



# Swelling and mechanical properties of superporous hydrogels of poly(acrylamide-co-acrylic acid)/polyethylenimine interpenetrating polymer networks

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## Abstract

Swelling and mechanical properties were investigated for superporous hydrogels (SPHs) of poly(acrylamide-co-acrylic acid)/polyethylenimine (P(AM-co-AA)/PEI) interpenetrating polymer networks (IPNs). Gelation kinetics of SPHs changed significantly according to the acidic condition of reactant. The compressive strength of neutralized SPHs decreased monotonically with AA concentration, while the maximum swelling was observed around the AA weight fraction of 0.4 for all PEI concentrations. The SPH samples composed of high concentrations of AA and PEI were easily cracked in water due to the swelling stress developed during water uptake. The swelling kinetics decreased with increasing PEI and PAA concentrations because of the high molecular entanglement and network density associated with ionic interaction between PAA and PEI molecules. For non-neutralized SPHs, the equilibrium water uptake decreased but the compressive strength increased with PEI and PAA concentrations by simple plasticization effect.

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## 1. Introduction

Hydrogels are three dimensional network polymers swellable in water. Their network structures are provided not only by typical covalent bonding but also by ionic, hydrogen, or even van der Waals interaction. Unique physical properties of hydrogels such as high water affinity, high thermal and mechanical stability, biocompatibility, etc. provided them with a variety of industrial applications [1]. Biomimetic and drug delivery applications are among them, as hydrogels are suitable materials not only for imitating the precise structure and function of living systems but for controlling the drug releasing pattern inside the living body. A variety of stimuli sensitive hydrogels [2,3] have been studied for these applications, but in many cases, slow response to environmental stimuli caused limitation to their effective use.

In relevance to the importance of fast response to

environmental change, a number of studies [4–12] have been conducted on the establishment of fast swelling or shrinkage of hydrogels. Introduction of pores in hydrogels was one of good trials for this purpose. The pores present in hydrogels create large surface area to accommodate lots of water in short time. Depending on the pore size, porous hydrogels are divided into microporous, mesoporous, macroporous and superporous hydrogels (SPHs). The standard pore size of each type of porous hydrogel is in the range from 10 to 100, 100 to 1000 nm, 1 to 100 and 10 to 1000  $\mu\text{m}$ , correspondingly. While microporous, mesoporous, and macroporous hydrogels are generally prepared by freeze drying [13], porogens [14–16], microemulsion [17], and phase separation methods [6–8,18], SPHs [19–25] are by simultaneous reactions of gelation and gas blowing [26,27].

Although large pores provide SPHs with fast and high water imbibe, they are mechanically too weak to sustain their functions for long time. Their molecular structures are easily destroyed when even small force is applied. They are hardly re-used once contacted with water. As these

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problems are attributed to low elastic strength of SPHs in water, this research aimed at the development of SPHs with enhanced elastic strength to keep their water holding ability for long-time.

Poly(acrylamide-co-acrylic acid) (P(AM-co-AA)) was chosen as the base material in this study because of its high water affinity and commercial availability. As P(AM-co-AA) SPH itself did not have enough mechanical strength in the swollen state, the interpenetrating polymer network (IPN) structure was considered. Polyethyleneimine (PEI) was chosen as the second polymer component for this role, because it had several advantageous properties like high hydrophilicity, biocompatibility, thermal stability as well as commercial availability. High resilient property can be provided by high molecular entanglement associated with high molecular weight and highly branched structure. PEI also can function as a cationic polyelectrolyte, and thus is strongly attracted to the anionic-charged organic molecule like AA. In this study, SPHs of P(AM-co-AA)/PEI IPN were prepared, and the effects of composition and neutralization on the swelling and mechanical properties were investigated.

## 2. Experimental

### 2.1. Raw materials

Acrylamide (AM) and acrylic acid (AA) were purchased from Aldrich Chemical Company (Milwaukee, WI). N,N'-methylenebisacrylamide (BIS, Aldrich) was used as crosslinking agent, and the redox pair of N,N,N',N'-tetramethylethylenediamine (TEMED, Aldrich) and ammonium persulfate (APS, Aldrich) as initiator. Sodium hydroxide (Fisher, Fair Lawn, NJ) was used as neutralization agent, sodium bicarbonate (J.T. Baker, Phillipsburg, NJ) as blowing agent, Pluronic PF 127 (BASF, Gurnee, IL) as foam stabilizer, and ethanol as wetting agent. Highly branched polyethyleneimine (PEI) with the weight average molecular weight of 750,000 g/gmol was purchased from Aldrich.

