Multiporous microstructure for enhancing the water absorption and swelling rate in poly(sodium acrylic acid) superabsorbent hydrogels based on a novel physical and chemical composite foaming system

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ABSTRACT: In this article, we report a novel physical and chemical composite foaming system, which was used to successfully prepare high-performance and low-cost composite superabsorbent [poly(sodium acrylic acid) (PAA–Na)] hydrogels based on acrylic acid by free-radical polymerization in a water bath under a nitrogen atmosphere without the use of any organic solvents. The prepared hydrogels showed superabsorbent properties, high water-absorption abilities and swelling rates, a lighter packing density, and a multi-porous microstructure. Fourier transform infrared spectroscopy and scanning electron microscopy revealed that the sodium dodecyl sulfate surfactant, sodium bicarbonate chemical foaming agent, and 1,1,2-trifluorotrichloroethane physical foaming agent were evenly distributed and grafted onto the PAA–Na matrix. Water-absorption, swelling rate, and packing density testing confirmed that the superabsorbent had a high water-absorption ability and swelling rate and a lighter packing density. Furthermore, we investigated the effects of different foaming agents, including chemical and physical foaming agents, on the swelling and water-retention capabilities of the superabsorbent hydrogels (SAHs). The results show that the combination of these foaming agents significantly improved the water-absorbing capacity. With the help of these foaming agents, we obtained PAA–Na hydrogels without any organic solvents for posttreatment or special porogens; this is an environmentally beneficial way to prepare SAHs for hygiene and biomedical products. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44149.

INTRODUCTION

Superabsorbent hydrogels (SAHs) are defined as three-dimensional networks of hydrophilic polymers with high absorption capacities up to several hundred times their dried weight. Because of their remarkable properties compared with those of traditional water-absorbing materials, such as cotton, pulp, and sponges,[1,2] they are widely used in many specialized applications, including drug-delivery systems, tissue engineering, immobilization of protein and cells, agriculture and horticulture, and sanitary products.[1,3–5] However, compared to a low water-absorption ability, the slow swelling rate is the major disadvantage of these superabsorbent materials, which are used worldwide, as they are made from petroleum-based monomers such as acrylic acid and acrylamide. Recently, several studies on improving the swelling rate of SAHs to expand their applications have been published; there studies have included research on the phase-separation technique,[6] freeze-drying method,[7] foaming technique,[8] and water-soluble porogens.[9]

From the previously reported results, we found that generally speaking, the swelling rate of SAHs is limited by the diffusion speed of water into the hydrogels. At the same time, the creation of porosity in the hydrogel structure influences the diffusion speed of water into the hydrogels. The most effective method for producing hydrogels with a fast swelling rate is to reduce the diffusional path length and the dimensions of the hydrogels. Recently, Chen *et al.*[10] synthesized superporous hydrogels that could swell in an aqueous solution. They believed that the fast swelling rate resulted from the absorption of water by capillary force and diffusion rather than by diffusion only, and the formed pores in the microstructure could form channels for capillary force. The process of foam formation by gas-forming agents resulted in oriented pore structures. Meanwhile, the techniques used to obtain the foam of hydrogels included physical foaming and chemical foaming. Physical foaming is achieved by gas injection (e.g., nitrogen injection) or the addition of a volatile liquid, but it results in inferior pores in distribution compared to chemical foaming. Chemical foaming is achieved by the blending of solid endothermic or exothermic chemical foaming additives with the polymer matrix.[11] Wang *et al.*[12] prepared porous superabsorbent resins (SARs) of poly(sodium acrylic acid) (PAA–Na), which was

obtained by the free-radical polymerization of partially neutralized acrylic acid with a surfactant as a foaming agent, and the water-absorbing capacity of the SARs was enhanced. The incorporation of sodium bicarbonate ($NaHCO_3$) and acetone for foaming system preparation greatly enhanced the swelling properties.[13,14] PAA–Na, which possesses the advantages of wide raw material sources, a simple synthesis method, and a low cost, has many acrylic acid groups, which are the kinds of hydrophilic groups that are conducive to the absorption of more moisture in superabsorbents. PAA–Na, with its porous structure, can be obtained from foam cladding in the PAA–Na network through a fast polymerization process.

