

Swelling and Mechanical Properties of pH-sensitive Hydrogel Filled with Polystyrene Nanoparticles

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ABSTRACT: We investigated the effect of organic filler and the degree of crosslinking on the performance of a hydrogel/filler system to control its diffusion and mechanical properties. A series of poly(acrylic acid) gels filled with polystyrene (PS) nanoparticles at well-controlled filler loading levels was synthesized by free radical polymerization in the presence of a crosslinking agent. Three different concentrations of the crosslinking agent (methylene bis-acrylamide), that is, 5 mg/(g of AAc), 10 mg/(g of AAc), and 20 mg/(g of AAc), were used. The hydrogel crosslinked to the least extent that included a high amount of PS showed fast swelling rates, high equilibrium swelling ratios, and the highest pH sensitivity. Three gel/filler combinations including the gel without filler, gel/filler mixture, and gel/filler copolymerization were considered. The PS particles of ~40 nm in diameter, which were used as the fillers, were prepared by microemulsion polymerization. Copolymerization of styrene and AAc having different reactivities ratios was achieved by a seed-microemulsion polymerization with the crosslinking agent. The gel/filler mixture showed the highest swelling rate and the gel/filler copolymer resulted in highly enforced mechanical properties and the highest pH sensitivity. The incorporation of filler by copolymerization to mechanically enforce the equilibrium swelling hydrogel was more efficient than the increase of crosslinking degree. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3574–3587, 2013

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INTRODUCTION

Hydrogels, which are three-dimensional polymer networks, are characterized by both hydrophilicity and insolubility in water and are capable of absorbing large amounts of water. The high water retention of hydrogels arises from the presence of water-solubilizing groups such as —OH, —COOH, —CONH₂, —CONH, or —SO₃H. Owing to its high hydrophilicity, low toxicity, biocompatibility, and similarity to natural tissues, hydrogels possess a wide range of applications and have gained much attention and focus of the scientific research community.^{1,2}

Hydrogels based on poly(2-hydroxyethyl methacrylate) are used as soft contact lenses.³ Hydrogels based on poly(sodium acrylate) are used as absorbents in disposable diapers.^{4–6} Ionic hydrogels are used as eroding reservoir devices in controlled drug-release systems.^{7,8} Applications for hydrogels depend on the ability to swell (especially in terms of swelling rate, equilibrium swelling ratio, and mechanical strength) from a collapsed state to a highly swollen state in water as a response to external stimuli such as composition and type of monomers,⁹ pH,¹⁰ salt concentration,¹¹ temperature,^{12–15} and ionization.^{16–18}

Huglin et al.^{19,20} investigated the swelling behavior of the hydrogel obtained by copolymerization with the hydrophilic AAc and hydrophobic methacrylic acid (MAc). They concluded that the swelling ratio was dependent on the ratio of AAc/MAc. With increasing amounts of carboxyl group incorporated, the equilibrium swelling ratio of the hydrogel increased. They also reported that the swelling ratio of 2-acrylamide-1-methyl-2-propane sulfonic acid hydrogel increased as a function of the ionization. Barrlales-Rienda and colleagues²¹ reported that hydrogen bonding had an effect on the dynamic swelling of poly(*N*-isopropylacrylamide-*co*-MAc) hydrogel. Below the isoelectric point of MAc, the swelling ratio of these hydrogels was independent of the concentration of MAc because of the hydrogen bonding between the carboxyl groups. Above the isoelectric point, the swelling ratio was proportional to the ionized MAc concentration. The swelling kinetics of a hydrogel depended on both the hydrophilic properties and the degree of crosslinking. Peppas group²² reported the effects of pH and ionic strength on the swelling behavior of an interpenetrating network of poly(vinyl acetate and poly(acrylic acid) (PAAc). With increase in the pH, the swelling ratio also increased. As the ionic strength was

stronger, ions in the solution surrounding the network increasingly counteracted the mutual repulsion of the ions fixed on the network itself and the swelling ratio decreased.

The major drawback of hydrogels is their mechanical weakness, especially when the materials reach the equilibrium swelling ratio. In the rubber industry, nanoparticles have been used as fillers to increase the mechanical strength of composites.^{23,24} The type of bonding between the base polymer and filler, the filler loading level, filler type, and filler dispersion are important. Neibl and coworkers²⁵ reported that the mechanical strength could be enhanced by the increase in the concentration of the filler, by using fillers with smaller particle sizes, and by improving the degree of dispersion of the filler. They demonstrated these effects by using polypropylene compounds as matrices and talc as the mineral filler. Schmidt²⁶ reported the reinforcing effect of fillers in styrene-butadiene rubber (SBR) and concluded that the filler size played a critical role in elastomer reinforcement and its chemical nature appears to be of secondary importance. This was attributed to the total surface area of the filler particles. As the total surface area was larger, the number of bonds and the strength of bonding between the base polymer and the filler increased. Filler dispersion is also a key factor determining the mechanical reinforcement. If fillers become agglomerated despite their small sizes, the particles do not play the expected role. For example, carbon black increases the abrasion resistance of SBR. However, agglomeration reduces its role as an abrasion resistance enhancer.

To improve the diffusion and mechanical properties of hydrogel, little attention has been devoted to the incorporation of hydrophobic organic filler into hydrogels. The ultimate goal of this study is to increase pH sensitivity and to enforce the mechanical properties, especially to resist the shear stress, of equilibrium swelling hydrogel by introducing hydrophobic polystyrene (PS) fillers into the system.

To achieve this goal, we encountered three challenges in the preparation of a filled hydrogel. The first challenge lay in the particle size. To maximize the reinforcing effect of the filler particles, their sizes must be as small as possible. The second challenge lay in the strong bonding between PAG and the PS fillers. The reactivity ratios of both styrene and AAc are very different²⁷ and it is challenging to fabricate the copolymer. The third challenge lay in the high dispersity of PS filler. Agglomeration of the fillers may lead to the failure of reinforcement in a system.

Therefore, in this study, the first step was to synthesize the mechanically reinforced pH-sensitive PAG by overcoming the abovementioned challenges. PS was prepared by microemulsion polymerization to minimize the particle size. Owing to the high concentration of sodium dodecyl sulfate (SDS) which is possible with addition of 1-pentanol, more micelles formed in microemulsion provided the maximized number of particle and the minimized particle size. Large surface area of all particles provided more ions on their surface.

Incorporation of PS particles into PAG was achieved by two different methods. In the first method, styrene and acrylic acid were copolymerized in the PS seed microemulsion with 50% of

conversion (F40PAG). With addition of crosslinking agent, water-soluble PAAc could be precipitated, and polymerized with styrene monomer on the surface of PS. During the time of swelling or external stimuli, PS covalently bonded to PAAc chain was not agglomerated.

In the second method, microemulsion polymerization of styrene was achieved in the swollen PAG at equilibrium (PAGPS). After the preparation of hydrogels, the dependence of swelling rate, equilibrium swelling ratio, and mechanical strength on the pH and the addition of filler were carefully studied.

EXPERIMENTAL

Materials

Styrene (purity, >90%), inhibited with stabilizer was purchased from J. T. Baker Chemical. The stabilizer was removed by washing with an alkaline solution. The styrene samples were washed with an equal volume of 10 wt % of NaOH solution thrice and subsequently thrice with an equal volume of deionized (DI) water. Potassium persulfate (purity, >99%) and acrylic acid (AAc, anhydrous, 99%) were purchased from Aldrich Chemical, SDS (purity, 98%) was purchased from OmniPur EMD, 1-Pentanol (purity, >99%) was purchased from Alfa Aesar Chemical, *N,N'*-methylenebisacrylamide (MBAAm) was purchased from Fluka, and ethylenediaminetetraacetic acid (EDTA) was purchased from Sigma. All these chemicals were used as received.