### 2.2. Synthesis of superporous hydrogels of P(AM-co-AA)/PEI IPNs

Monomer aqueous solution, 25 parts, composed of 50% (w/v) AM and 50% (w/v) AA was mixed with 5.5 parts of 2.5% (w/v) BIS, 2.5 parts of 10% (w/v) PF 127, and 1 part of 20% (v/v) TEMED. Stock solutions were prepared for different compositions of AM/AA weight ratios of 1.0/0, 0.8/0.2, 0.6/0.4, 0.4/0.6, 0.2/0.8 and 0/1.0. To each stock solution, 15 wt% PEI aqueous solution was added to obtain final PEI/monomer weight ratios of 2.5/100, 5/100 and 10/100, respectively.

Polymerization reaction was conducted in the borosilicate glass culture tube (Corning, New York, NY) with the

dimension of 100 (ID) × 1600 mm (L). After 1.65 ml of stock solution and the predetermined amount of PEI aqueous solution were placed in the culture tube, pH was adjusted to 5.0 by adding 50% (w/v) sodium hydroxide aqueous solution. After introduction of 60 μl of 20% (w/v) APS solution, 80 mg of blowing agent of sodium bicarbonate was added. While the mixture was vigorously stirred with the spatula or vortex generator at room temperature, polymerization reaction was completed in a few minutes. The products were stored in the convection oven for complete drying.

### 2.3. Measurement of gelation kinetics

As the polymerization reaction proceeded, the viscosity continuously increased until the full network structure (gel structure) was formed. The gelation time was defined as the duration time for gel formation after addition of initiator (APS). It was measured by a simple tilting method; it was determined by the duration time until the reactant mixture was no longer descending in the tilted tube position.

### 2.4. Measurement of swelling behavior

Cylindrical SPH samples were cut to have around 7 mm length. The samples in 0.15–0.2 g were placed in distilled water at room temperature. Each sample was weighed periodically until no weight change was observed. Equilibrium swelling ratio was determined as the weight of final (equilibrium) water uptake divided by the weight of dry polymer.

### 2.5. Measurement of mechanical strength

SPHs swollen to equilibrium in water were placed on the bench comparator (Ames, Waltham, MA). Differently scaled loads up to 1500 g were successively applied on the top of each sample. The ultimate compressive strength was determined as the compressive force at breakage divided by cross-sectional area of sample in contact with the load, 5.07 cm<sup>2</sup>. Five measurements were performed at room temperature, and the average value was taken as the ultimate compressive strength.

## 3. Results and discussion

### 3.1. pH adjustment of stock solution

The relationship between the pH of stock solution and the consumption amount of NaOH aqueous solution for different reactant compositions is shown in Fig. 1. More amount of NaOH solution was required to neutralize the reactant composed of higher concentration of AA, as AM aqueous solution has non-ionic (pH = 6.3 at 50 wt%) but AA anionic characteristic (pH = 1.3 at 50 wt%). On the