However, until now, there have been few reports on chemical and physical foaming agent composite superabsorbents. In this study, a novel foaming system composed of the surfactant sodium dodecyl sulfate (SDS) with the foam stabilizer sodium chloride (NaCl), the chemical foaming agent $NaHCO_3$, and the physical foaming agent 1,1,2-trifluorotrichloroethane (CFC-113) was used in the preparation of porous PAA–Na resins under an N_2 atmosphere. We focused on studying the influence of the types of foaming agent and the combination of three foaming agents on the porous structure and water-absorbing capacity of the composites. Furthermore, the porous morphology, water-absorption ability, swelling rate, and packing density were investigated through water-absorption testing, swelling rate testing, packing density measurement, and scanning electron microscopy (SEM), respectively. Compared with $3.12\,g\,g^{-1}\cdot s^{-1}$, the highest swelling rate reported in the literature as far as we know,[12] we successfully obtained SAHs with foaming agents with a swelling rate of $3.90\,g\,g^{-1}\cdot s^{-1}$.

EXPERIMENTAL

Materials
The acrylic acid (98%), inner crosslinker [analytical reagent (AR)], and redox initiator (AR) was purchased from Zhejiang Satellite Petro Chemical Co. (Zhejiang, China). SDS (AR) and CFC-113 (AR) were obtained from Aladdin Reagent Co. (Shanghai, China). Sodium hydroxide (NaOH; AR), NaCl (AR), alcohol (AR), and $NaHCO_3$ (AR) were obtained from Hangzhou Shuanglin Chemical Co. (Zhejiang, China).

Synthesis of the PAA–Na Hydrogels
PAA–Na was synthesized with two different foaming agents. An optimized two-porogen procedure was used as follows.

The acrylic acid monomer (100 mL) was partially neutralized with NaOH solution (44.4 g of NaOH + 100.0 g of H_2O) in a 40 °C water bath under a nitrogen atmosphere. Then, the inner crosslinker solution (0.8 mL) and SDS (3 mmol or 0 mmol) were gently added to the monomer mixture. The monomer and inner crosslinker solutions were poured into a 500-mL beaker equipped with a magnetic stirrer and a thermometer to monitor temperature changes during the exothermic reaction. Then, the system was heated to 48 °C, and other components were added to the mixture in the following sequence: 1.6 g of a 10 wt % aqueous solution of redox initiator (the proportion of oxidation to reduction initiator was 1:1), NaCl, CFC-113, and $NaHCO_3$. The amounts of foaming agents in each experiment are listed in

Table I. Detailed Formulas of the PAA–Na Resins with the Addition of Different Types of Foaming Agents

Added agent	N	N1	N1′	N2	N3	N4
SDS (mmol)	0	3	3	3	3	3
NaCl (mmol)	0	0	3	3	3	3
CFC-113 (mL)	0	0	0	0	25	25
$NaHCO_3$ (mmol)	0	0	0	12	0	12

Table I. After the addition of the initiator, the temperature and viscosity of the reaction mixture rapidly increased to reach the gelation point. The products were removed from the beaker and dried in a forced-draft oven for 5 h at 100 °C so they could reach a constant weight. The dry products were ground with a hammer-type minigrinder and screened. The obtained particles were stored in well-sealed bottles away from moisture and light.

Comparable nonporous PAA–Na without any surfactant or foam stabilizer was prepared by a similar procedure with surfactant-added samples. The hydrogels were designated as N, N1, N1′, N2, N3, and N4 with the addition of different types of foam agents. For example, N1 PAA–Na hydrogel designation signifies that 3 mmol of SDS was added to the system.

Swelling Studies of the PAA–Na Hydrogels
For swelling studies, the dried PAA–Na hydrogels were placed in the required aqueous swelling media. An amount of 0.20 g of dried sample was immersed in 500 mL of distilled water in beakers (500 mL) at room temperature. To make sure the absorption reached equilibrium, the samples were tested after they were immersed in distilled water for 24 h. At regular time intervals, the hydrogels were taken out of the water, blotted with filter paper to remove excess water present on the hydrogel surface, and weighed. After weighing, the samples were kept back in the medium until the weight of the swollen hydrogel showed no change. Average values of the three samples were taken for each sample, and the water content (%) at different time intervals for each hydrogel was calculated with eq. (1):

$$Q_{eq} = \frac{m_2 - m_1}{m_1} \qquad (1)$$

where Q_{eq} is the practical equilibrium water absorption (g/g), m_2 is the weight of the swollen hydrogel (g), and m_1 is the weight of the dried hydrogel (g).

