

Preparation and Swelling Behavior of Superporous Hydrogels: Control of Pore Structure and Surface Property

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Abstract. Superporous hydrogels (SPHs) with interconnected pores of several hundreds micrometers were prepared using radical polymerization of acrylic acid (AA) and acrylamide (AAm) in the presence of *N,N'*-methylenebisacrylamide (BIS). A gas blowing method using bicarbonate as a foaming agent was applied to introduce the porous structure under different pH conditions (pH 2~7). The pore structures of the prepared SPHs were examined by a scanning electron microscope. The SPHs obtained at pHs of 4.5 and 4.75 were observed to have a interconnected pore structure with homogeneous distribution and swell to an equilibrium state within several minutes. The O₂ plasma reactor has been used for surface modification of SPHs. The plasma-treated SPHs showed much faster swelling behavior due to the improvement of surface hydrophilicity. The swelling ratio of SPHs was also enhanced by using a wetting agent, such as triacetin and glycerol, during a washing procedure.

Introduction

Most dried hydrogels have a glassy nature, but become rubbery or flexible in the swollen state, where they imbibe a large content of water. When introduced into aqueous environments, they start to swell by absorbing water. Since slow diffusion limits water absorption into glassy hydrogels, it takes a long time ranging from a few hours to several days for the hydrogels to swell to the equilibrium state depending on their shape and dimension. A fast swelling (or water absorption) could be achieved by making the hydrogels in the form of micro-sized particles that have extremely short diffusion path length, but with a dimensional limitation [1-3]. Therefore, the use of hydrogels has been excluded in situations which require fast swelling kinetics or instantaneous responses.

Over the past years, we have developed a series of superporous hydrogels (SPHs) that show both fast swelling and superabsorbent properties [4-7]. The superporous structure could be prepared by using a gas blowing technique that could generate an interconnected pore structure to form open channels for fast water absorption by capillary force. Because the water absorption is accomplished primarily by capillary force, the equilibrium swelling has been achieved within several minutes. The swelling or mechanical property has been further improved by incorporation of hydrophilic polymer grafts or interpenetrating polymer network structure to the hydrogel [8, 9].

In this study, to enhance the swelling rate of the SPHs the pore structure and surface have been modulated. The pore structure has been optimized by varying the pH condition of reaction media and the pore surface has been modified to increase the surface hydrophilicity through oxygen plasma treatment and the use of a wetting agent such as triacetin or glycerol that can lead to a higher swelling rate.

Experimental

Materials. Acrylic acid (AA, 99%), Ammonium persulfate (APS, 98%), *N,N'*-methylenebisacrylamide (BIS, 99%), and *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99%) were purchased from Sigma-Aldrich Korea. Acrylamide (AAM, 98.0%) and PF127 were obtained from Fluka and BASF, respectively. Sodium bicarbonate was obtained from Duksan Pure Chemicals, Co.(Korea). The reagents were used as received in our study.

Preparation of AA/AAM SPHs. The process for making the SPHs is shown in Fig. 1. The SPHs were prepared by polymerization of water-soluble monomers, AA and AAM, in the presence of BIS as a cross-linking agent. AA (10% w/v), AAM (15% w/v), BIS (0.25% w/v) and PF127 (0.5% w/v) were dissolved in distilled water. The pH value of the solution was adjusted from 2 to 7 by adding 8 M NaOH solution. The monomer solutions (8 ml) were placed into polypropylene conical tubes (50 ml) and then APS (0.6% w/v) and TEMED (0.4% w/v) were added. After 3.5 min, sodium bicarbonate powder (5% w/v) was added to the solutions with vigorous stirring using a spatula to generate and distribute gas bubbles evenly throughout the reaction solution. The solutions were kept for 30 min to ensure complete polymerization. The resultant SPHs were dehydrated in ethyl alcohol and placed in a vacuum oven at 60°C for 12h. In case of using wetting agents for surface modification, each wetting agent (5% w/v in ethyl alcohol) was added before drying process.

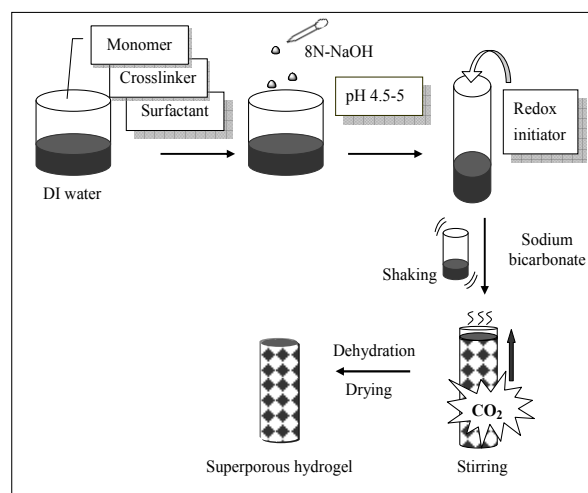


Figure 1. Synthetic procedure for superporous hydrogels.