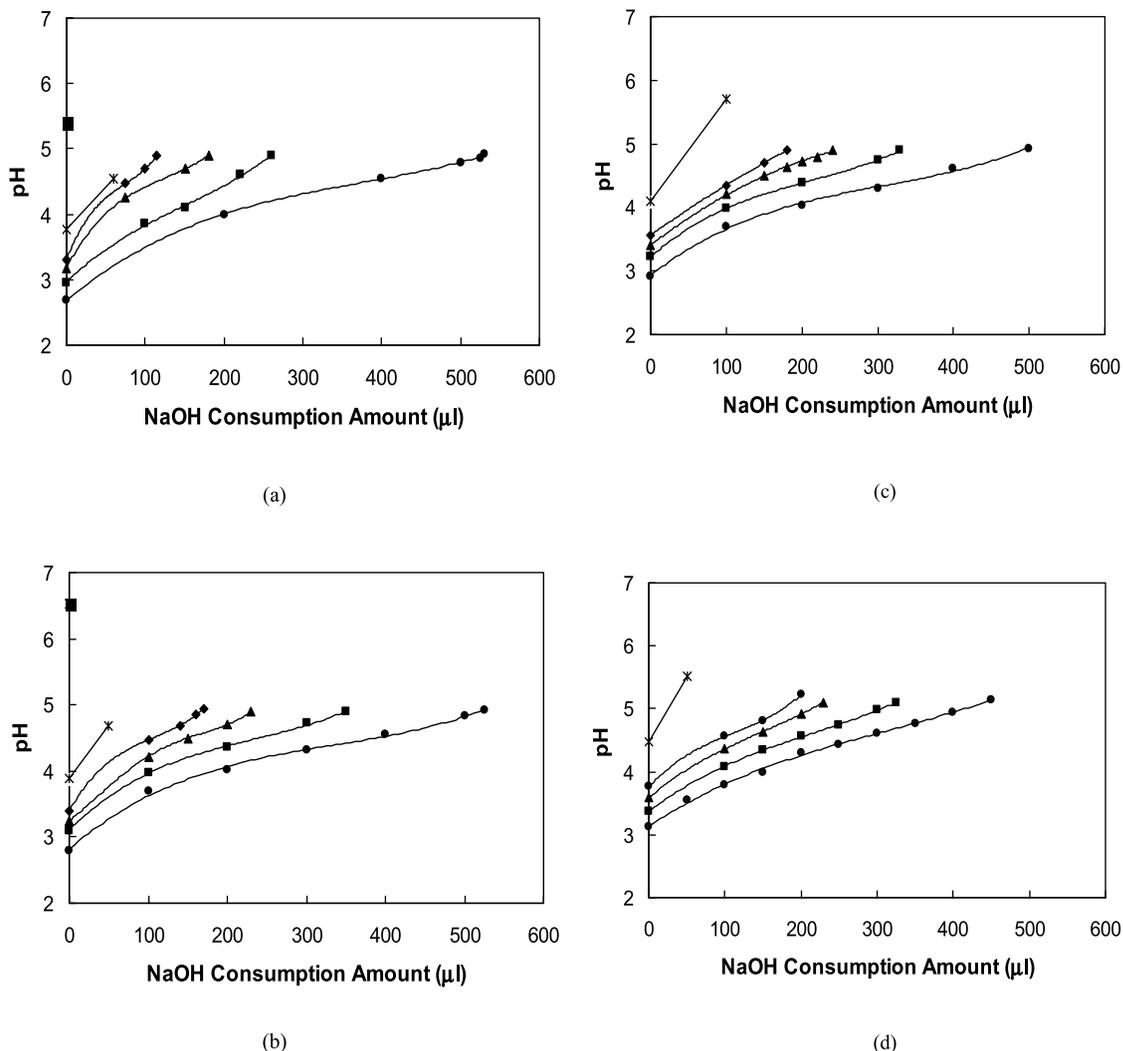


Fig. 1. NaOH consumption amount to adjust the pH of reactant for the synthesis of P(AM-co-AA)/PEI IPN SPHs when 15 wt% of PEI aqueous solution was incorporated to have the weight ratio of PEI to monomer of (a) 2.5/100, (b) 5/100, (c) 7.5/100 and (d) 10/100, respectively. Each curve indicates AM to AA weight ratio of 0/1.0 (●), 0.2/0.8 (■), 0.4/0.6 (▲), 0.6/0.4 (◆), 0.8/0.2 (\*), and 0.96/0.04 (■), respectively.

other hand, less amount of NaOH was required to neutralize the reactant when more PEI was incorporated because PEI is cationic in aqueous solution state.

### 3.2. Gelation kinetics

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 shapes by completion of reaction when blowing agent is introduced too early, and they cannot even be formed when introduced too late. The gelation kinetics gives good information determining the introduction time of blowing agent.