Packing Density of the PAA–Na Hydrogels
The dried hydrogels were naturally free fallen into a fixed-volume container, and then, the redundant part was carefully removed by a ruler without pressing. The packing density was calculated with eq. (2):

$$\text{Packing density} = \frac{m_2 - m_1}{V} \qquad (2)$$

where m_2 is the weight of the container filled with hydrogels (g), m_1 is the weight of the empty container, and V is the volume of the container. Each test was repeated five times to obtain the mean value of the packing density with an error range of less than 5%.
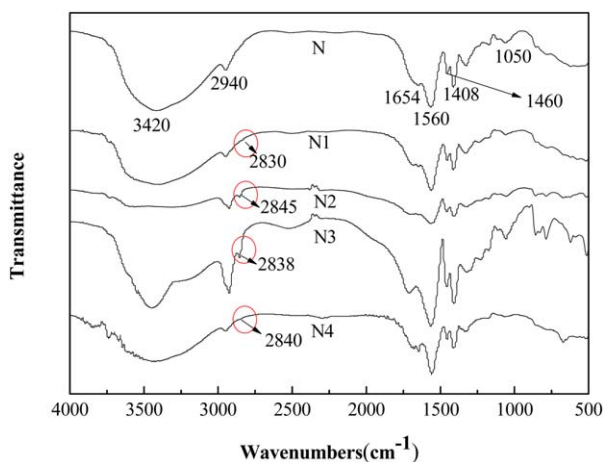
Figure 1. FTIR spectra of the washed N, N1, N2, N3, and N4 under a nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fourier Transform Infrared (FTIR) Analysis

FTIR spectroscopy was measured on a Nicolet Nexus FTIR 6700 spectrophotometer in the 4000–400 cm^{-1} region with KBr pellets.

Internal Microstructure of the PAA–Na Hydrogels

The surface morphology of the hydrogels was investigated with SEM (Hitachi SEM-S4700). These dried hydrogels were stuck with carbon tape and coated with gold before we took the measurements.

RESULTS AND DISCUSSION

FTIR Spectroscopy Analysis of the PAA–Na Samples

The FTIR spectra of the washed N, N1, N2, N3, and N4 samples under a nitrogen atmosphere are shown in Figure 1. For the FTIR spectra of N, the broad absorption peaks at about 3420 cm^{-1} were ascribed to the O—H stretching vibrations of PAA–Na and the bonding of water molecules. The peaks at 2940 cm^{-1} was assigned to the C—H stretching and bending vibrations. The absorption bands at 1654 and 1050 cm^{-1} were the C=O asymmetrical stretching vibrations. The band at 1573–1560 cm^{-1} was attributed to the —COO asymmetrical stretching of —COO— groups, and that at 1460–1408 cm^{-1} was attributed to the —COO symmetrical stretching of —COO— groups. Bands resulting from —CH$_2$— symmetric stretching vibrations were observed in the case of the surfactant-added samples at 2845–2830 cm^{-1}; this verified the presence of surfactant molecules.[15] Sample N had no new peak at 2845–2830 cm^{-1}. This implied that the surfactant was evenly dispersed in the PAA–Na matrix.

Internal Microstructure of the PAA–Na Hydrogels

The morphologies of the dried hydrogels were analyzed by SEM. The microstructures of the hydrogels made from the addition of different types of foam agents are shown in Figure 2. Sample N [Figure 2(a)] showed a smooth surface with no obvious pores, whereas some pores existed on the surfaces of N1, N1′, N2, N3, and N4 [Figure 2(b–f)] when the samples had the surfactant SDS added. This result was in accordance with the

packing densities of N1, N3, and N4 shown in Table II, in which the samples with more pores had a lighter packing density. The samples with the surfactant SDS added produced bubbles easily; thus, they could be wrapped in the polymeric network during the process of polymerization. As reported in the literature, pores improved the contact area between the polymeric network and external solution and endowed the samples with additional space to hold more water. This facilitated the water absorption and swelling rate of the PAA–Na resin.[16]

A comparison of Figure 2(b) with Figure 2(c) showed many more pores in Figure 2(c) because of the addition of the foam stabilizer NaCl, which increased the stability of foams and prolonged the existing time of the bubbles. Hydrogels with added CFC-113 or NaHCO$_3$ showed a different type of porous structure with more pores on the surface [Figure 2(b–f)]. In our case, with the addition of the surfactant SDS, the foam stabilizer NaCl, the low-boiling-point liquid CFC-113, and the chemical foaming agent NaHCO$_3$, the PAA–Na hydrogels had more pores and a lighter packing density. As a result, sample N4 had the potential for high water absorption.