Surface modification of SPHs by oxygen plasma treatment. A plasma reactor system was used for surface modification of SPHs. The equipment is a bell-jar type reactor with an output impedance of 50 ohms and with radio frequency of 13.56 MHz (Model EPPS 2000, PLASMART Inc. Korea). The oxygen flow rate was measured by mass flow controller (MFC, Brooks, Japan, Model 5850E). The SPH samples (12mm in diameter and 2 mm in thickness) were positioned on the sample die. The whole system was initially evacuated up to 10^{-5} Torr. The powers supplied to external electrode were set at 100W and the samples were treated for 30 or 60 sec.

Characterization. Surface and inner pore structures of dried SPH samples were observed by SEM. The contact angles of SPHs were measured by a drop computerized goniometer (DSA 100, KRÜSS, Germany). Because SPHs are not directly available for the measurement due to the porous structure, the control hydrogels with the same chemical compositions were synthesized without the foaming process and used for comparison. The weight swelling ratio of the SPHs was calculated from the equation, $S = (W_s - W_d) / W_d$. Here, W_s and W_d are the weights of swollen and dried SPH, respectively. The percentage swelling of SPHs was defined as $\% \text{ swelling} = (S_t / S_{eq}) \times 100$. Here, S_t and S_{eq} are the swelling ratio measured at a time (t) and the equilibrium swelling ratio, respectively.

Results and Discussion

Preparation of SPHs. As listed in Table 1, various SPHs based on AA and AAM were synthesized from different pH conditions (pH=2~7). The polymerization rate was significantly dependent upon the pH of the reaction solutions when the redox initiator was used. The superporous structure could not be formed below pH=4 and above pH=5, while the hydrogel with good pore structure could be prepared from the pH values of 4.5 and 4.75. To make a homogenous superporous hydrogel, the polymerization rate should be synchronized with the foaming process. In the low pH range below 4,

the foaming started too early in comparison with the polymerization rate and finished before gelation, resulting in non-porous or partially porous hydrogels. On the other hand, in the high pH range above 5 the gelation reaction was completed before the foaming process was activated. This resulted in modestly porous but heterogeneous hydrogels. As shown in Table 1, the hydrogels with poor pore structure showed a lower swelling ratio and required a longer swelling time. The pH of the reaction solution is one of most important factors for controlling the porous structure of SPHs.

Table 1. Synthetic results for superporous hydrogels

Sample	AA [% w/v]	AAm [% w/v]	pH ^{a)}	T _{eq} ^{b)} [sec]	Pore structure	S _{eq} ^{c)}
AA/AAm01	10	15	2.40	8820	poor	16
AA/AAm02	10	15	3.00	10800	poor	15
AA/AAm03	10	15	4.00	1800	poor	14
AA/AAm04	10	15	4.50	180	good	700
AA/AAm05	10	15	4.75	420	good	725
AA/AAm06	10	15	5.00	720	poor	540
AA/AAm07	10	15	6.00	12420	poor	60
AA/AAm08	10	15	7.00	14400	poor	57

a) The pH value of monomer stock solutions. b) Time required for equilibrium swelling. c) Equilibrium swelling ratio. d) The other chemicals were fixed as the following: BIS = 0.25 %w/v, Pluronic® F127 = 0.5 %w/v, sodium bicarbonate = 5 %w/v. e) The amount of initiator was fixed as the following: APS = 0.6%w/v, TEMED = 0.4 %w/v.

Pore structures of SPHs. The morphological studies of SPHs were performed by SEM and the results are presented in Fig. 2. The figure shows that the SPHs obtained at pH 4.5 and 4.75 have the best pore structures where the pores of even size were interconnected to create open channels. They swelled to the equilibrium state within several minutes. The SPHs prepared at low pH range (pH 2~4) did not have homogenous pores due to too slow reaction rates in acidic conditions. For SPHs obtained at pH 6 and 7, gas bubbling was not generated due to lack of acidity. If the polymerization proceeds too slowly or too rapidly, pores did not form or formed poorly.