Fig. 2 shows the concentration dependence of gelation time for both neutralized and non-neutralized systems. Neutralized reactants were cured much faster than non-neutralized ones, as the redox type initiator activated much faster at neutralized condition. For both systems, increase of PEI concentration reduced gelation time because it

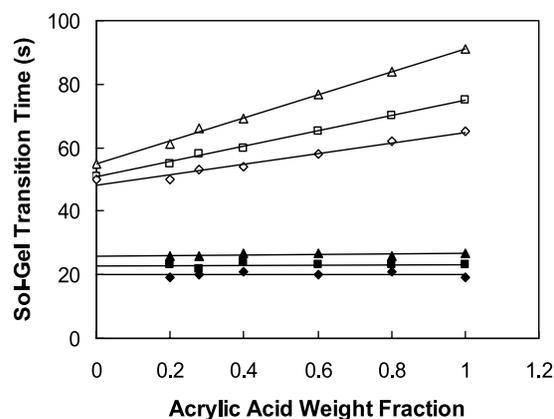
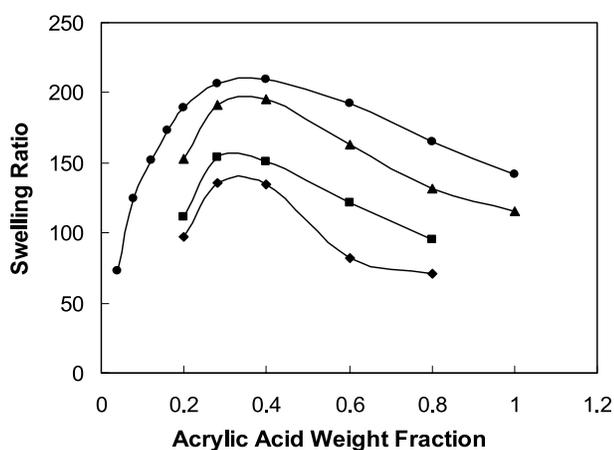


Fig. 2. Monomer concentration dependence of sol-gel transition time during the synthesis of P(AM-co-AA)/PEI SPHs when PEI was added in the weight ratios of PEI to monomer of 2.5/100 (▲, △), 5/100 (■, □), and 10/100 (◆, ◇), respectively. Filled symbols indicate neutralized samples and open symbols non-neutralized ones.

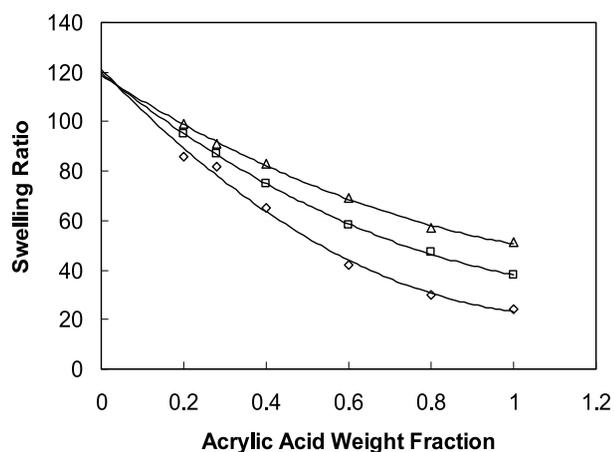
decreased the reactant acidity. Gelation times of non-neutralized samples slightly decreased with AA concentration for the same reason. Gelation times of neutralized samples were so short, about 20 s, that their concentration dependence was not as distinguishable as that of non-neutralized ones. From the relationship between the gelation time and reactant composition, the introduction time of blowing agent was chosen as 20 s before the completion of gelation for non-neutralized samples. For neutralized ones, however, blowing agent was introduced as soon as possible after addition of initiator.

### 3.3. Equilibrium swelling ratio

Fig. 3(a) and (b) show equilibrium swelling behaviors of



(a)



(b)

Fig. 3. Monomer composition dependence of equilibrium swelling ratio of (a) neutralized and (b) non neutralized SPHs of P(AM-co-AA)/PEI IPNs for different PEI concentration: Each curve represents the weight ratio of PEI to monomer of 0/100 (●), 2.5/100 (▲, △), 5/100 (■, □), and 10/100 (◆, ◇), respectively. Filled symbols indicate neutralized samples and open symbols non-neutralized ones.

neutralized and non-neutralized P(AM-co-AA)/PEI SPHs, respectively. For both systems, equilibrium swelling ratios changed significantly according to the polymer composition. As shown in Fig. 3(a), it does not change monotonically with monomer concentration. Instead, maximum swelling ratios are observed around the AA weight fraction of 0.4 for all PEI concentrations. This composition dependence was caused by the difference in both pore structures (sizes) and water absorbencies of component polymers.