Water Absorption and 0.9% Saline Absorption of the PAA–Na hydrogels

The effects of the foam agent on the absorption behavior of the hydrogels in water at 25 °C are shown in Figure 3. This figure shows the foam-agent-dependent absorption behavior of the hydrogels in water. It indicates that the type of foam agent had a great influence on the water absorption of the SARs. What is more, the absorption behavior of the hydrogels in 0.9% saline at 25 °C also showed [in Figure 3(b)] the same trend in changes. However, it was interesting that water absorption in 0.9% saline was about tenfold less than the absorption in water. When the electrolyte solution (0.9% saline) was added, the swelling capacity increased with decreasing salt concentration.[17] The water-absorption order for different types of foam-agent-added samples was N4 > N2 > N3 > N1′ > N1 > N. The anionic surfactant SDS had a positive effect on the water absorption and the 0.9% saline absorption. The surfactant could form a large number of bubbles under stirring to introduce a multiporous microstructure into the polymeric network in an aqueous environment. The porosity reduced the packing density (Table II) and played multiple roles in enhancing the water absorption and responsive rate of the SARs.[18]

In a comparison of N1 with N1′, the water absorption of N1′ was higher than that of N1. When the foam stabilizer NaCl was added, it enhanced the surface activity of the solution and the strength of the foam film. So, the addition of NaCl substantially improved the foam stability and decreased the liquor surface tension. A high foam stability prevented bubbles from destroying the foam, and more pores could be formed in the polymeric network; this resulted in a slowing of the rate of liquid loss through the foam film and a reduction in the gas permeability. The foam lifetime could be prolonged, and the foam stability was improved. Thus, the packing density was lower and the water absorption was higher in NaCl with SDS added than in the SDS-only samples. As shown in Figure 2, the water absorption of N2 was higher than that in N1′. It was obvious that NaHCO$_3$ reacted with the acrylic acid monomer to produce
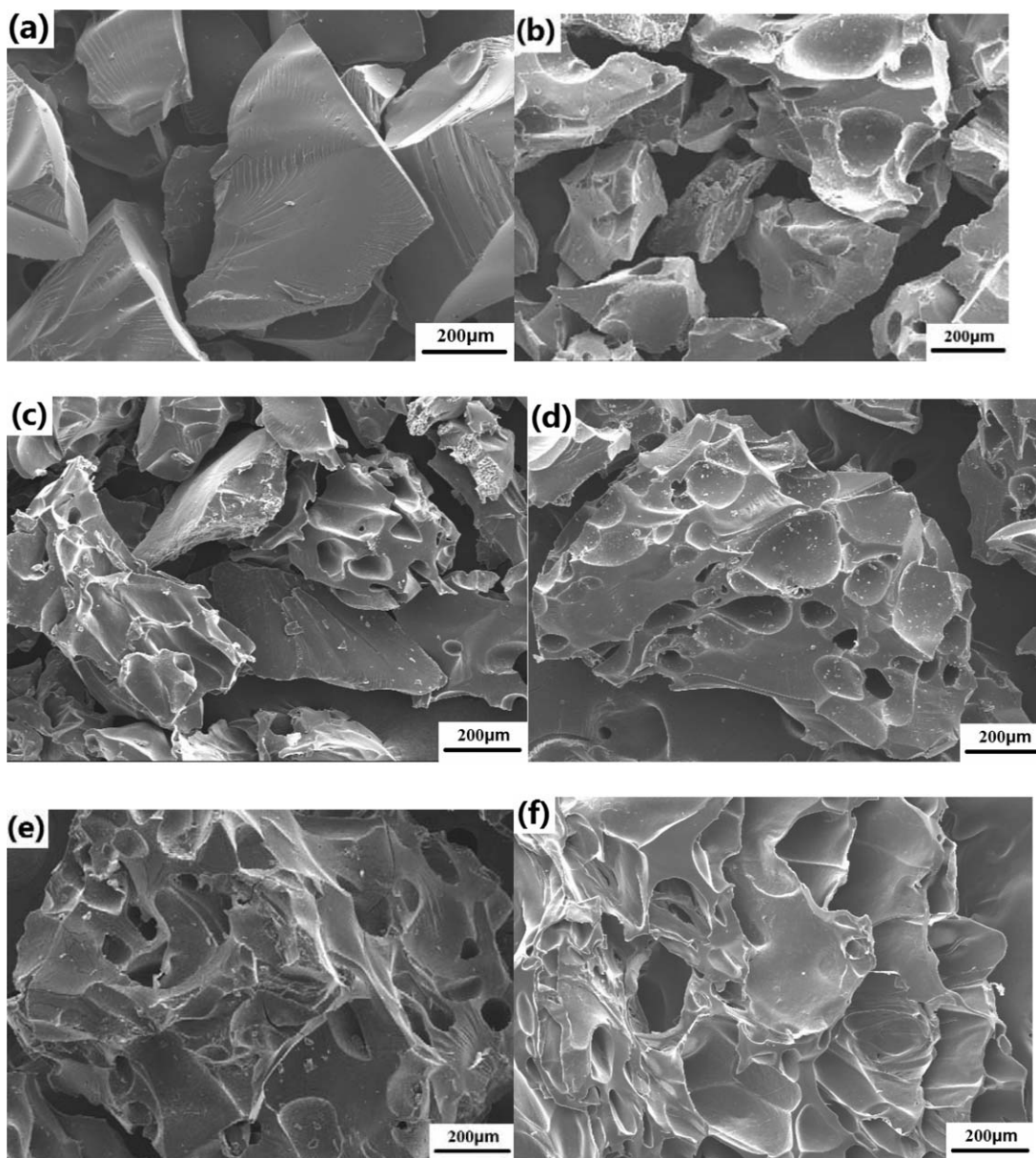
Figure 2. SEM images with the addition of different types of foaming agents of the PAA–Na resins: (a) N, (b) N1, (c) N1′, (d) N2, (e) N3, and (f) N4.

