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Polymer composition and acidification effects on the swelling and mechanical properties of poly(acrylamide-co-acrylic acid) superporous hydrogels

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Abstract—Poly(acrylamide-co-acrylic acid) (poly(AM-co-AA)) superporous hydrogels (SPHs) were synthesized and the acidification effects on the swelling and mechanical properties were studied. Gelation exotherms were measured to determine the optimum introduction time for adding a blowing agent. The gelation kinetics decreased with increasing the AA concentration. The maximum equilibrium swelling was observed around an AA weight fraction of 0.4, but the compressive strength decreased monotonically with increasing the AA concentration. Poly(AM-co-AA) SPHs were much less swollen in acidic solution than in distilled water of pH 6.7. The swelling ratio decreased with increasing acidity (decreasing pH). Reduction of water absorption content by acidification led to considerable increase in the mechanical strength.

Key words: Hydrogel; polyacrylic acid; porosity; swelling; mechanical test.

INTRODUCTION

Superporous hydrogels (SPHs) [1–7] were recently developed for their potential applications in controlled drug delivery, especially for developing oral gastric retention devices. SPHs are characterized by a three-dimensional network structure with numerous pores in relatively large sizes ranging from micrometers to millimeters. The fast and high water absorbent property is accommodated by the presence of interconnected pores and this provides SPHs with many applications in various fields including horticulture, water sealing or caulking ability in civil constructions

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and hygienic and biomedical areas. The current SPHs, however, possess rather poor mechanical strength, mainly due to their extreme swelling property. As SPHs absorb a lot of water, they are easily cracked in water when even small force is applied. As the decrease of mechanical strength is mainly caused by high water absorbency, understanding the relationship between equilibrium water swelling and mechanical strength of SPHs is very important.

In poly(acrylamide-co-acrylic acid) (poly(AM-co-AA)) SPHs, neutralization of poly(AM-co-AA) with metal hydroxide leads to considerable increase of water absorption due to ionization of AA [8, 9]. As the synthetic process of poly(AM-co-AA) SPHs requires addition of sodium bicarbonate [2, 3], poly(AM-co-AA) becomes highly neutralized during gelation. The neutralization extent is a key parameter affecting the swelling and mechanical properties of poly(AM-co-AA) SPHs. In this study both the neutralized and acidified poly(AM-co-AA) SPHs were synthesized and the effects of polymer composition and neutralization extent on the equilibrium swelling and mechanical properties were investigated.

MATERIALS AND METHODS

Synthesis of SPHs

To 1.25 g of the aqueous monomer solution, composed of 50% (w/v) acrylamide (AM, Aldrich, Milwaukee, WI, USA) and 50% (w/w) acrylic acid (AA, Aldrich), were added 0.275 g of 2.5% (w/v) N,N′-methylenebisacrylamide (BIS, Aldrich), cross-linking agent, 0.125 g of 10% (w/v) Pluronic F127 (BASF, Gurnee, IL, USA), foam stabilizer and 0.05 g of 20% (v/v) N,N,N′,N′-tetramethylethylenediamine (TEMED, Aldrich), initiator. The reactant mixture was placed in a 1 cm (I.D.) × 16 cm (*l*) borosilicate glass culture tube (Corning, New York, NY, USA) and then neutralized to pH 5.1 by addition of 50% (w/v) sodium hydroxide aqueous solution.

Polymerization reaction was initiated by adding 60 μl of 20% (w/v) ammonium persulfate (APS, Aldrich) solution, which is the other component of the redox pair, to the reactant mixture. Foaming reaction was triggered by addition of sodium bicarbonate (J.T. Baker, Phillipsburg, NJ, USA), while the mixture was vigorously stirred with a spatula. The polymerization reaction was conducted at room temperature for different monomer compositions; AM/AA weight ratios were 1 : 0, 0.8 : 0.2, 0.6 : 0.4, 0.4 : 0.6, 0.2 : 0.8 and 0 : 1.

Some SPHs were placed in 0.01, 0.1, or 1 M HCl aqueous solution to equilibrium and then washed with distilled water. The water absorbed in SPHs was extracted with ethanol. The processed SPHs were stored in the convection oven for complete drying.

Polymerization reaction exotherms

Since the polymerization reaction is exothermic, the heat generated during the polymerization reaction provides good information about the reaction kinetics. The temperature change of the reactant was monitored during polymerization by placing a thermocouple in the reactor tube. The thermocouple was connected to a personal computer through a temperature controller (model 3000, LFE Instruments). Data acquisition software was used for their analysis.