It has been reported that the highly branched sites in PEI are separated by secondary amine groups, with one branch occurring for every 3–3.5 nitrogen atoms along the linear chain as shown in Fig. 4(a). This branching distribution provides presumably spheroid-shaped molecules possessing many charged nitrogen atoms, and this imparts cationic functionality to PEI as shown in Fig. 4(b). As AA polymer component has anionic nature, there is a strong ionic interaction between AA and EI molecules in IPN systems. Not only tight network structure, but also high molecular entanglements were developed by the presence of high MW and highly branched PEI molecules. For this reason, higher concentration of AA or PEI led to production of smaller pores and thus absorption of less water amount. When AA concentration was too low, however, the curing reaction proceeded so fast that large pores could not be generated. As the water absorbency of homo polyacrylamide (PAM) was lower than that of homo poly(sodium acrylate), the water swelling ratio decreased with AM concentration when AA weight fraction was lower than 0.4. This trend was more prominent for higher PEI concentration.

Fig. 3(b) shows equilibrium swelling properties of non-

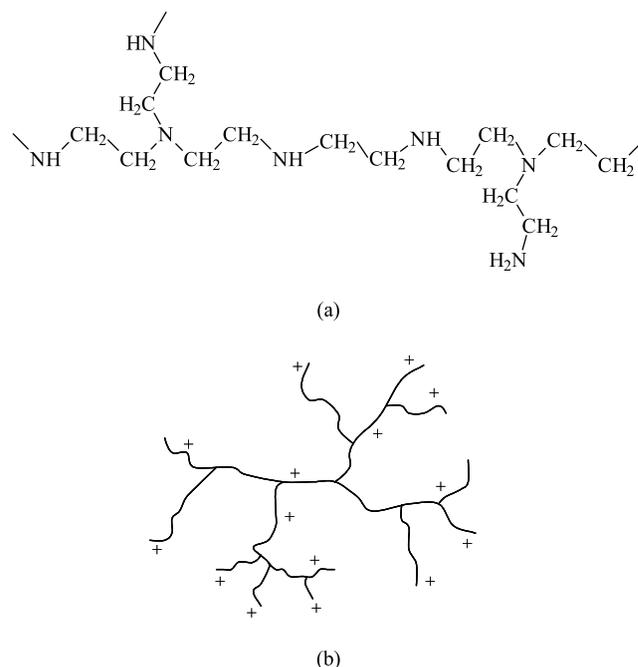


Fig. 4. Schematic representation of (a) chemical structure of branched PEI and (b) charge distribution in branched PEI.

neutralized P(AM-co-AA)/PEI SPHs. Swelling ratios of non-neutralized SPHs were much lower than those of neutralized ones, because the decreased fixed charge concentration in the gel phase reduced ionic contribution to swelling pressure. The composition dependence of swelling behavior was mainly caused by inherent swelling capacities of component polymers. As the equilibrium water uptake of homo PAM was higher than that of homo PAA when no ionic charge was involved, the swelling ratio increased with increasing AM concentration. The PEI concentration effect on the swelling behavior of non-neutralized system was similar to that of neutralized one.

Fig. 5 shows the effect of crosslinking agent concentration on the swelling ratio of non-neutralized P(AM-co-AA) SPHs. The water uptake decreased with increasing BIS concentration, as tighter network structure was created by presence of more BIS. The copolymer composition effect was the same as above.

### 3.4. Swelling kinetics

Figs. 6 and 7 show polymer composition dependence of swelling kinetics for neutralized and non-neutralized SPHs, respectively. In Fig. 6, increasing AA or PEI concentration considerably decreased the water sorption rate, because the interaction enhancement between PEI and PAA molecules led to reduction of pore sizes of SPHs. The PEI concentration effect on the absorption kinetics reduced for AM weight fractions higher than 0.8, as not many AA molecules were involved in interaction with PEI molecules. In Fig. 6(c), the water sorption rate is not significantly decreased when PEI is incorporated lower than 5 wt%, but it takes only 2 min to reach equilibrium when PEI is added at 5 wt%.