CO_2 gas. As the polymerization process occurred and the solution viscosity increased, it was difficult for CO_2 to escape from the polymer network. It was enshrouded in the polymer porous structure formation. Thus, the packing density was lower, and the water absorption was higher. In a comparison of N3 with N1′, the sample N3 with added CFC-113 had a higher water absorption. The low-boiling-point liquid CFC-113 (48 °C) turned into a gas when the reaction temperature increased

sharply; this left many holes in the polymer matrix. As result, the sample with added CFC-113 had the potential to retain water. In a comparison of all of the samples, N4 had the best ability to hold water. In our case, with the addition of the surfactant SDS, the foam stabilizer NaCl, the low-boiling-point liquid CFC-113, and the chemical foaming agent $NaHCO_3$, the PAA–Na hydrogels held much water and had the best water absorption.

Table II. Packing Densities with the Addition of Different Types of Foaming Agents of the PAA–Na Resins

SAR	N	N1	N1′	N2	N3	N4
m_2 (g)*	3.82 (0.02)	3.40 (0.02)	3.32 (0.02)	3.25 (0.04)	3.36 (0.05)	2.87 (0.02)
Packing density (g/mL)	0.87 (0.01)	0.76 (0.01)	0.74 (0.02)	0.72 (0.01)	0.75 (0.01)	0.62 (0.05)