Microstructure of pores

The microstructure of pores generated in poly(AM-co-AA) SPHs was investigated using scanning electron microscope (SEM, Hitachi, S-2400, Japan). Samples with different AM/AA weight ratios, from 1.0 : 0 to 0 : 1.0, were used for this investigation.

Equilibrium swelling and compressive strength measurement

Cylindrical-shaped SPHs were cut in lengths of 5–10 mm, weighing 0.15–0.2 g. Samples were placed in distilled water and were periodically weighed at room temperature until no weight change was observed. The equilibrium swelling ratio was defined as the weight of an equilibrium swollen SPH divided by the weight of a dried SPH. The same measurements were repeated at least three times for each neutralized and acidified sample. The average value was taken for the determination of the equilibrium swelling ratio.

A bench comparator (Ames, Waltham, MA, USA) was used to measure the compressive strength of water-swollen SPHs. Samples were located on the bench comparator and a series of cylindrical loads were applied to the top of each sample. The ultimate compressive strength was determined as the applied force (weight) divided by the load contacting area when samples were broken.

RESULTS AND DISCUSSION

Polymerization kinetics

The amount of sodium hydroxide solution necessary to adjust the pH of the monomer solution to 5.1 was measured for different monomer compositions, as shown in Fig. 1. As the AA concentration in the monomer solution increased, a larger amount of sodium hydroxide solution was required for neutralization.

The rate of gelation is very important to determine the time to introduce a blowing agent. Too early introduction of a blowing agent during gelation results in formation of foams that may not last long enough until the completion of the gelation process. Introducing a blowing agent too late may not even generate a foam due to completion of the cross-linking reaction. To determine the optimum introduction time for a blowing agent, the polymerization reaction kinetics were measured by tracking the reaction exotherms. Figure 2 shows the temperature profiles during polymerization reactions right after the initiator was introduced to the monomer mixtures. In Fig. 2, the gelation induction time is defined as the

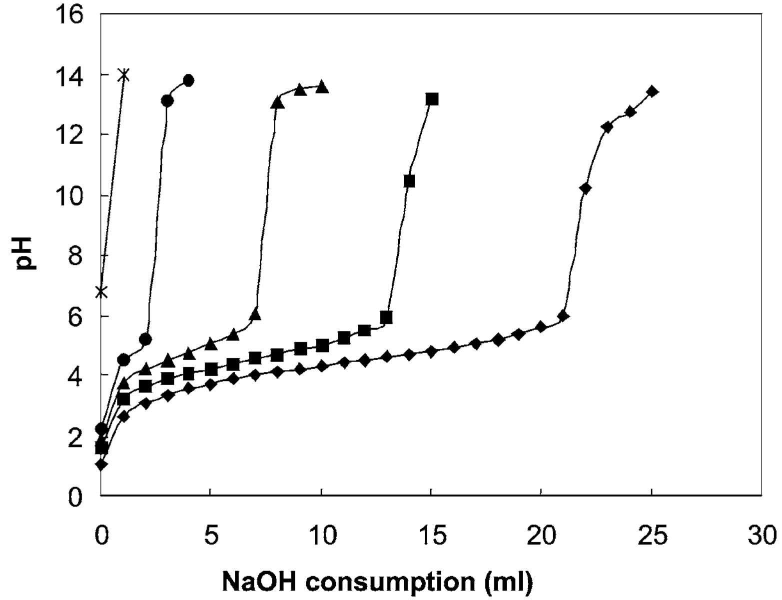


Figure 1. The amount of NaOH solution (50%, w/v) necessary to adjust the pH of the monomer solution for the synthesis of poly(AM-co-AA) with different AM/AA weight ratios. The AM : AA ratio were 0.25 : 0.75 (◆), 0.5 : 0.5 (■), 0.75 : 0.25 (▲), 0.9 : 0.1 (●) and 1.0 : 0 (×).