Non-neutralized samples showed rather higher swelling kinetics than neutralized ones. While the equilibrium swelling behavior was mostly governed by fixed charge

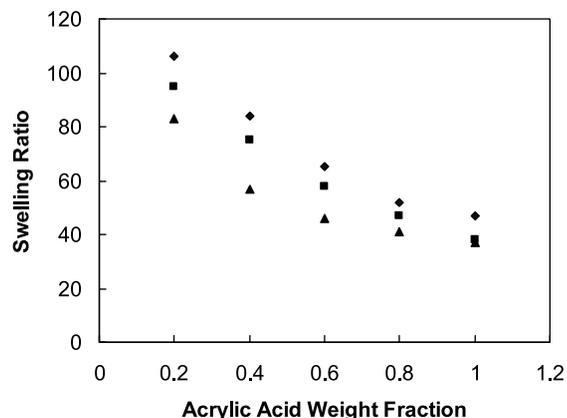
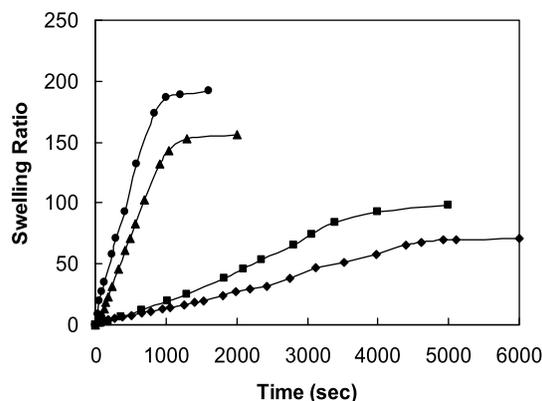
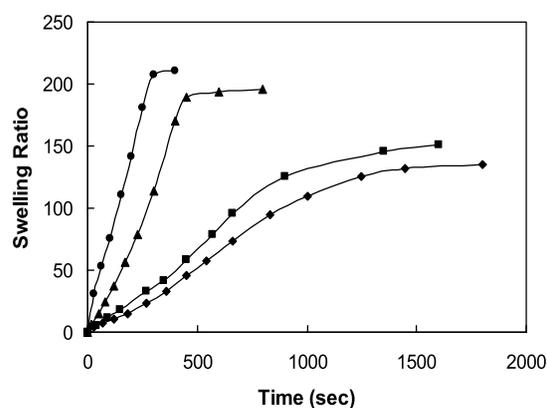


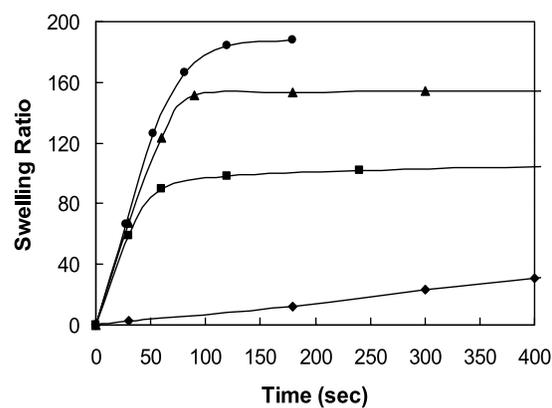
Fig. 5. Monomer composition dependence of equilibrium swelling ratio of non neutralized SPHs of P(AM-co-AA)/PEI IPNs including PEI to monomer weight ratio of 5/100 for different crosslinking agent concentrations: Each curve indicates the crosslinking agent concentration of 0.5 (◆), 1 (■), and 2 wt% (▲), respectively.