Polymerization and Gelation

Microemulsion was prepared by catastrophic phase inversion method. To produce water-in-oil emulsion first, 10 g of water was added slowly to the mixture of styrene, 1-pentanol, and SDS. After the transparent water-in-oil emulsion was formed, water was added until the phase is inverted to oil-in-water emulsion. This mixture was agitated for 10 min at room temperature, and then stored at 4°C for 24 h to obtain the equilibrium. Polymerization was conducted in 1000-mL kettle with four necks. Before the polymerization, the reactor was immersed in a thermostatic water bath. A water-cooled condenser was connected to the reactor and nitrogen was bubbled continuously into the reactor liquid to remove oxygen while stirred with 1-in paddle stirrer. The reactor containing water was heated to a temperature of 70°C. Styrene microemulsion was added and equilibrated for 20 min with stirring at 300 rpm. After equilibrating, potassium persulfate initiator was added. Polymerization proceeded at a constant temperature for 25 min. PS latex was poured into methanol, and precipitates were separated and washed with DI water and methanol.

Samples for conversion rate measurement were collected at polymerization time intervals, and dropped into 100-mL pre-labeled and preweighed beakers. Each beaker was weighed and placed in a hood with the ventilation to remove unreacted monomer for 2 days. Monomer-removed samples were placed in vacuum oven at 50°C for 3 days. Samples were taken out and placed at room temperature to cool down before weighed. Samples were dried more if constant weight was not observed. Gravimetric conversion rate measurement assumed that monomer was dispersed uniformly in the dispersion. The equivalent

amount of monomer could be calculated based on the weight of each sample and the weight % of monomer initially charged.

$$X_c = \frac{(W_2 - W_0) - (W_1 - W_0) \times C_{\text{initiator}}}{(W_1 - W_0) \times C_{\text{monomer}}} = \frac{W_p}{W_p + W_m} \quad (1)$$

W_0 is the weight of empty beaker, W_1 is the weight of beaker after latex sample which was dropped in, and W_2 is the weight of beaker after drying. $C_{\text{initiator}}$ and C_{monomer} were given by the weight ratio of the corresponding ingredient charged and the weight of total charge. W_p is the weight of polymer and W_m is the weight of monomer.

The hydrogel was synthesized in a polymerization reactor equipped with a magnetic stirring bar, reflux condenser, nitrogen inlet, and thermometer. The monomer solution was prepared by dissolving 16 g of acrylic acid in 43 mL of DI water with the addition of 0.08 g (5 mg/(g of AAc)), 0.16 g (10 mg/g of AAc), or 0.32 g (20 mg/(g of AAc)) of MBAAM and 0.06 g of EDTA as an accelerator. This monomer solution was placed in the reactor, stirred, and deoxygenated by bubbling with nitrogen gas through the solution for 20 min. The initiator stock solution contained 10 mL of DI water and 0.38 g of ammonium persulfate. After 20 min of nitrogen bubbling and heating up the reaction mixture to 60°C, the initiator solution was added to the reaction mixture and was maintained at the same temperature of 60°C for two hours. The obtained gel product was thoroughly washed with DI water and was measured with a densimeter. In order to remove the unreacted monomer and water-soluble fraction of the polymer, the gel product was washed five times for 2 days at room temperature.

Swelling Ratio and Density

Six pH solutions were first prepared to examine the effect of pH on the swelling behavior of the hydrogel. To prepare solutions with pHs of 2.0, 2.4, and 3.3, stock solution of HCl (pH 2.0) and NaOH (pH 13.0) was diluted with DI water to reach the desired pHs. In brief, 3.0M of sodium acetate was diluted 30 times to obtain a buffer solution with pH 4.8. In total, 0.5M of Tris-HCl was diluted five times to obtain a buffer solution exhibiting pH 7.6. The buffer solution of pH 10.0 was purchased from VWR. The pH value of the DI water used as a swelling solvent was ~5.8. With pH meter, it took about 20 h for the pH value to be stabilized because ions were rare in the solution.

The washed hydrogels were cut into six pieces and dried in a vacuum oven at 60°C. The dried weight and swelling rate of each hydrogel in DI water were monitored for the first 5 h. The equilibrium swelling ratio was determined when the swelling ratio remained unchanged for more than 3 days.

To observe the pH sensitivity, the swollen hydrogel in DI water at equilibrium was placed into each buffer solution. It took 5 days to get the equilibrium swelling ratios in different pH values. The synthesis of the hydrogel was repeated thrice to obtain the average swelling ratio. Therefore, at a particular pH value, the equilibrium swelling ratio of a single hydrogel sample was measured thrice and the values were averaged and the standard deviation was obtained.

The density of the swollen hydrogel at equilibrium was measured 10 times to get the average value. The density of the dried gel was calculated using a material balance. The weight in the air (W_a) was measured by a densimeter to obtain the swelling ratio. As the hydrogel could be shattered easily when its swelling ratio was high, the test solution was carefully removed from the beaker by suction and the hydrogel was subsequently lightly tapped with a paper towel to remove the water on the surface. This allowed hydrogels to be weighed without breaking. Swelling ratio (Q_w) is calculated from eq. (2).

$$Q_w = \frac{W_s - W_d}{W_d} \quad (2)$$

where W_s is the weight of the hydrogel after swelling, W_d is the weight of dried hydrogel.

Mechanical Property

Measurements of the rheological properties of the hydrogel were performed in the dynamic shear oscillation mode (frequency sweep) and in the strain rate-controlled oscillation mode (amplitude sweep). To characterize the viscoelastic properties of the PS bead-filled hydrogels, rheological measurements were carried out with a rheometer (MCR 301, Physica, Anton Paar) using a cone and plate configuration (diameter, 25 mm). The hydrogel samples were loaded onto the lower plate, the upper fixture was lowered, and the humidity chamber was placed around the sample to prevent dehydration during data collection. Temperature, which was fixed at 20°C, was controlled by a water bath circulator. In the amplitude sweep mode, the strain rate during an oscillation cycle varied. The measurement of amplitude sweep was carried out at a constant angular frequency of 10 rad/s. A total of 100 points were scanned with a time interval of 15 s between each point.

RESULTS AND DISCUSSION

Preparation of Poly(acrylic acid) Hydrogel Filled with PS Beads

Hydrogel has been widely studied to control the swelling rate and equilibrium swelling ratio, especially in environment and biomedical applications.^{28,29} Hydrophilic monomers have been polymerized with crosslinking agent to produce hydrogel. Recently, hydrogel modification has been focused on the copolymerization; different ratios of monomers, hydrophilic or hydrophobic property, and type of copolymer.³⁰ Free radical polymerization is the easier way to prepare, and to control the property by the feed condition including the addition of filler when compared to the block-copolymerization prepared by anionic polymerization, ATRP, or RAFT.³¹ Seed-polymerization with crosslinking agent is the effective way in a copolymerization of two monomers having much different reactivity ratios, such as styrene and acrylic acid.

In microemulsion polymerization, surfactant concentration exceeds over critical micelle concentration (CMC) during the polymerization which leads to the existence of mixed micelles. Mixed micelle consists of surfactant, cosurfactant, and small amount of monomer in the palisade layer. The core of micelle

is composed of monomer and cosurfactant. After 4% conversion, all the monomers in the core of mixed micelles diffuse out, and those droplets become empty micelles.³² Therefore, PAAc chains copolymerize with styrene not in the mixed micelle, but in the particle phase.

To prepare PS filler, microemulsion polymerization of styrene was carried out with SDS as the anionic surfactant and 1-pentanol as the cosurfactant. PS of 40 nm in diameter was formed with a conversion of 50%. For a course of polymerization, particle diameter was not changed to conversion in an appreciable degree rather it was around 40 nm.