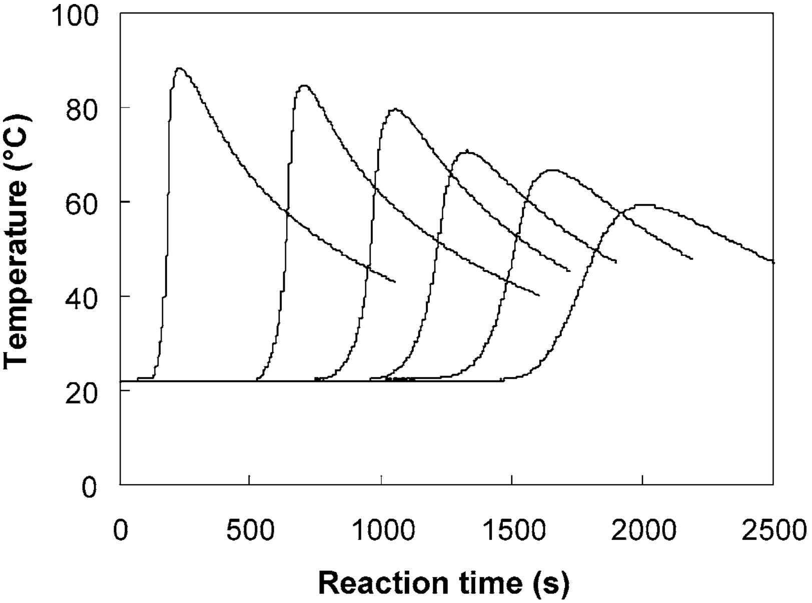


Figure 2. Reaction exotherms during the cross-linking polymerization of poly(AM-co-AA) neutralized to pH of 5.1 for different AM : AA weight ratios. The AM/AA ratios are, from left to right, 1 : 0, 0.8 : 0.2, 0.6 : 0.4, 0.4 : 0.6, 0.2 : 0.8 and 0 : 1.

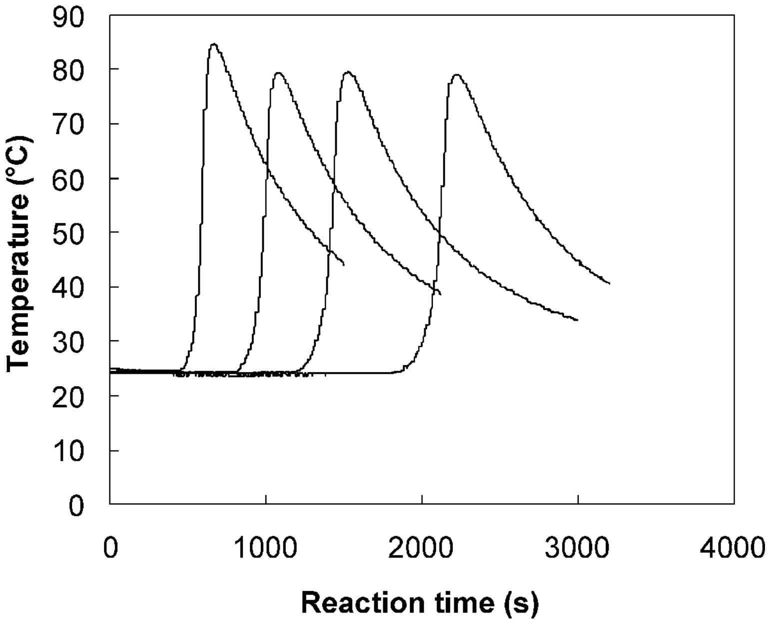


Figure 3. Reaction exotherms during the polymerization of poly(AM-co-AA) with the AM : AA weight ratio of 0.6 : 0.4. Samples were adjusted, from left to right, to pH 5.3, 5.1, 4.9 and 4.7.

time when the reaction temperature first starts to rise and gelation completion time as the time when the reaction temperature reaches the peak. As shown in Fig. 2, both the gelation induction and gelation completion time increase with increasing AA concentration. This indicates that as the AA concentration increases, the polymerization reaction becomes slower, even at the same pH. The pH dependence of the reaction exotherms for poly(AM-co-AA) SPHs with an AM/AA weight ratio of 0.6 : 0.4 is shown in Fig. 3. As the pH of the monomer solution decreased from 5.3 to 4.7, significant delays in the gelation induction and completion times were observed. Clearly, pH is one of the most important factors controlling the polymerization kinetics and so has a large impact on the synthesis of SPHs.

For preparation of SPH samples in this experiment, the blowing agent was introduced 1 min before the gelation induction time. Figure 4 shows the blowing agent introduction time as a function of the acrylic acid concentration. The blowing agent introduction time increased almost linearly with AA concentration.