(a)



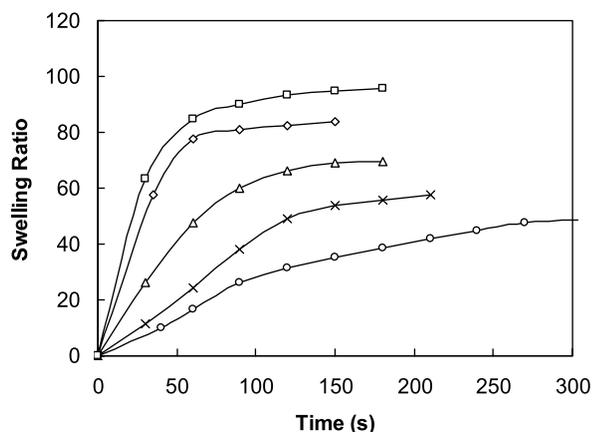
(b)



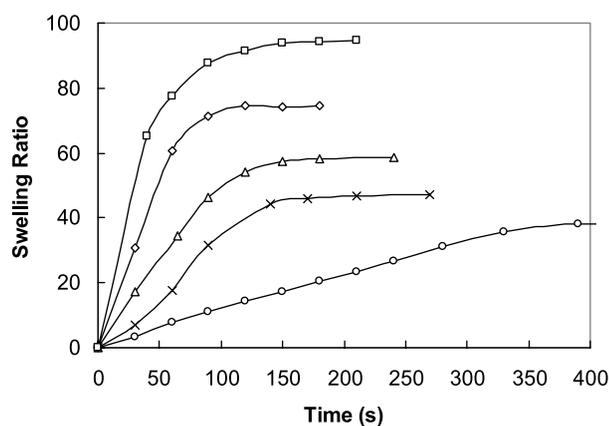
(c)

Fig. 6. Dynamic swelling behavior of neutralized SPHs of P(AM-co-AA)/PEI IPNs with different AM to AA weight ratios of (a) 0.4/0.6, (b) 0.6/0.4, and (c) 0.8/0.2, respectively. Each curve indicates the PEI to monomer ratio of 0/100 (●), 2.5/100 (▲), 5/100 (■) and 10/100 (◆), respectively.

concentration in polymer systems, the swelling rate mostly by the pore size associated with the gelation kinetics. As gelation reactions of non-neutralized samples started later and propagated more slowly than those of neutralized



(a)



(b)

Fig. 7. Dynamic swelling behavior of non-neutralized SPHs of P(AM-co-AA)/PEI IPNs with different PEI to monomer weight ratios of (a) 2.5/100 and (b) 5/100 respectively. Each curve indicates AM to AA weight ratio of 0/1.0 (O), 0.2/0.8 (x), 0.4/0.6 ( $\Delta$ ), 0.6/0.4 ( $\diamond$ ), and 0.8/0.2 ( $\square$ ), respectively.

samples, there was enough manipulation time to develop larger and more stable bubbles. For this reason, the equilibrium swelling times for non-neutralized samples, less than 2 min, were much shorter than those for neutralized ones.

### 3.5. Ultimate compressive strength

Fig. 8(a) and (b) show ultimate compressive strengths of neutralized and non-neutralized SPHs in equilibrium water swollen states, respectively. The mechanical strength of neutralized samples increased with increasing PEI concentration because of the reduction of equilibrium water sorption amount. This plasticization effect was applied when the AA weight fraction was lower than 0.5. The compressive strength, however, slightly decreased with AA concentration when it was higher than 0.5, and even

cracking occurred when it was close to 1. The weakness of compressive strength at high concentration of AA was presumably caused by the swelling stress accumulated during the water uptake. When the polymer molecules are not relaxed so fast as water diffusion, stresses can be developed and accumulated during swelling processes. When this swelling stress is too highly developed, samples are easily cracked by even minute external forces. As the stress relaxation rate decreased with increasing molecular entanglement and chemical or physical crosslinks, higher concentration of AA and PEI resulted in lower compressive strength, often accompanying with cracking.

