31	0.39	0.35
97.20	0.79	0.93	0.89	0.27	0.23	0.27
162.10	0.67	0.87	0.79	0.23	0.23	0.26

$\alpha_{[salt]}$ = swelling in salt solution/swelling in distilled water.

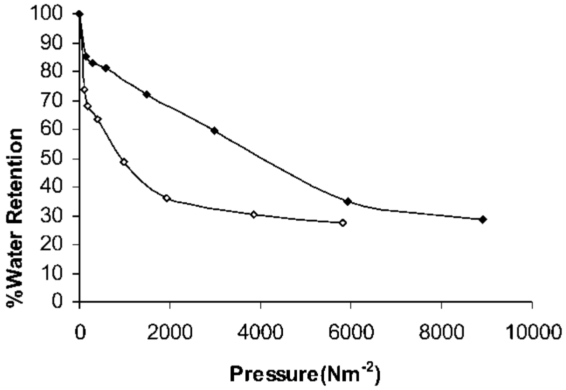


Figure 8. Effect of external pressure on percent water retention of superporous hydrogels prepared with (–O–) 64.8 × 10^{-3} mM and (–■–) 162.1 × 10^{-3} mM of crosslinking agent.

The result can be explained on the basis of the fact that in the gels the concentration of the crosslinker is the same. It means that the two polymers are crosslinked to almost the same extent, thus exhibiting almost similar flexibility. When the swollen gels are put under varying loads, the two samples demonstrate nearly the same fractional compressibility (which was measured in the terms of height of the compressed gels relative to their heights in the fully swollen state), and hence, percent retention. Here, it is interesting to see that as the composition of two superporous samples was the same (except the amount of porogen used) the macromolecular chains contained nearly the same number of $-COO^-$ groups in the two samples. So, the quantity of water bound to these groups through H– bonding interactions was nearly the same. This may be the reason for almost same water retention capacity of two samples. Therefore, it appears that the gel synthesized with 60 mg of porogen possesses higher porosity within the network and these interconnected pores are responsible for the higher water uptake at a faster rate. But, the same relative compressibility results in almost similar percent water retention of the two superporous gels. It should be reiterated here, that due to porous structure,

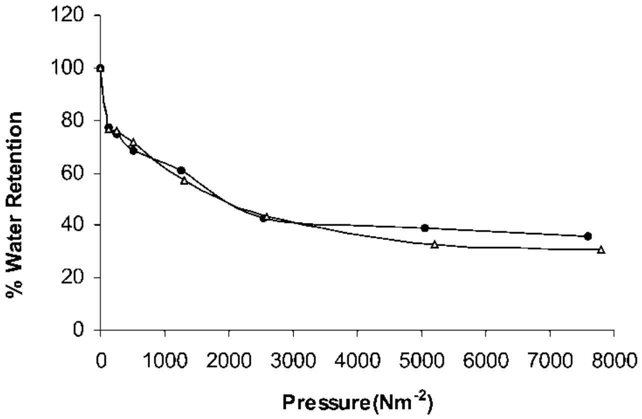


Figure 9. Effect of external pressure on percent water retention of superporous hydrogels prepared with (-●-) 47.61 × 10^{-2} mM and (–△–) 71.4 × 10^{-2} mM of gas blowing agent.

the surface area of gel exposed to invading solvent increases, thus resulting in a higher water uptake. Finally, it can be concluded that the superporous gels the synthesized with same concentrations of monomers and crosslinker, but varying amounts of porogen, demonstrate different water uptake but possess almost the same percent water retention.

Ultimate Compressive Strength (UCS)

One of the most important requirements for a super absorbent hydrogel to be used as a gastroretentive system is its structural integrity. A superporous hydrogel system must be able to withstand the pressure exerted in the stomach by peristaltic waves resulting from contractions in a distal stomach. The maximum stomach contraction pressure in humans is nearly 4900–6800 Nm^{-2} (24), although this number reflects only the direct compression pressure. In fact, the presence of other forces such as abrasion and shear forces would increase the actual pressure on hydrogels. Therefore, for a superporous hydrogel to be maintained as an integral dosage form in the stomach, it must be able to withstand a pressure greater than 4900–6800 Nm^{-2}. The actual value of pressure that a gastroretentive dosage form must withstand can be determined from animal experiments, the values, mentioned above, can be used as a baseline for laboratory experiments. However, in a number of applications, the superporous hydrogels swollen in distilled water, are required to retain their structural integrity. Therefore, superporous hydrogels prepared with varying amounts of monomer acid and crosslinking agent were allowed to equilibrate in simulating gastric fluid as well as in distilled water and their UCS was determined.