To characterize the polymerization, polymerization rate (R_p), number of particle (N_p), monomer concentration in polymer particles $[M]_p$, and average number of radicals per particle (\bar{n}) were collected from eq. (3) where N_A is the Avogadro number (6.02×10^{23}). Propagation rate constant at 70°C was $3.29 \times 10^5 \text{ cm}^3/\text{mol}\cdot\text{s}$.³³

$$R_p = -\frac{dM}{dt} = k_p[M]_p \frac{\bar{n}N_p}{N_A} \quad (3)$$

Conversion rate was gained by a gravimetric measurement, and particle size was obtained by TEM as shown in Figure 1. From eq. (4), R_p could be found. $[M]_0$ is the feed concentration of monomer.

$$R_p = [M]_0 \frac{dX_c}{dt} \quad (4)$$

Number of particle was obtained from eq. (5) and particle size (D_p diameter).

$$D_p = \left(\frac{6[M]_0 X_c}{\pi d_p N_p} \right)^{1/3} \quad (5)$$

Equation (5) was derived from balance equation of ($[\text{gram of monomer}]/[\text{density of monomer}] \times \text{conversion} = (\text{density of particle}) \times (\text{number of particle})$). X_c is the conversion rate. Density of PS, d_p is 1.05 g/cm^3 .²⁷ From eqs. (3) to (5), $[M]_p$ and \bar{n} were found. At $X_c = 0.08$, R_p was $2.13 \times 10^{-6} \text{ mol/s}$, D_p was 37 nm, N_p was $1.107 \times 10^{14}/\text{cm}^3$, $[M]_p$ was 0.12 mol, and \bar{n} was 0.292. At $X_c = 0.5$, R_p was $2.22 \times 10^{-6} \text{ mol/s}$, D_p was 40 nm, N_p was $5.478 \times 10^{14}/\text{cm}^3$, $[M]_p$ was 0.06 mol, and \bar{n} was 0.113. As the polymerization progressed, $[M]_p$ and \bar{n} were decreased and N_p was increased. D_p and R_p did not change significantly.

Two methods were used to introduce the PS beads into PAG. In the first method, the PS beads were incorporated by microemulsion polymerization of styrene in swollen PAG at equilibrium (and these samples will henceforth be termed as PAGPS-gel/filler mixture). In the second method, copolymerization of styrene and acrylic acid in the PS microemulsion was carried out with conversion of 50% (and these samples will henceforth be termed as F40PAG-gel/filler copolymer). PAG is described in Figure 2(a). The difference between PAGPS and F40PAG is schematically compared in Figure 2(b,c).

Figure 3 illustrates the preparation of PAGPS and of equilibrium swelling hydrogels. Preparation ingredients of PAG, PAGPS, and F40PAG were shown in Tables I, II, and III,

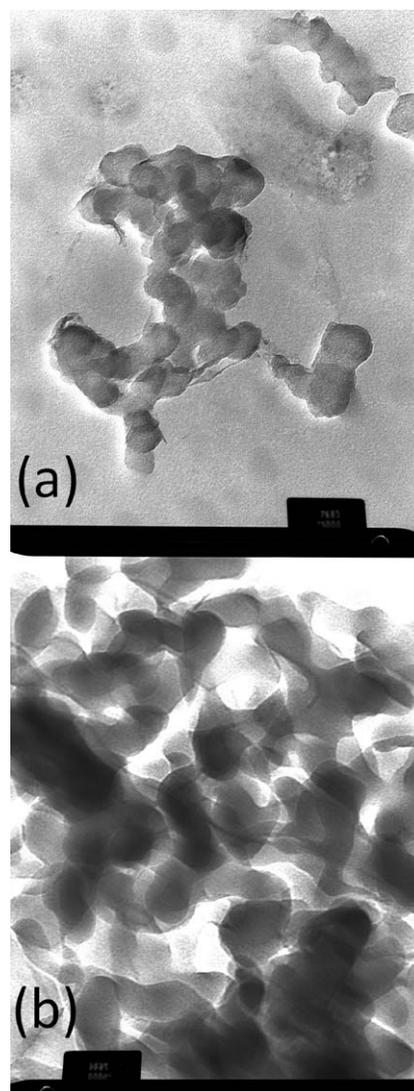


Figure 1. Transmission electron micrographs of PS prepared by microemulsion polymerization. In brief, (a) 37 nm in diameter at 8% conversion and (b) 40 nm in diameter at 50% conversion.

respectively. F40PAG is referred to as a block copolymer. One part consists of a homogeneous styrene block portion and the other part consists of acrylic acid and styrene, but the composition of styrene is small (0.86 g of styrene and 16 g of acrylic acid in the initial condition, molar ratio of styrene : acrylic acid is $[\text{St}] : [\text{AAc}] = 1 : 26.87$), that is, molar fraction of AAc is 0.964. It is more like a block copolymer. According to Slawinski,³⁴ in a copolymerization reaction of styrene and AAc, if the molar fraction of AAc is 0.965 in the feed condition, the value becomes 0.8 in a copolymer in the seeded emulsion polymerization at 70°C. The main reason, except the reactivity ratio of two monomers, that the portion of two monomers in a copolymer is different is owing to the polymerization rate. AAc polymerizes 85 times³⁵ and 125 times³⁴ faster than styrene at 85 and 70°C, respectively, in the aqueous phase.

Linear PAAc is a water-soluble polymer which is not precipitated, but the crosslinking agent makes it precipitate. In microemulsion, the amount of styrene molecules on the particle phase is inversely

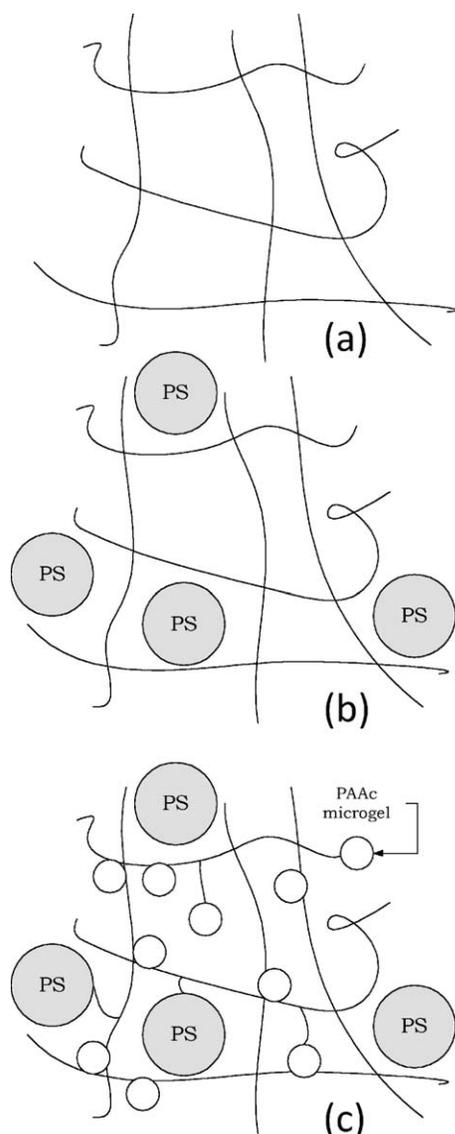


Figure 2. Schematic illustration of (a) PAG, (b) PAGPS, and (c) F40PAG. PAG is the pure PAAc hydrogel. PAGPS includes PAG, PS, and empty micelles which are mixed. F40PAG is the PAG that PS and PAAc are covalently bonded.

proportional to the conversion rate, $[M]_p$ is approximately equals to $[M]_0(1 - X_c)$.³⁶ Styrene monomer in the particle phase is mostly consumed to increase the number of particle rather than the particle propagation. At 8 and 50% of conversion, R_{ps} were similar, instead we observed a fivefold increase in N_p . It is considerable to calculate the probability of these styrene radicals diffused out of particle phase whether to enter into the micelle or the particle, or to meet propagating PAAc chain. However, it is hard to obtain the contact probability owing to lots of variables such as micelle concentration, diffusing rate, PAAc radical concentration, and defect ratio of hydrogel during the polymerization.

Solubility of styrene in water is very small (0.03 g of styrene per 100 ml of water at 20°C).²⁷ Therefore, polymerization of styrene in the aqueous phase rarely occurred and oligomeric crosslinking PAAc radicals (1) continuously propagate in the aqueous phase,

(2) form the loop causing deactivation of radical, such as the termination in the polymerization, (3) have a small chance to meet the styrene radical which transferred from the particle to the aqueous phase, or (4) form PAAc microgel owing to the presence of empty micelles in the microemulsion, which act like crosslinking points or crystallites. The existence of the PAAc microgel in the PAAc-PS macrogel (F40PAG) is thought to provide more strength, resulting in the improved mechanical strength.