Standard deviations from the two test samples are shown in parentheses. *m_2 is the weight of the container filled with hydrogels (g).
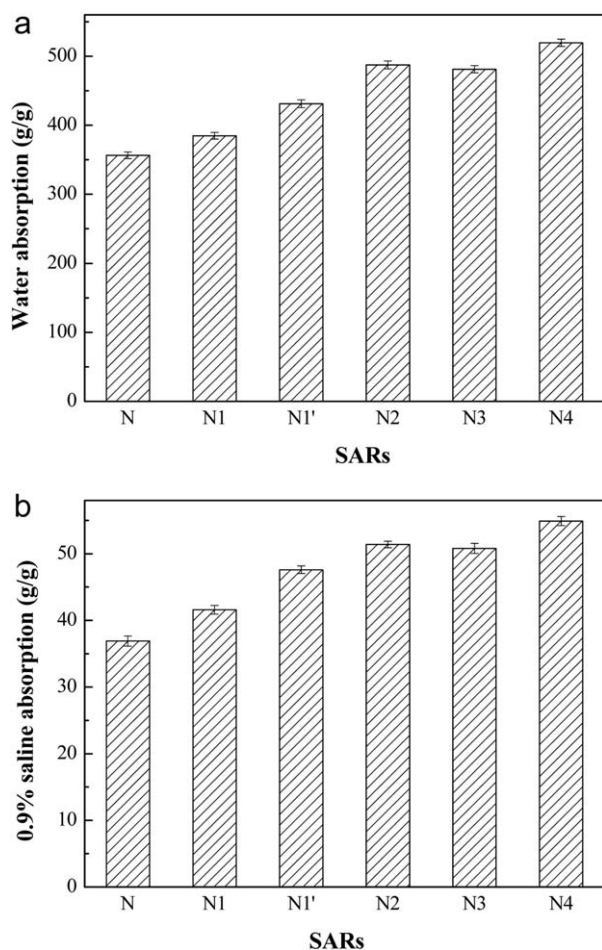
Figure 3. (a) Water absorption with the addition of different types of foaming agents of the PAA–Na resins under an N_2 atmosphere and (b) 0.9% saline absorption with the addition of different types of foaming agents of the PAA–Na resins.

Table III. Swelling Kinetic Parameters for the Addition of Different Types of Foam Agents of the PAA–Na Resins

SARs	Q_{eq} (g/g)	Q_{∞} (g/g)	k_{is} (g g^{-1}·s^{-1})
N	298	308	2.54
N1	368	377	3.68
N1′	406	420	3.69
N2	430	446	3.71
N3	426	441	3.73
N4	466	483	3.90

with the intercept and slope of the lines and are presented in Table III.

Figure 4 shows the swelling behaviors of the N, N1, N1′, N2, N3, and N4 samples, the data of which were obtained from two testing samples. In a comparison of N with N1, it was shown that the swelling rate of N1 in distilled water was higher than that of N1. Regardless of the foaming agents used, all of the
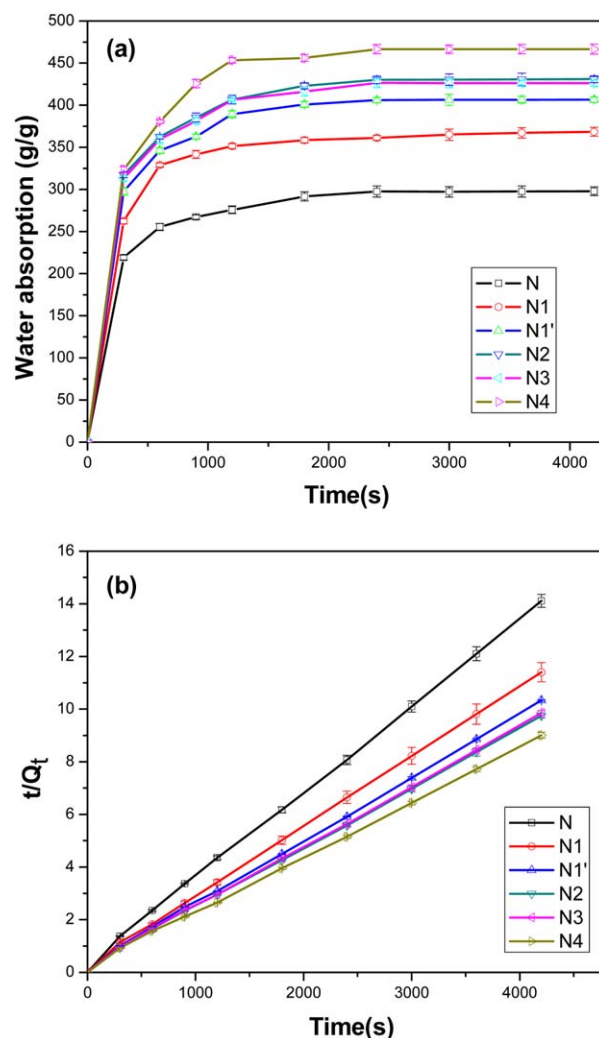
Swelling Rates of the PAA–Na Hydrogels