Figure 10 depicts the ultimate compressive strength (UCS) of fully swollen superporous hydrogels containing varying amounts of crosslinker in the range from 32.4×10^{-3} mM to 226.8×10^{-3} mM in the distilled water. The results indicate that initially the compressive strength increases with the increase in concentration of crosslinker and reaches the optimum value of 8840 Nm^{-2}. However, as the crosslinker content increases beyond 97.9×10^{-3} mM, the UCS begins to decrease. This finding can be explained by the fact that UCS of a swollen polymer depends upon a number of factors such as degree of hydration, porous nature of the polymer matrix, elasticity of

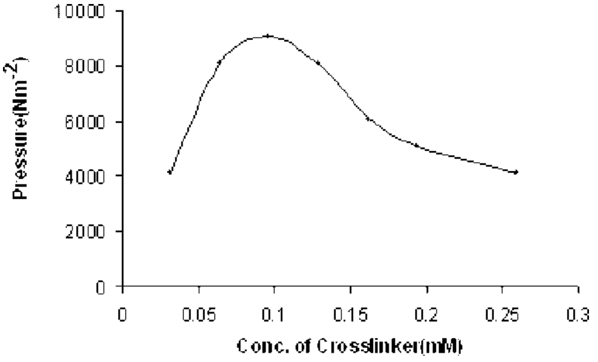


Figure 10. Ultimate compressive strength of superporous hydrogels swollen in distilled water as a function of crosslinker concentrations.

the macromolecular chains, etc. It has been discussed previously that water uptake decreases with an increase in the concentration of crosslinker. Therefore, the initial increase in UCS with crosslinker concentration may be attributed to the decrease in the water uptake of the superporous hydrogels. When the concentration of crosslinker is increased further beyond 97.9×10^{-3} mM, in spite of a decrease in the equilibrium water uptake, the UCS now begins to decrease. It appears that the observed decrease in UCS of less swollen hydrogels now may be attributed to the formation of a less porous and rather brittle polymer network for hydrogels prepared with higher concentrations of crosslinker. In fact, when the content of the crosslinker is increased beyond 97.2×10^{-3} mM, the gelation process becomes fast or the gelation time decreases sharply. With the decrease in gelation time, bubbles are not produced in sufficient number due to enhanced viscosity of the gelation media. In this way, the porosity of the resulting polymer network decreases. The decrease in porosity makes the network less elastic or more rigid. Moreover, the increasing contents of crosslinker also results in the formation of rather tight or brittle networks. This finally causes a decrease in the UCS of swollen networks. In this way, it can be concluded that the swollen superporous hydrogel with 97.2×10^{-3} of crosslinker possess maximum compressive strength in the distilled water.

As stated in the beginning of this section, the superporous hydrogel must possess fair UCS in order to be used as gastric retention devices. To investigate this, the superporous hydrogels with varying amounts of monomer acrylic acid, in the 1.38 Mm to 11.10 mM range, were synthesized, equilibrated in the artificial gastric fluid of pH 1.2 and tested for their ultimate compressive strength. The results, as shown in Figure 11, clearly indicate that for the samples with the acrylic acid content 1.38 Mm to 6.93 mM the ultimate compressive strength is quite low, falling within the 4086 Nm^{-2} to 807 Nm^{-2} range. However, as the monomer acid content increases beyond 4.16 mM, there is a sharp increase in the UCS and the superporou hydrogel with acid content 11.10 mM possesses the highest compressive strength, nearly 31036 Nm^{-2}. This variation in UCS with monomer acid content can be explained as follows:

Initially, for the gels with a acid content within the 1.38 mM to 4.16 mM range, the gelation took place at a faster rate and the reaction medium became highly viscous in a