Owing to the presence of PS beads and micelles in the microemulsion during its preparation, the efficiency of the crosslinking agent during the polymerization can be expected to be lower than that in the case of PAG. In other words, the probability of the chains growing from MBAAM to meet a monomer molecule is lower. It has been previously reported that this inefficiency of the crosslinking agent can cause higher number of small loops, which cause the formation of microgels and heterogeneity in the network.^{37,38} Also, because of the empty micelles present and the polymerization rate of AAC, PAAc microgel and macrogel were formed at the same time.

Swelling Rate of Hydrogels

According to Flory,³⁹ the swelling ratio of a hydrogel in an aqueous solution is a function of its characteristic properties such as crosslinking degree, affinity toward water molecules, degree of ionization of functional groups, and the characteristics of the swelling medium such as pH, ionic strength, and temperature. However, the effect of organic filler on the swelling rate has been rarely published.

The swelling rates of the hydrogels in DI water are plotted in Figure 4. The samples used for measuring the swelling rates were PAG, PAGPS, and F40PAG with low (8), medium (16), and high (32) crosslinking. Thus, the gels were characterized by the swelling rate in terms of the crosslinking degree, gel/filler mixture, and gel/filler copolymerization.

Three characteristic regions of the swelling ratio with swelling time are distinguished in all the swelling curves, the second-order swelling part, a linear swelling part, and a saturation

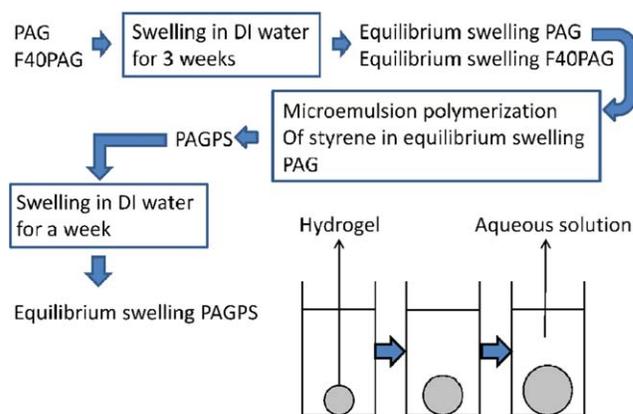


Figure 3. Procedure of swelling hydrogels to obtain the swelling rate and the equilibrium swelling ratio. It took about 3 weeks for dried PAG and F40PAG to reach the equilibrium swelling ratio. Swelling rate in the first 5 h was observed to get how fast the water molecules were diffused in. Maximum capacity of water uptake was obtained by measuring the equilibrium swelling ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Recipe of PAAc Hydrogel (PAG)

	Water (g)	Acrylic acid (g)	MBAAm (g)	EDTA (g)	Ammonium persulfate (g)
PAG8	53	16	0.08	0.06	0.38
PAG16	53	16	0.16	0.06	0.38
PAG32	53	16	0.32	0.06	0.38

Table II. Recipe of Polystyrene Bead-Filled PAAc Hydrogel (PAGPS)

	Equilibrium swollen PAG8 (g)	Equilibrium swollen PAG16 (g)	Equilibrium swollen PAG32 (g)	Microemulsion ^a (g)
PAG8PS	107.9 (0.46) ^b			418.6
PAG16PS		28.5 (0.61) ^b		418.6
PAG32PS			20.3 (0.86) ^b	418.6

^aMicroemulsion includes the following: water, 350 g; styrene, 13.6 g; SDS, 38.5 g; 1-pentanol, 1.6 g; potassium persulfate, 0.07 g.

^bWeight of dried gel—equilibrium swelling ratio: 235.16 (PAG8), 46.1 (PAG16), and 23.6 (PAG32).

range or plateau. Nicolas and coworkers⁴⁰ have described the step-by-step swelling of a hydrogel by an acoustic impedance method. During the process of water sorption, three different parts including a dry part, a water absorbing part, and a water saturated part can be observed. When the hydrogel reaches the swollen state at equilibrium, the whole part is saturated with water. There are four steps required to progress from the dry state to the swollen state at equilibrium. They are (a) dried state (22% transmitted), (b) rigid solid core coexisting with water absorbing part (transmitted, 22–24%), (c) water-absorbing state (no core, 30–46% transmitted), and (d) water-saturated state (equilibrium swelling, 46% transmitted). Disappearance of the core is the threshold of transmittance and density. Therefore, the end of nonlinear second-order swelling could be regarded as the disappearance of the rigid solid core part in the hydrogel, which is observed at 20 min of swelling in PAG, 12 min of swelling in PAGPS, and 40 min of swelling in F40PAG. Swelling rate was different with crosslinking degree, but the time when the rigid core was disappeared was independent of the crosslinking degree.

In addition to this explanation, it can be assumed that one more transition region, that is, a water-absorbing state to water-saturated state, exists. In this region, the water-absorbing part and the water-saturated part coexist. The second transition in PAG8PS is observed at 120 min.

Between these two transition periods, a linear swelling part was observed in all the swelling rate of hydrogel. Figure 4(a) shows

the swelling rate distinguished by the slope, time (s) versus swelling ratio. PAG8 was 2×10^{-3} , PAG8PS was 5.3×10^{-3} , and F40PAG8 was 5×10^{-5} in the slope. When PS filler was added as a mixture, water-absorbing rate became 2.6 times faster. However, when PS was incorporated by polymerization, it was 40 times slower. In case of high crosslinking hydrogel, the rate was 3 times faster in gel/filler mixture, and 2.5 times slower in gel/filler copolymerization than in PAG. That is, the addition of PS as a mixture into PAG accelerated swelling rate 2.6–3 times regardless of the crosslinking degree. It was inferred that PAG8PS had more PS filler than PAG32PS. Slopes of F40PAG linear swelling were not much different from the crosslinking degree, that is 5×10^{-5} to 4×10^{-5} .

Swelling rates of F40PAG8 and PAG32 were compared to elucidate the effects of the filler addition by copolymerization and of the increased crosslinking density. In Figure 4(a,c), to reach the swelling ratio of 1.17, F40PAG8 took 139.5 min, and PAG32 took 122.5 min. In the comparison of slopes of linear swelling part, PAG32 showed two times faster swelling than F40PAG8, 1×10^{-4} and 5×10^{-5} , respectively.

For the medium crosslinking hydrogels, PAG16PS also exhibited a higher swelling rate than PAG16 and the PS beads acted as accelerators, facilitating swelling. As the swelling progressed, the mesh size of the hydrogel became larger, which provided more mobility for the PS beads in the network. The swelling rate of F40PAG16 was slow. However, the gap in the swelling rate between F40PAG16 and PAG16PS was smaller than that between

Table III. Recipe of Polystyrene Bead-Filled PAAc Hydrogel (F40PAG)

	Microemulsion ^a (g)	Acrylic acid (g)	MBAAm (g)	EDTA (g)	Ammonium persulfate (g)
F40PAG8	53	16	0.08	0.06	0.38
F40PAG16	53	16	0.16	0.06	0.38
F40PAG32	53	16	0.32	0.06	0.38

^aMicroemulsion includes the following: water, 44 g; styrene, 0.8 g; polystyrene, 0.8 g; SDS, 4.9 g; and 1-pentanol, 2.1 g.