In addition to the water absorbency of SARs, the swelling rate also plays an important role in various application fields, such as in the biomedical, environmental, and pharmaceutical areas. The swelling rates of the SARs were dependent on the compositions of the polymers, the multiporous microstructure, and the external conditions. In this part of the study, the swelling rates of different foam agents with surfactant in distilled water were investigated (Figure 3). Initially, the swelling rate increased and then began to level off after 600 s until the equilibrium swelling was achieved. The effect of different foam agents with the surfactant on the swelling kinetic behaviors were analyzed by a Schott's pseudo-second-order swelling kinetics model,[19] as described in eq. (3):

$$\frac{t}{Q_t} = \frac{1}{k_{is}} + \frac{1}{Q_{\infty}} t \qquad (3)$$

where Q_t is the water absorption at time t, Q_{∞} is the theoretical equilibrium water absorption, and k_{is} is the initial swelling rate constant. Graphs of t/Q_t verse t gave straight lines with a relatively good linear correlation coefficient; this indicated that the swelling rate of the samples obeyed Schott's theoretical model. The swelling parameters, such as k_{is} and Q_{∞}, could be calculated

Figure 4. (a) Swelling kinetic curves and (b) t/Q_t–t graphs of N, N1, N1′, N2, N3, and N4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

superporous hydrogels reached swelling equilibrium within 2000 s. The addition of a proper amount of SDS gave rise to an initial absorption rate through the generation of a multiporous microstructure in the three-dimensional polymeric network. In a comparison of N1 with N1′, the addition of the foam stabilizer significantly improved the foam stability, made the foam surface denser, increased the surface elasticity, and decreased the volume of a single bubble, which became more uniform and small, so that the foams were more difficult to break. Therefore, as depicted previously, N1′ had more pores in the surface [Figure 2(c)], a lower packing density (Table II), and more foams formed in the polymeric network. Moreover, the multiporous microstructure facilitated the easier entrance of the water molecules into the polymeric network. The porosity of the samples contributed to the enlargement of the surface area to speed up the diffusion rate of water molecules and improve the swelling rate of the samples.

As shown in Figure 4, the swelling rate of N2 was higher than that of N1′. It was obvious that $NaHCO_3$ reacted with the acrylic acid monomer to produce CO_2 gas. As the polymerization process occurred and the solution viscosity increased, it was difficult for the CO_2 to escape from the polymer network. It was enshrouded in the polymer porous structure formation. In a comparison of N3 with N1′, the sample N3 with added CFC-113 had a higher swelling rate. The low-boiling-point liquid CFC-113 (48 °C) turned into a gas as the reaction temperature increased sharply; this left many holes in the polymer. As a result, the sample with added CFC-113 had the potential to retain water. In a comparison of all the samples, N4 had the best ability to hold water. In our case, the best foaming agent was made up of the surfactant SDS, the foam stabilizer NaCl, the low-boiling-point liquid CFC-113, and the chemical foaming agent $NaHCO_3$. When the foam agent addition sequence and the reaction time were controlled, the polymer produced lots of bubbles or pores in polymerization, the packing density was greatly reduced, the formation of the pores in the part was interconnected, and finally, a water channel was formed in the polymer network.

CONCLUSIONS

Superabsorbent PAA–Na resins were prepared by a free-radical solution polymerization reaction with the surfactant SDS, the foam stabilizer NaCl, the chemical foaming agent $NaHCO_3$, and the physical foaming agent CFC-113 as foam templates to achieve a multiporous microstructure for enhancing the water absorption and swelling rate. The results show that the combination of these foaming agents significantly improved the water-absorbing capacity, and compared to PAA–Na resins without porous structures, the packing density decreased from 0.87 to 0.62 g/mL, the water absorption improved from 356 to 519 g/g, the 0.9% saline absorption improved from 37 to 55 g/g, and the swelling rate was enhanced from 3.12 to 3.90 g g^{-1}·s^{-1}. When the foam agent addition sequence and the reaction time were controlled, the polymer could produce lots of bubbles or pores in polymerization; this greatly reduced the packing density, the formation of

the pores in the part was interconnected, and finally, a water channel was formed in the polymer network. Therefore, we used the synergistic effect of the system of a special surfactant, a foam stabilizer, a chemical foaming agent, and a physical foaming agent to improve the water absorption and swelling rate of the superabsorbent PAA–Na resins. The use of this method to fabricate hydrogels could potentially facilitate the development of materials for hygienic applications and prevent the use of any organic solvents, including in diapers for babies and adults, sanitary napkins, soil water-holding agents, wound dressings, and cooling gels in medical applications.

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