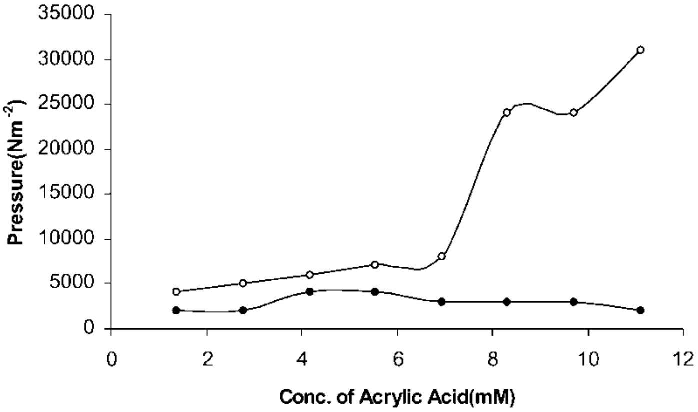
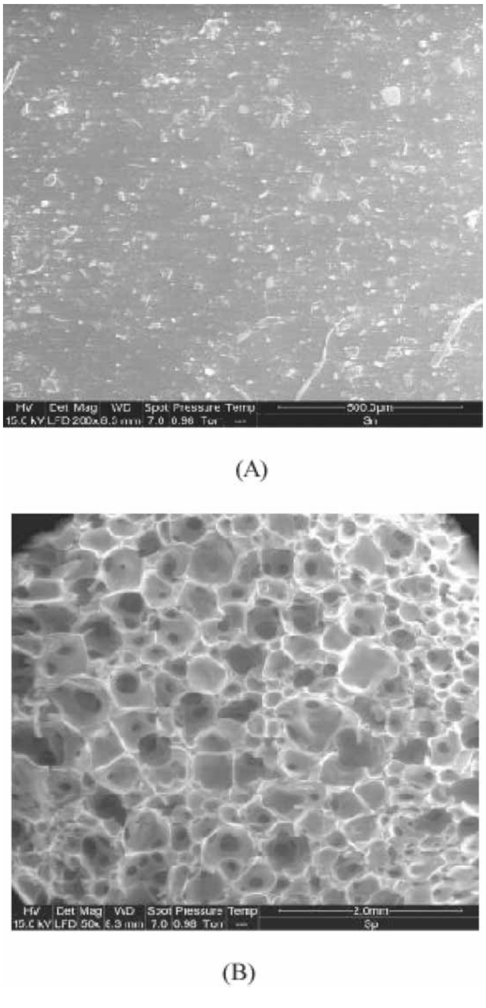


Figure 11. Ultimate compressive strength as function of concentration of monomer acid in superporous hydrogels, swollen in a medium of pH1.0 (–○–) and distilled water (– ● –) at 30°C.

short time. So the CO_2 gas bubbles could not be produced in sufficient number and the gel thus formed was less porous. In addition to this, when gel is placed in a buffer solution of pH 1–2, the H–bonding interactions among the –COOH groups along the polymeric chains provide a compact structure to the gel (25). This accounts for low compressive strength initially. However, when the concentration of AAc is increased, the gelation time increases, and so the porogen produces a sufficient number of gas bubbles before the gelation medium becomes highly viscous. This results in the formation of a network with higher porosity. Due to a porous structure and small degree of hydration, the UCS continues to increase. However, when the AAc content increases beyond 6.93 mM, there is a drastic increase in the compressive strength of hydrogels. This may be attributed to the fact that because of relatively lower gelation time (i.e., 40 ± 3 for gel with 6.93 mM acid) the porogen was added 20 sec before the gelation time was reached and so the bubbles had sufficient time to acquire proper shape within the gelling network. Therefore, the well-formed porous structure with low water content resulted in the



(A)

(B)

Figure 12. SEM of (A) non porous hydrogel; (B) porous hydrogel.

sudden increase in the UCS. The increase in acid content beyond 8.30 mM did not cause much increase in UCS. Finally, it can be concluded that the superporous gels with acid content more than 6.93 mM possess a higher degree of compressive strength and may prove to be good candidates for gastric retention.

The UCS of superporous gel equilibrated in distilled water are depicted in the Figure 11. As shown, the values of compressive strength are much lower than those for the samples swollen in artificial gastric fluid of pH1.2. The observed low values can be attributed to the high degree of swelling of these samples, particularly with monomer acid concentration in the range 5.55 to 11.04 mM (please see Figure 6). The low compressive strength for samples with a higher AAc content may also be due to swelling stress accumulated during the water uptake, when the polymer molecules are not relaxed as quickly as water diffuses in, causing stress can be developed and accumulated during swelling process, therefore, samples are easily cracked. However, the samples with a monomer acid content below 5.5 mM exhibit comparatively less water uptake, but they also show low compressive strength. This can be attributed to the fact that since the gelation time for these samples is sufficiently low, the bubbles could not be formed in a large number, thus resulting in the formation of a polymer network with a smaller number of pores and less flexibility. In this way, there is great difference between the compressive strength profiles of superporous gels with varying acid contents, when swollen in artificial gastric fluid of pH 1.2 and in distilled water.