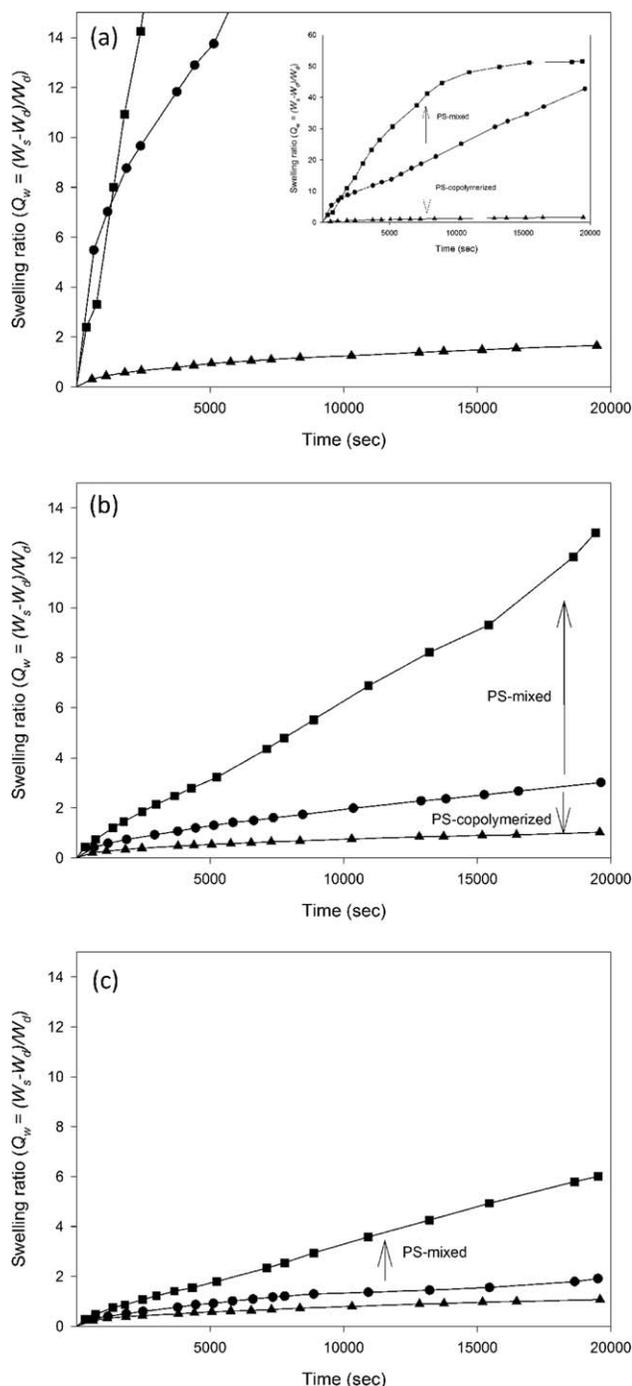


Figure 4. (a) Effect of filler incorporation on the swelling rate of the low crosslinking hydrogel in DI water (●) PAG8, (■) PAG8PS, and (▲) F40PAG8. (b) Effect of filler incorporation on the swelling rate of the medium crosslinking hydrogel in DI water (●) PAG16, (■) PAG16PS, and (▲) F40PAG16. (c) Effect of filler incorporation on the swelling rate of the high crosslinking hydrogel in DI water (●) PAG32, (■) PAG32PS, and (▲) F40PAG32.

F40PAG8 and PAG8PS and was not as high as that between F40PAG32 and PAG32PS.

For all the samples examined, as the crosslinking degree increased, chain mobility and swelling rate reduced. PAG8 and

PAG8PS having the more flexibility of the PAAc backbone in an aqueous solution showed much higher swelling rates than F40PAG8. PAG8PS swelled faster than PAG8 during the first 5 h as shown in Figure 4(a). Differences in the swelling rates between these two hydrogels could be owing to the addition of the PS beads. It could be inferred that the sulfonic ions on the surface of the PS beads contributed to the extension of the PAAc chains with uptake of water. In contrast, F40PAG8 shows the lowest swelling rate. The decreased water uptake was owing to the fact that the PS filler particles were chemically bonded to PAAc chains and the produced PAAc microgels acted as crystallites, providing more rigidity to the hydrogel.

PAAc has the hydrophilic side chain, and PS has been prepared with the anionic surfactant, SDS. Swelling in DI water, the rate of water uptake in PAGPS may be explained by the equivalence in the gel phase and in the outer medium phase. Khokhlov and coworkers⁴¹ reported that the anionic surfactant over CMC was evenly distributed between the anionic gel phase and the solution. Different from PAG and F40PAG, PAGPS includes unfixed PS inside gel. In the process of swelling in DI water, anionic empty micelles, whose size range is from 5 to 10 nm in diameter,³⁹ could diffuse out to solution, and water molecules could penetrate into the gel phase. This exchange was thought to promote the swelling in DI water.

As a result, the addition of PS filler particles and the different methods of their incorporation induced different swelling rates. PAGPS showed the fastest swelling rate owing to the flexible chains of PAAc and an abundance of ionized groups on the surface of the added PS beads. In contrast, F40PAG showed the slowest swelling rate which may be ascribed to the higher number of chemical bonding sites between PS fillers and PAAc chains and microgels.

Equilibrium Swelling Ratio/Mesh Size of PAG/Volume Fraction of PS Filler of F40PAG and PAGPS

The equilibrium swelling ratio (Q_{w-eq}) was obtained when the hydrogel was saturated with water and stopped swelling. The equilibrium swollen state took 3 weeks to occur. Figure 5 shows

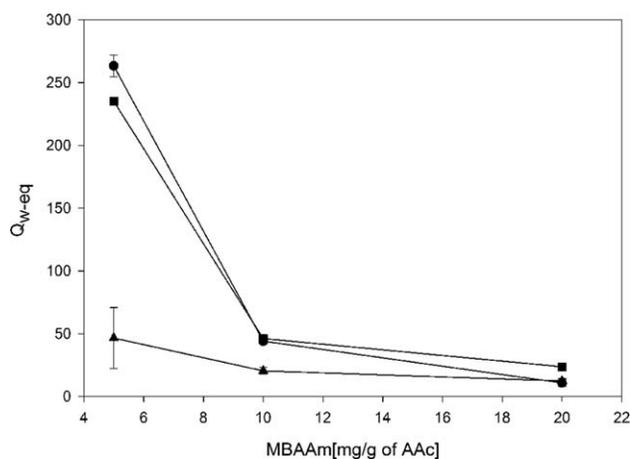


Figure 5. Equilibrium swelling ratios (Q_{w-eq}) of hydrogels in DI water, (●) PAG, (■) PAGPS, and (▲) F40PAG. Q_{w-eq} of PAG8 and PAG8PS were significantly higher than others.

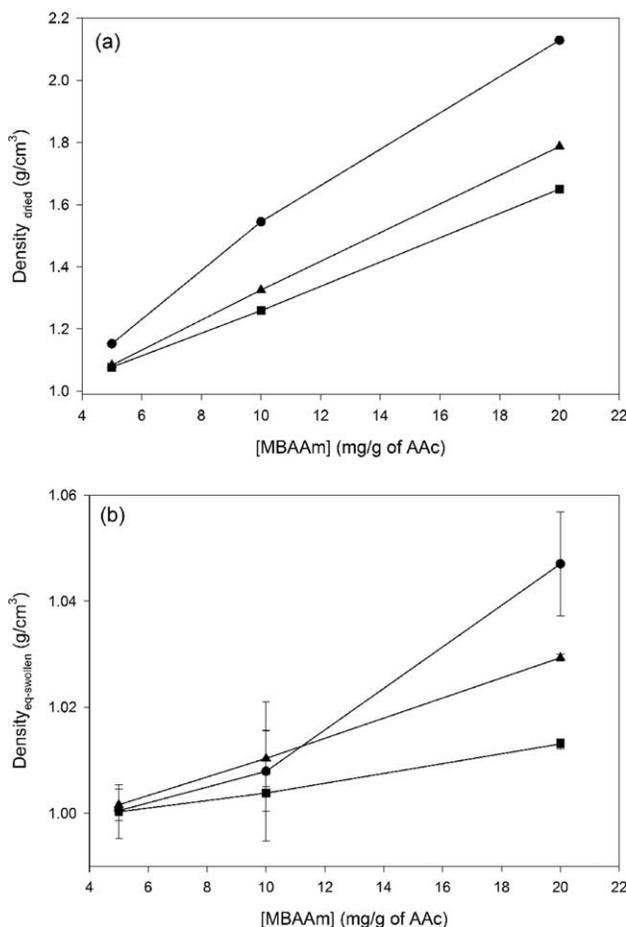


Figure 6. Densities of (a) dried hydrogels (b) equilibrium swollen hydrogels, (●) PAG, (■) PAGPS, and (▲) F40PAG.