Pore structure

Figure 5 shows the pore structures of poly(AM-co-AA) SPHs with AM/AA weight ratios of 1.0 : 0, 0.6 : 0.4, 0.2 : 0.8 and 0 : 1.0, respectively. Pores were quite uniformly distributed and their diameters ranged from 50 μm to 200 μm. As the gelation kinetics were different for each system, the pore size was different for different composition. At AM/AA ratios of 1.0 : 0 and 0.6 : 0.4 (Fig. 5, top left and top right), the gelation started and completed while the gas bubbles were

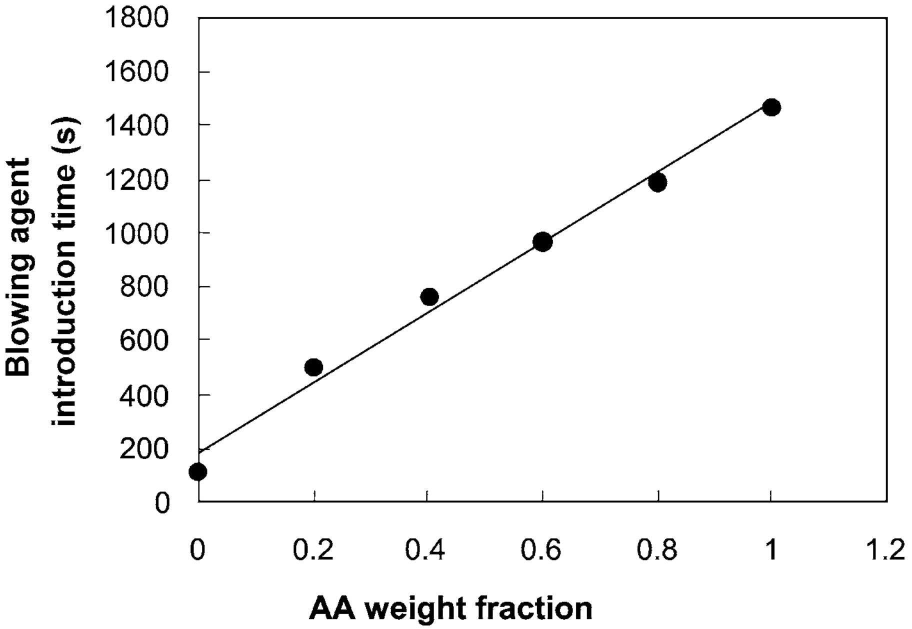


Figure 4. Blowing agent introduction time as a function of polymer composition when the pH of reactant was adjusted to 5.1.

actively forming and this resulted in highly open pore structures. At the other end of the scale, where the AM/AA ratios were 0.2 : 0.8 and 0 : 1.0 (Fig. 5, bottom left and bottom right), the gelation began and ended slower as compared with the bubble formation and maintenance of the foam structure and thus many of the pores were closed. When the AA/AM ratio was about 0.5 : 0.5, formation of open pore structures was optimum.

Equilibrium swelling and mechanical behavior of neutralized SPHs

Figure 6a shows the equilibrium swelling ratio of the neutralized poly(AM-co-AA) SPHs at pH 5.1. The swelling ratio did not change monotonically with monomer concentration. Instead, the maximum swelling ratio was observed around an AA weight fraction of 0.4. This result was caused by the difference in both the pore structure of synthesized polymers and the inherent properties of component polymers. At very high AA concentrations the gelation reaction was too slow to stabilize bubbles and, thus, produce large but partially blocked pores at the end of the reaction, leading to less swelling. At low AA concentrations, on the other hand, the swelling ratio decreased with increasing AA fraction due to the increase in hydrophilicity of AA.

Figure 6b shows the compressive strength of neutralized SPHs swollen in water. Inverse relationship between the compressive strength and swelling ratio was expected by simple plasticization effect. The compressive strength, however,