Swelling rate of surface-modified SPHs. The O₂ plasma reactor was used for surface modification of SPHs. As shown in Fig. 3, the plasma-treated SPHs show much faster swelling behavior. In case of AA/AAm05, the time for equilibrium swelling was significantly decreased from 420 s to 100 s. The swelling rate became faster with longer plasma treatment. The hydrophilicity of hydrogels was compared by contact angle measurements. The contact angle values before and after plasma surface treatment were 53 and 27, respectively. On the other hand, SEM analysis showed that such plasma treatment had no significant effect on the surface

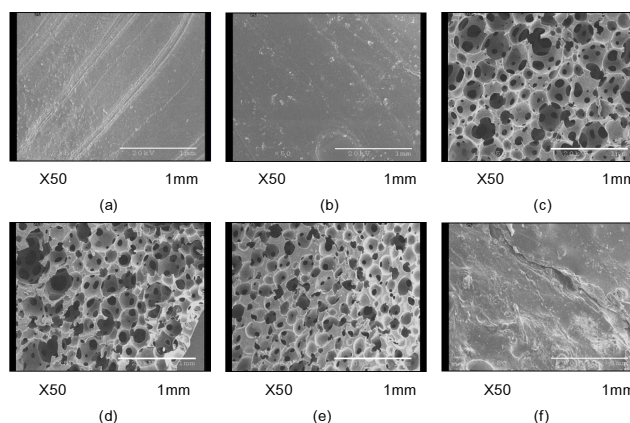


Figure 2. SEM images of hydrogels: (a) pH=3.0, (b) pH=4.0, (c) pH=4.5, (d) pH=4.75, (e) pH=5.0, and (f) pH=6.0.

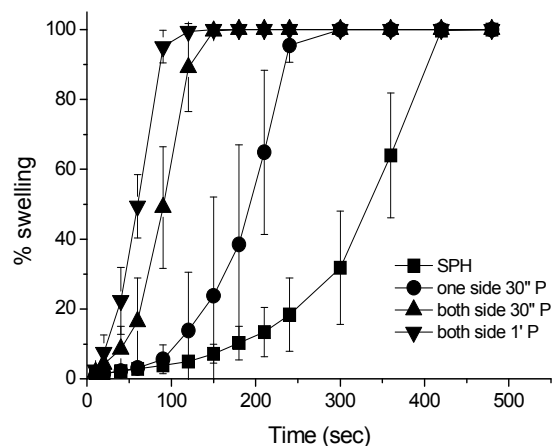


Figure 3. Swelling kinetics of O₂ plasma-treated hydrogels.

morphology (data not shown). As a result, the enhanced swelling kinetics is due to the improved hydrophilicity of the hydrogel surface through O₂ plasma treatment.

The swelling rate of SPHs can be also enhanced by adding wetting agents such as triacetin and glycerol during washing procedures. Through contact angle measurements it was observed that the surface hydrophilicity increased after adding wetting agents (contact angle=20). As shown in Fig. 4, the equilibrium swelling times of the modified SPHs was significantly reduced in comparison with that of the unmodified SPH sample.

The swelling ratios of all the SPHs synthesized ranged from 400 to 700 depending on the pore structure. Usually the swelling ratio can be modulated by controlling the amount of BIS used. Thus, various kinds of SPHs showing different swelling ratios and rates can be prepared for specific uses.

Conclusions

Superporous hydrogels with a fast swelling to a large swelling ratio were prepared using a gas blowing method synchronized with radical polymerization of water-soluble monomers. The pore structure could be optimized by controlling the pH of reaction media and the superporous hydrogels with interconnected pore structure could be obtained from the pH range of 4~5. The hydrogels modified by O₂ plasma treatment showed much improved swelling kinetics due to high hydrophilicity of pore surface. Additionally, the use of wetting agents were also effective to improve the swelling rate by 2~3 times. These SPHs with fast swelling and superabsorbent properties can be useful for biomedical applications where the instant swelling to a large volume is critical or advantageous.

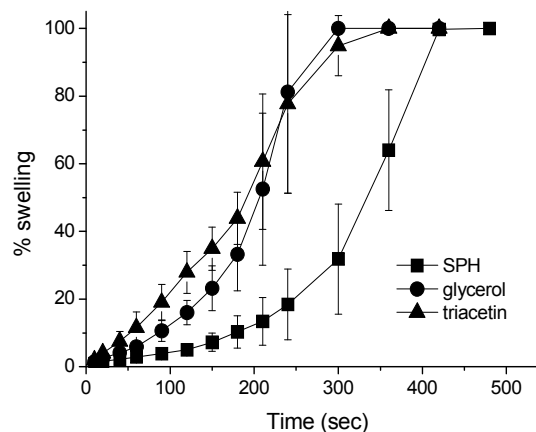


Figure 4. Swelling kinetics of surface-treated hydrogels by wetting agents.

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