Q_{w-eq} of each hydrogel in DI water. Q_{w-eq} of low crosslinking hydrogels was compared. Q_{w-eq} s of PAG8, PAG8PS, and F40PAG8 were 263, 235, and 47, respectively. PAG8PS was faster than PAG8 in the swelling rate, but lower than PAG8 in Q_{w-eq} . PAG8 and PAG8PS with low crosslinking degree exhibited much higher Q_{w-eq} than hydrogels in other medium and those with high crosslinking. However, F40PAG8 showed relatively low Q_{w-eq} value. Hydrogels with medium crosslinking were similar although F40PAG16 showed low Q_{w-eq} values. In the case of highly crosslinked hydrogels, the Q_{w-eq} values were not very different.

In PAG, PAG16 was 44, and PAG32 was 11 in Q_{w-eq} . In other words, PAG16 was 6 times, and PAG 32 was 24 times lower than PAG8 in Q_{w-eq} . The relationship between the increased range of crosslinking degree (x) and the decreased range of Q_{w-eq} (y) was approximately, $y = 1.5(x^2)$. However, this rule was not able to be applied to gel/filler mixture and gel/filler copolymer, that is in PAGPS and F40PAG. In PAGPS, PAG16PS was 46, and PAG32PS was 24 in Q_{w-eq} . PAG16PS was 5 times and PAG32PS was 10 times lower than PAG8PS in Q_{w-eq} . In the same way, F40PAG16 was two times and F40PAG32 was four times lower than F40PAG8 in Q_{w-eq} .

The average molecular weight (M_{ct}) between crosslinks, which is a nominal value estimated from the initial composition, was

determined from eq. (6).⁴² In molecular weight, AAc is 72 g/mol and MBAAm is 154 g/mol. Initial feed concentration of AAc was 16 g. Three different amounts of MBAAm were 0.08, 0.16, and 0.32 g.

$$M_{ct} = \frac{1}{2} \times \frac{[AAc]}{[MBAAm]} \quad (6)$$

$$\text{where } [MBAAm] = \frac{\text{g of } [MBAAm]}{154}, [AAc] = \frac{16}{72}$$

Equation (6) has been established based on the assumption that MBAAm has four active sites, and the value that the total number of mole of AAc is divided by 4 is the number of mole attached in one direction to a mole of MBAAm. Therefore, that value is doubled between MBAAm molecules. M_{ct} s were 15,400, 7700, and 3850 g/mol at 0.08, 0.16, and 0.32 g of MBAAm. Equation (6) does not involve the swelling ratio and any interaction parameters with water molecules. It can be inferred that these M_{ct} s are from the dried gel with 100% crosslinking efficiency and without any physical entanglements. The exact M_{ct} value is hard to obtain, but inefficiency of crosslinking agent results in the higher M_{ct} , and the physical entanglements induce the effect of lowering M_{ct} . Those two opposite effects are offset in a degree.

Equation (7) was derived by Merrill and coworkers^{43,44} Free energies of mixing and swelling in respect to the solvent molecule from Flory's theory³⁹ were applied. Chemical potentials of solvent in a gel and in a bulk are same when a gel reaches the equilibrium swelling is a precondition, that is $\partial\Delta F/\partial n_1 = 0$.

$$\frac{1}{M_{cs}} = \frac{2}{M_n} - \frac{\ln(1-\Phi_{vd}) + \Phi_{vd} + 0.498(\Phi_{vd})^2}{\rho_g V_1 \left[(\Phi_{vd})^{1/3} - \frac{1}{2}\Phi_{vd} \right]} \quad (7)$$

where M_n is the number average molecular weight of PAAc (93,368 g/mol), Φ_{vd} the volume fraction of dried sample in an equilibrium swelling gel, ρ_g the equilibrium density of gel, and V_1 is the molecular volume of water.

Interaction parameter (χ) of PAAc to water is 0.498.²⁷ Molar volume of water is 18 cm³/mol. Densities of equilibrium swelling PAG8, PAG16, and PAG32 were 1.0005, 1.0309, and 1.0372 g/cm³, respectively, as shown in Figure 6(b). Number average molecular weight of linear PAAc, 93,368 g/mol, was obtained from gel permeation chromatography. Volume fractions of dried gel in equilibrium swelling gels were found in equilibrium swelling ratios. Molecular weights between crosslinks derived from eq. (7) were 46,647, 44,532, and 18,093 g/mol for PAG8, PAG16, and PAG32.

The distance, that is mesh size (ξ), between crosslinks was calculated using eq. (8). V_d is the volume fraction of the polymer gel in the equilibrium swelling state, which can be calculated from the swelling ratio and the density. M_c is the molecular weight between crosslinks. In brief, 0.154 (nm) is a carbon-carbon chain length and 0.186 was derived from $(2C_n/M_r)$.⁴⁵ C_n is Flory's characteristic ratio, 6.7 of AAc,³⁹ and M_r is the molecular weight of repeating unit, 72 g/mol of AAc.

$$\xi = 0.154 \times (v_d)^{-1/3} \times (0.186 \times M_c)^{1/2} \quad (8)$$

Table IV. Densities and Volume Fractions of Dried Hydrogels

Crosslinking degree	PAG		F40PAG		PAGPS	
	Density (g/cm ³)	Φ_v PS	Density (g/cm ³)	Φ_v PS	Density (g/cm ³)	Φ_v PS
Low(8)	1.15	0	1.08	0.350	1.07	0.889
Medium(16)	1.54	0	1.33	0.356	1.26	0.584
High(32)	2.13	0	1.79	0.288	1.65	0.449

ζ_s were derived and compared from eq. (6) (M_{ct}) and eq. (7) (M_{cs}). For PAG8, PAG16, and PAG32, ζ_s from M_{ct} were 52.9, 20.9, and 9.3nm, and ζ_s from M_{cs} were 92.0, 49.4, and 20.1 nm. In each PAG, values were approximately 43–58% different, and this might be owing to the efficiency of the crosslinking agent. According to the modeling from Bowman and coworkers,³⁷ the degree of heterogeneity was 25% with beginning of the polymerization, and slightly more than 60% at 100% conversion.

To characterize the crosslinking degree and the loading level of the PS filler particles in the hydrogels, the densities of hydrogels were measured. Figure 6(b) shows the densities of the swollen hydrogels at equilibrium. In each type of hydrogel, with increase in the crosslinking degree, the density increased. In hydrogels with low crosslinking, densities are similar, but the equilibrium swelling ratios showed significant differences. It can be inferred that the smaller amount of water uptake of F40PAG8 makes it close to that of PAG8 owing to the presence of PS beads that were chemically bonded to the PAAc chains.

Figure 6(a) was derived from the densities of the swollen hydrogels at equilibrium and from eq. (9).^{43,44}

$$\frac{1}{\rho_g} = \frac{W_a}{\rho_a} + \frac{W_w}{\rho_w} \quad (9)$$

where ρ_g is the density of swollen gel, ρ_a the density of dried PAG, ρ_w the density of water, W_a the weight fraction of PAG, and W_w is the weight fraction of water.

By comparing the densities of PAG and PAGPS, the volume fraction of PS could be calculated.

The density of atactic PS is known to be 1.05 g/cm³.²⁷ The dried weight of PAG, as listed in Table II, was used. In the light of the protocol used for obtaining PAGPS, the conversion rate of PS in each different crosslinking hydrogel was different: the conversion was ~100% in PAG8PS, 62% in PAG16PS, and 48% in PAG32PS. This result showed that the degree of crosslinking ratio affected the polymerization rate. It can be inferred that in the highly crosslinked hydrogel, the movement of radicals was significantly interrupted by the PAAc chains.