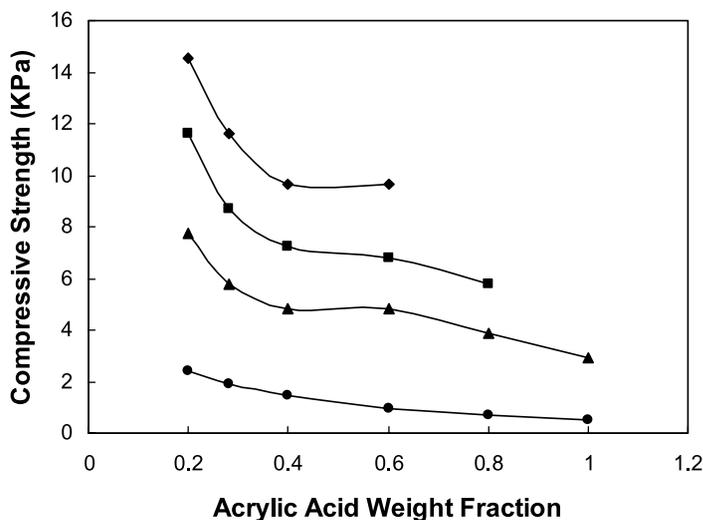
As shown in Fig. 8(b), the polymer concentration dependence of compressive strength of non-neutralized polymers is quite different from that of neutralized ones. Compressive strengths of non-neutralized samples increased with increasing AA concentration. As water absorption contents in non-neutralized systems were not as high as those of neutralized ones, swelling stress was not highly developed. Thus, the composition dependence for non-neutralized samples could be explained mostly by simple plasticization effect. Absorption of more amount of water resulted in lower strength. The maximum strength shown in Fig. 8(b) is 0.29 MP. It was simply because the strength higher than this value could not be technically measured by limitation of experimental equipment.

## 4. Conclusions

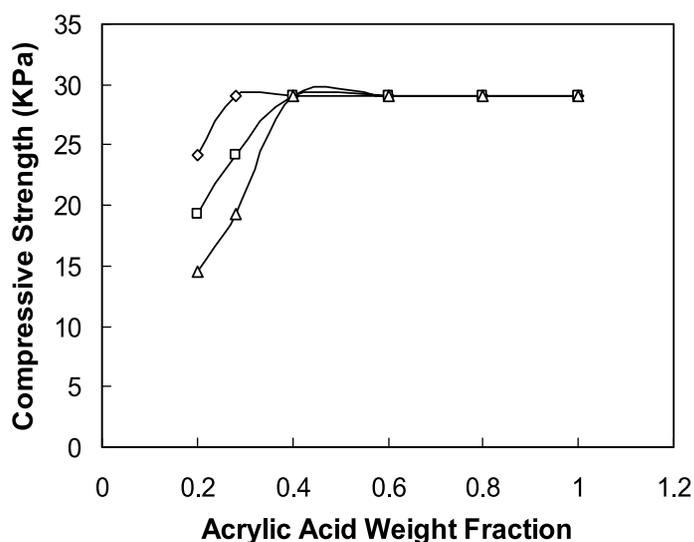
Swelling and mechanical properties were studied for a series of SPHs of P(AM-co-AA)/PEI IPNs prepared. The gelation time increased with increasing AA or decreasing PEI concentration, as the redox type initiator activated much faster at neutralized condition. The maximum equilibrium swelling ratios were observed at the PAA weight fraction of around 0.40 for neutralized samples, but it decreased monotonically with PAA concentration for non-neutralized ones. For both systems, the equilibrium uptake decreased with increasing PEI concentrations because of high the molecular entanglement of PEI and high physical interaction between PEI and PAA molecules.

The swelling kinetics was also significantly affected by polymer composition. Slower water sorption was shown at higher concentrations of PEI or PAA. This concentration dependence was more prominent for neutralized samples, because pores of neutralized samples were not fully developed due to shortage of gelation time as well as high interaction between PEI and PAA molecules.

The mechanical strength of water swollen SPHs increased with PEI concentration for both systems. For non-neutralized samples, the increase of AA concentration led to increase of compressive strength by simple plasticization effect. For neutralized samples, however, the increase of AA concentration decreased the compressive strength, and even cracking occurred when PAA concentration was



(a)



(b)

Fig. 8. Polymer composition dependence of ultimate compressive strength of (a) neutralized and (b) non-neutralized SPHs of P(AM-co-AA)/PEI IPNs for different PEI concentration: Each curve represents the weight ratio of PEI to monomer of 0/100 (●, ○), 2.5/100 (▲, △), 5/100 (■, □), and 10/100 (◆, ◇), respectively. Filled symbols indicate neutralized samples and open symbols non-neutralized ones.

close to 1. It was because the swelling stress was accumulated during the water uptake in highly crosslinked and entangled molecular structure.

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