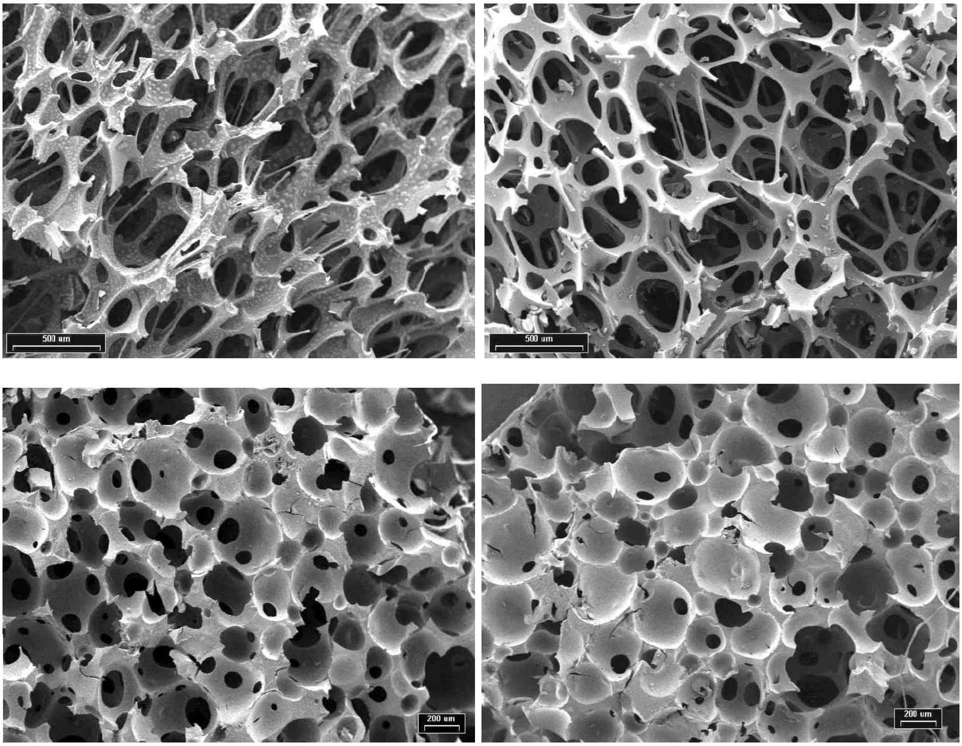
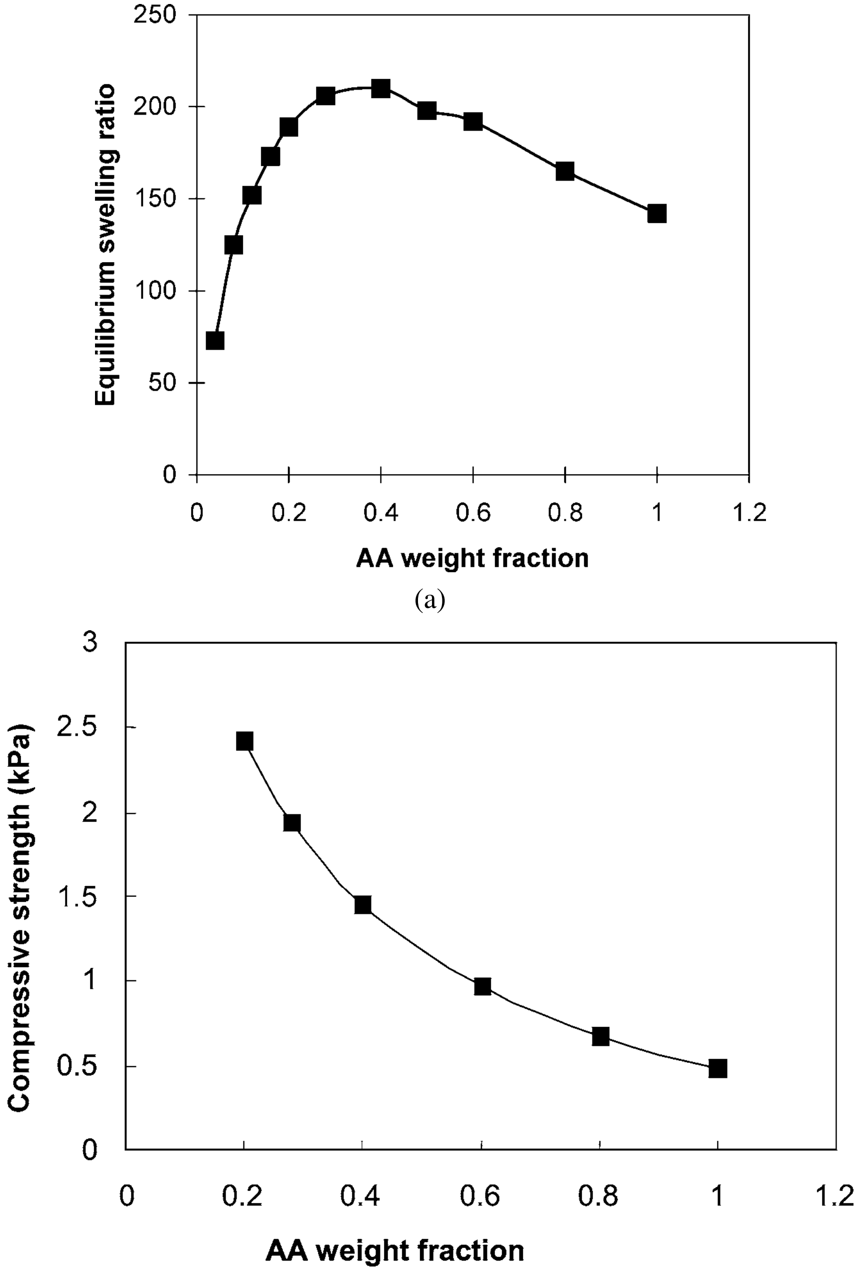