To obtain the volume fractions of the PS filler particles in F40PAG, the conversion rate of AAc was assumed to be 100%. Then, the weight of PS and SDS was considered. The density of the initial PS emulsion was estimated to be 0.95 g/cm³ because the conversion rate was 0.5. The density of styrene at 80°C is known to be 0.85 g/cm³.²⁷

As summarized in Table IV, the filler loading level was lower in the highly crosslinked hydrogel. Even if the concentration of PS

was higher in PAGPS, the equilibrium swelling ratio and swelling rate of F40PAG were lower than that of PAGPS owing to the chemical bonding between the PS filler particles and PAAc chains in F40PAG

Equilibrium Swelling Ratio of pH-Sensitive PAAc Hydrogels

Q_{w-eq} of a hydrogel with less crosslinking in a different pH range is shown in Figure 7(a). In the pH range of 2.0–3.3, the difference in the Q_{w-eq} values is insignificant. Q_{w-eq} increased when the pH increased from 4.8 to 7.5. In the pH range of 7.5–10.0, Q_{w-eq} of PAG8 was constant, Q_{w-eq} of F40PAG8 was increased, and Q_{w-eq} of PAG8PS was decreased. In the pH range of 4.8–7.5, slopes of PAG8 and PAG8PS were steep, which indicated that most carboxyl groups of AAc were ionized. Owing to the larger mesh and mobile PS, the chelation of sodium ions between ionized carboxyl groups and sulfonic ions could be formed on the surface of the PS particles. However, this was not observed in PAG8. In F40PAG8, because of the high heterogeneity and fixed PS to the main PAAc backbone, it was assumed that the screen effect was not occurred.

Q_{w-eq} s of hydrogels crosslinked to a medium extent in different pH ranges are shown in Figure 7(b). Q_{w-eq} of PAG16PS was slightly decreased although Q_{w-eq} s of PAG16 and F40PAG16 were increased in the pH range of 7.5–10.0. Q_{w-eq} was inversely proportional to the crosslinking degree. Highly crosslinked hydrogels showed the lowest Q_{w-eq} . Figure 7(c) shows that Q_{w-eq} s in the pH range of 2.0–7.5 were not significantly sensitive to pH. At pH 10.0, F40PAG32 showed the highest Q_{w-eq} and PAG32PS showed the lowest Q_{w-eq} .

The driving force of swelling or shrinking is the presence of mobile counter ions. Ions can diffuse into and out of the hydrogel when a salt especially, a 1 : 1 salt such as NaCl or KCl is added. The increase in the concentration of mobile counter ions inside the hydrogel is possible in the process of balancing out the ion concentration inside and outside the hydrogel. Therefore, as the concentration of added salt increases, swelling ratio can be decreased, especially when the chains are more flexible.⁴⁶ In addition, based on the Donnan equilibrium theory, increase in concentration of H⁺, Cl⁻, or Na⁺ in water can make these ions to attach on the boundary of the gel phase and shield the opposite charge inside gel because of which, the osmotic pressure can be decreased.^{47,48} Considering the two theories, first the concentration of the mobile counter ions inside and outside hydrogel is increased. Next, those counter ions attach on the boundary of the gel phase and interrupt the water uptake. This explanation is well established in cases of PAG8 and PAG8PS as shown in Figure 7(a).

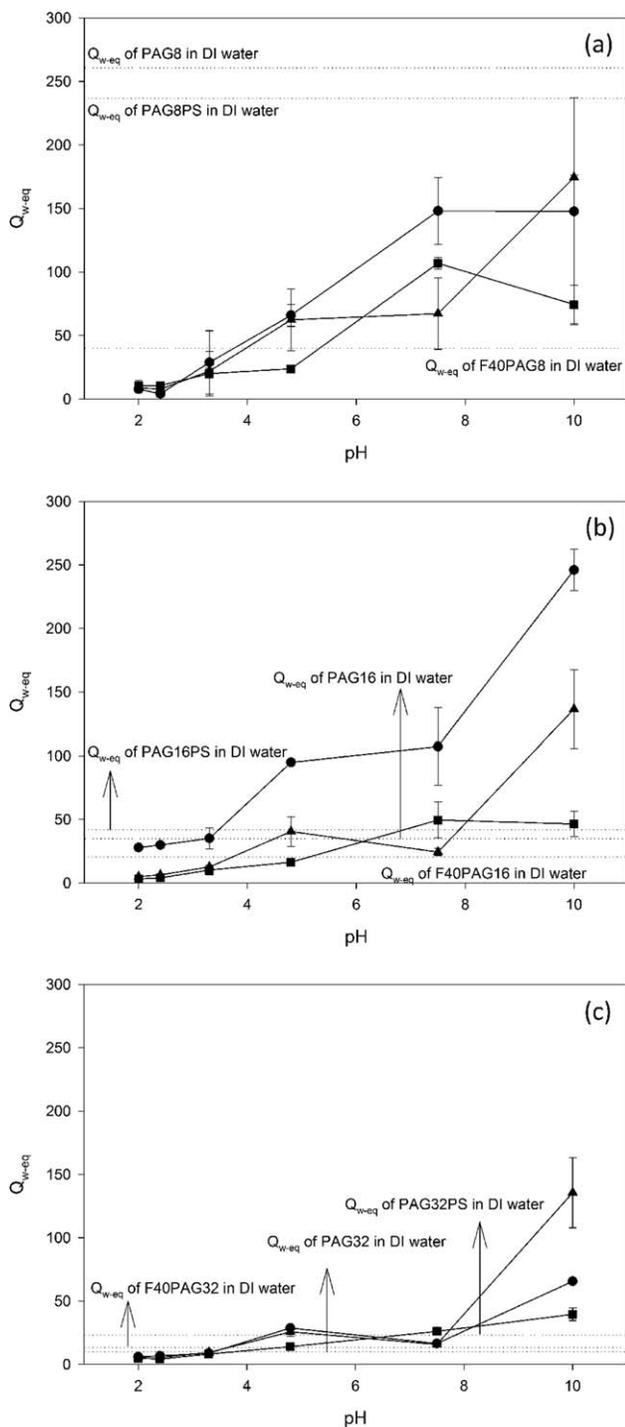


Figure 7. (a) Equilibrium swelling ratios of low crosslinking hydrogels as a function of pH, (●) PAG8, (■) PAG8PS, and (▲) F40PAG8. (b) Equilibrium swelling ratios of medium crosslinking hydrogels as a function of pH, (●) PAG16, (■) PAG16PS, and (▲) F40PAG16. (c) Equilibrium swelling ratios of medium crosslinking hydrogels as a function of pH, (●) PAG32, (■) PAG32PS, and (▲) F40PAG32.

However, for the higher crosslinking degrees, or for more heterogeneity, that was not seemed to be applied for a course of pH ranges, and might be caused by the relatively low

concentration of salt in buffer solutions. Q_{w-eq} s were compared at pH buffer solutions and at DI water. In Figure 7(b,c), Q_{w-eq} s of PAG16 were 42.7 at pH 3.3 and 44 at DI water. The pH value, where Q_{w-eq} in DI water met, was 3.3 for PAG32 as well. Q_{w-eq} of PAG32 was 9.1 at pH 3.3, and was 10.8 at DI water. pK_a of AAc has been reported in the range of 4.8–5.0.^{49,50} The degree of the ionization of carboxyl group was speculated with comparison of Q_{w-eq} at pHs 4.8 and 2.0. The value of pH of 4.8 was regarded as an equivalence point, and pH 2.0 was the point where all the carboxyl groups formed hydrophobic hydrogel bonding. The maximum swelling degree induced by ~100% ionization was observed at pH 10. Q_{w-eq} s of PAG16 were 26.5, 86.6, and 257.6 at pH values of 2.0, 4.8, and 10.0. When compared to the lowest Q_{w-eq} , half deprotonation increased Q_{w-eq} about three times, and all ionization induced the nine times higher Q_{w-eq} . At pH 3.3, about 3% of carboxyl group was ionized.

For the hydrogels filled with PS, sulfonic group as the strong acid on the surface of particles was thought to be ionized in DI water. These ionized PS and PAAc particles were considered together with carboxyl group of PAAc chain to check whether the degree of ionization was more than 50% or not.