Porosity and Buoyancy of Superporous Hydrogels

The photograph in Figure 12 shows SEM of hydrogel prepared with and without the presence of a gas blowing agent in the feed mixture. Figure 12(A) represents almost a non-porous network which has been prepared without using $NaHCO_3$ in the reaction mixture. However, Figure 12(B) represents a highly porous network synthesized by using 47.6×10^{-2} mM of porogen in the feed mixture. To make a superporous hydrogel with uniform and interconnected pores, the monomer solution must have good foaming and foam stabilizing mechanism. Figure 12(B) shows that the pores are large in size, but they are not interconnected. This may probably be due to the fact that

Table 2

Porosity, pore volume and buoyancy behavior of superporous hydrogels with varying amounts of porogen, crosslinker and monomer acid successively

Property of superporous hydrogel	Concentration of gas blowing agent mM × 10^{-2}			Concentration of crosslinker mM × 10^{-3}			Concentration of monomer acid mM		
	0.00	35.71	71.42	32.43	97.29	162.15	1.38	5.55	9.26
d_a	0.918	0.187	0.150	0.258	0.139	0.118	0.264	0.275	0.093
d_T	1.106	0.429	0.601	1.274	0.686	0.364	0.424	0.669	0.370
P	0.17	0.565	0.751	0.798	0.798	0.676	0.378	0.589	0.749
Vp ($cm^3 g^{-1}$)	0.185	3.016	5.003	3.091	5.737	5.727	1.429	2.142	8.051
Buoyancy[a]	S	F	F	F	F	F	F	F	F

[a] The test was performed with five samples.

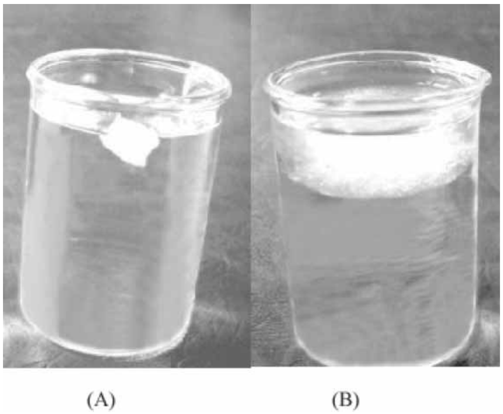


Figure 13. Photograph showing buoyancy behavior of superporous hydrogel sample (control set). (A). State of hydrogel sample just immersed in the distilled water. (B) State of hydrogel sample nearly 30 sec after immersing in distilled water.

during the preparation of this sample most of the gas bubbles might not have been generated within the solution as the gelation time for this sample was very short (nearly 18 ± 2 sec) and therefore the gelation medium acquired sufficient viscosity very quickly and so many of the bubbles could not be produced in a highly viscous medium and the retained bubbles were not enough to form interconnected channels.

We also determined the density, porosity, total pore volume and buoyancy of various superporous hydrogels prepared by varying concentrations of porogen, crosslinking agent and monomer acid in the feed mixtures (see Table 2). It is clear that all the superporous samples synthesized possess the buoyancy, except the one, which was prepared in the absence of porogen. A close look also reveals that the apparent density d_a for the sample prepared without using $NaHCO_3$ has a higher value thus indicating an almost non-porous polymer network formation. Likewise, its pore volume is nearly 30 to 80 times less than those of other samples, providing further evidence of non-porous hydrogel formation.

The photograph in Figure 13 depicts the floating behavior of control set. It was found that the moment the superporous gel was put in the distilled water, it began to float. In fact, we did not observe any time-lag. The gel swelled completely in nearly 30 sec.

Conclusions

It can be concluded from the above study that water uptake behavior of superporous hydrogels depends upon a number of factors, such as the amounts of crosslinker and monomers, concentration of porogen, gelation time, etc. For a definite concentration of monomer acid, the superporous gels possesses the maximum water uptake. The increase in concentration of blowing agent results in enhanced water uptake. However, the water absorbency decreases with crosslinker content. The presence of divalent ions like Ni^{2+} in the swelling medium causes a great decrease in the water uptake of superporous gels. The gels exhibit fair ultimate compressive strength in the artificial gastric fluid while it is quite low for gels swollen in the distilled water. Moreover, the gels with a higher degree of crosslinking exhibit greater percent water retention under varying loads.

Finally, nearly all the hydrogel samples, prepared with varying amounts of crosslinker, blowing agents and monomer acid possessed the buoyancy, except the gels prepared without a pore generating agent.

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