Figure 5. SEM microphotographs of poly(AM-co-AA) SPHs with AM/AA weight ratios of 1.0 : 0 (top left), 0.6 : 0.4 (top right), 0.2 : 0.8 (bottom left) and 0 : 1.0 (bottom right). Magnification = 50×.

decreased monotonically with the AA concentration, while water swelling ratio showed maximum around an AA weight fraction of 0.4. The decrease in both swelling ratio and mechanical strength with the AA concentration above 0.5 is due to the high tendency of cracking induced by relatively slow mechanical relaxation to the external stress.

Equilibrium swelling and mechanical behavior of acidified SPHs

Figure 7 shows the equilibrium swelling ratios of poly(AM-co-AA) SPHs in HCl aqueous solution of different concentrations. The swelling behavior of SPHs in 0.1 M HCl aqueous solution is expected to be similar to that in the gastric liquid. Comparison of Figs 6 and 7 shows that the swelling ratios of neutralized polymer gels in acidic solutions are much lower than those in neutralized water. The swelling ratio decreased with increasing HCl concentration (decreasing pH). Most sodium ions attached in the carboxylic group of AA molecules were exchanged with protons in the acidic environment. When this occurred, polymer molecules were not fully extended in acid solution, due to the reduced repulsive interaction between the polymer chains. As this trend was more considerable in more acidic conditions, the swelling ratio decreased with increasing acidity up to the certain acidic environment



(a)

(b)

Figure 6. Composition dependence of equilibrium swelling ratio (a) and ultimate compressive strength (b) of poly(AM-co-AA) SPHs. Experimental error range is in ±5%.

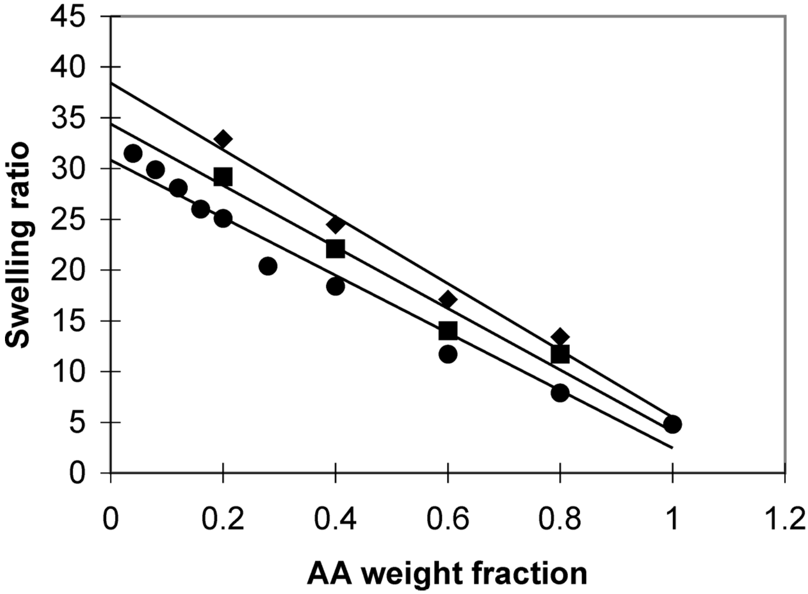


Figure 7. Equilibrium swelling ratio of neutralized poly(AM-co-AA) SPHs in 1 (●), 0.1 (■) and 0.01 M (◆) HCl aqueous solution, respectively.

where all metal ions were fully replaced by protons. For the polymer samples at the same HCl concentration, the swelling ratio increased with increasing AM weight fraction as the water affinity of homo-polyAM is higher than that of acidified homo-polyAA. Furthermore, lower AA concentration resulted in lower intermolecular hydrogen bonding between AA moieties, resulting in higher swelling.

Figure 8 shows the equilibrium swelling behavior of poly(AM-co-AA) SPHs in distilled water. SPH samples were firstly acidified in HCl solutions with different pH values. The equilibrium water swelling ratio of acidified poly(AM-co-AA) SPHs was much lower than those of neutralized ones. The swelling ratio in distilled water decreased monotonically with the acidic concentration of HCl solution that was used to acidify SPHs. The presence of charges on neutralized polyAA and the requirement of neutralization in the bulk systems provided an ionic contribution to the total swelling capacity [10–14]. The decrease in the charge density of the acidified gel reduced ionic contribution to swelling pressure and thus reduced water absorption. Swelling ratio increased with increasing AM concentration up to its weight fraction of around 0.8, beyond which no further increase was observed because smaller pores were developed for higher AM concentration.

Reduction of water absorption content by acidification led to considerable increase in the mechanical strength. The compressive strength was so high that samples were not cracked until the two end surfaces met under the load of 0.29 MPa, the maximum pressure that could be applied using the present equipment.

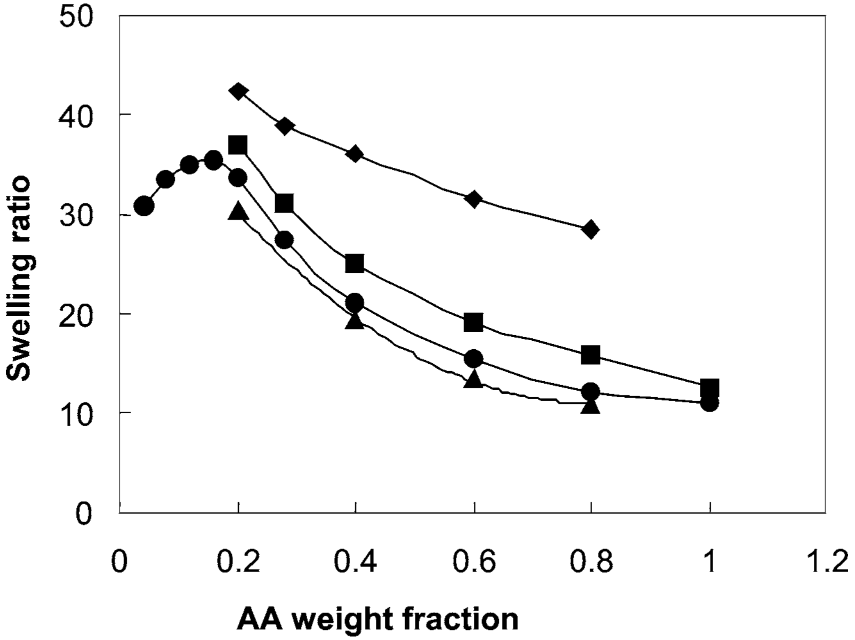


Figure 8. Equilibrium swelling ratio of poly(AM-co-AA) SPHs in distilled water. Samples were acidified in 10 (▲), 1 (●), 0.1 (■) and 0.01 M (◆) HCl aqueous solution, respectively, before swelling experiment.

CONCLUSIONS

SPHs of poly(AM-co-AA) were prepared and the acidification and composition dependence of swelling and mechanical properties were investigated. In the preparation of SPHs, the introduction time of a blowing agent was determined from the gelation kinetics measured by the polymerization reaction exotherms. The neutralization extent of reactant was controlled by addition of NaOH aqueous solution. The gelation rate became slower with increasing the AA fraction in copolymers when neutralization extent (pH) was fixed, but it increased with pH with the same polymer composition. The pores were quite uniformly distributed and their diameter ranged from 50 μm to 200 μm. The maximum equilibrium swelling was observed around the AA weight fraction of 0.4 for neutralized samples, but it decreased monotonically with the AA fraction for acidified SPHs. Acidification reduced water absorption considerably because acidification resulted in no ionic contribution to swelling pressure. The neutralized SPH samples with high AA concentrations were easily cracked in water, but acidified ones showed high mechanical strength even at very high AA concentrations. The difference of this mechanical behavior between the two polymeric systems was caused by both stress relaxation and plasticization effect.

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