Q_{w-eq} s of F40PAG8, F40PAG16, and F40PAG32 in DI water were 46.5, 20.4, and 12.3, respectively. Owing to the incorporated PS, pK_a value could not be estimated. However, from the highest Q_{w-eq} (Q_h) and the lowest Q_{w-eq} (Q_l), Q_{w-eq} at pK_a could be obtained by, $([Q_h/Q_l]^{0.5}) \times Q_l$. Based on this assumption, Q_{w-eq} at pK_a s of F40PAG8, F40PAG16, and F40PAG32 were 38, 26, and 21. The value of pK_a of F40PAG was in the range of 3.3–3.9. In DI water, over half of the carboxyl and sulfonic groups of F40PAG8 were ionized, but less than half of them were ionized for F40PAG16 and F40PAG32. This is related to the polymerization process of F40PAG. Less amount of crosslinking agent might increase the number of PAAc particle having the sulfonic ion on the surface and connected to the main backbone chain.

In the same way, Q_{w-eq} at pK_a s of PAG16PS and PAG32PS were 13 and 12. The value of pK_a of PAGPS was approximately 3.8. Q_{w-eq} s of PAG16PS and PAG32PS in DI water were 44 and 11. Therefore, over half of the PAG16PS were ionized, but less than half of the PAG32PS were ionized in DI water. As summarized in Table IV, PAG16PS included more than 14% of PS more than PAG32PS.

The difference between Q_h and Q_l for the whole range of pH was the largest in F40PAG. The Q_{w-eq} difference was 15–19 times, but in PAG and PAGPS, it was 9–12 times. Therefore, F40PAG was the most pH-sensitive hydrogel.

Rheological Properties of F40PAG

Elastomeric materials have the reinforcing filler, generally divided into carbon black or silicas.⁵¹ The size of these fillers is in the range of 10–100 nm scale in diameter. When these fillers are chemically or physically incorporated onto the main chain, its shear property is improved.⁵² Carbon black is the main filler in the automotive tires. The property of amorphous elastomer such as SBR is divided into two aspects, resilience and strength.

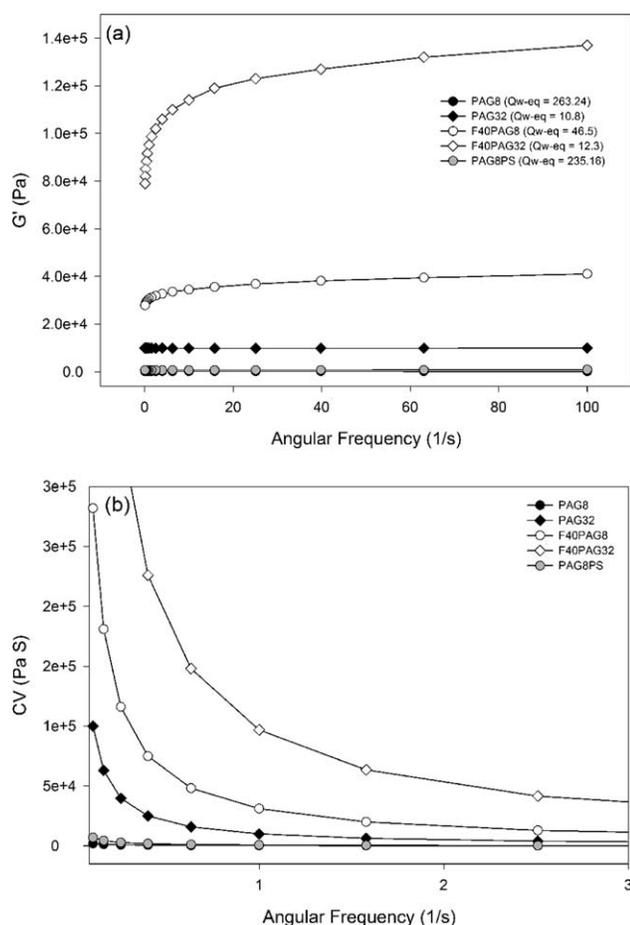


Figure 8. (a) Storage modulus and (b) CV of PAG8, PAG32, PAG8PS, and F40PAG8 to observe the effect of PS incorporation method on the shear properties, amplitude γ was 5%.

Resilience, the elastic property, can be introduced by vulcanization process. Strength is reinforced by the incorporation of fillers, carbon black (<300 nm), nonblack filler (10–8000 nm), calcium carbonate (<1000 nm). As the filler size is smaller, reinforcing effect is more efficient.⁵³

Inorganic materials have been used as fillers, and its application has been successful to enforce the mechanical property of the industrial product. However, no articles studied the incorporation of organic filler, especially PS, to the elastomer. PS, which is thermoplastic, is the most widely used inexpensive organic material. F40PAG is the PS incorporated PAG chemically. Its pH sensitivity was higher than that of PAG or PAGPS, for the equilibrium swelling hydrogel. In addition to pH sensitivity, its efficiency to strengthen the shear property of equilibrium swelling hydrogel was also higher than increasing the crosslinking degree.

Figure 8 shows the storage modulus (G') and the complex viscosity (CV) of PAG8, PAG32, PAG8PS, F40PAG8, and F40PAG32. G' of PAG8PS, that is the PS was physically incorporated into PAG8, was not improved. G' of more densely crosslinked PAG32 was observed at 10k Pa. But, G' of F40PAG8 was

27–40k Pa. Crosslinking degree of PAG32 is four times higher than that of PAG8, but its G' was lower than that of F40PAG8. CV of F40PAG8 was also higher than that of PAG32. At the low angular frequency (1/s), CV of PAG32 was 100k pa·s and CV of F40PAG8 was 300k pa·s. In Q_{w-eq} , PAG8 was 263, PAG32 was 10.8, and F40PAG8 was 46.5. Therefore, F40PAG8 showed more improved property than PAG32 in all aspects, such as the ability of water uptake, pH sensitivity, G' , and CV. G' and CV of F40PAG32 were increased significantly from those of PAG32 and F40PAG8. G' of F40PAG32 was in the range of 80–130k Pa. This value is about three times higher than that of F40PAG8, and 8–10 times higher than that of PAG32.

Corresponding to variations in the structure of the gel that resulted from swelling, the CV increased as the matrix–filler interaction or bonding became stronger. The difference in viscosity was more profound at low shear rates. As the shear rate increased, the network was destroyed by the shearing force, which induced a sharp decrease in viscosity. It can be noted that the surface has been ionized to improve the filler dispersity. However, that ionization strongly promoted the attraction between the filler and the matrix, resulting in adsorption or entanglement of the polymer chains on the filler surface, especially in pH solution, in the process of swelling, or under the external physical pressure. Eventually, in the high shear rate region, complex viscosities of all samples were similar, as against that observed in the low shear rate region. Figure 8(b) shows the effect of the addition of filler and shear rate on the CV. As the shear rate decreased, the CV was higher. For both Q_{w-eq} and CV, F40PAG8 was higher than PAG32.

Hydrogels with low crosslinking tended to be shattered when they reached Q_{w-eq} although F40PAG8, which was not as weak as PAG8 and PAG8PS, also showed low swelling ratios in DI water. The incorporation of PS as fillers, especially by copolymerization, is thought to be more effective in hydrogels with lower crosslinking to improve the mechanical strength. The PAAc chains of F40PAG are not as flexible. It is worth bearing in mind that the incorporated PS and PAAc microgels that act as crystallites play a major role in fixing the PAAc network.

The swelling ratio is intimately related to the mechanical strength of the hydrogel. The dried hydrogel is in a rigid solid state, whereas the swollen hydrogel at equilibrium is pliable owing to the high affinity to water molecules and the absence of physical entanglements. Most of the previously proposed methods to improve the mechanical strength have involved increasing the crosslinking density, changing the reaction conditions, and changing the chemical composition. By increasing the crosslinking density, the mechanical strength can be significantly increased, although changes in properties other than the strength such as swelling rate, equilibrium swelling ratio, or pH sensitivity are likely to occur. Therefore, F40PAG having three different crosslinking densities were examined for the stress–strain relationship.

Stress–strain curves are important in the view of engineering applications because they provide information such as the yielding point and shear modulus (G). Shear modulus is a

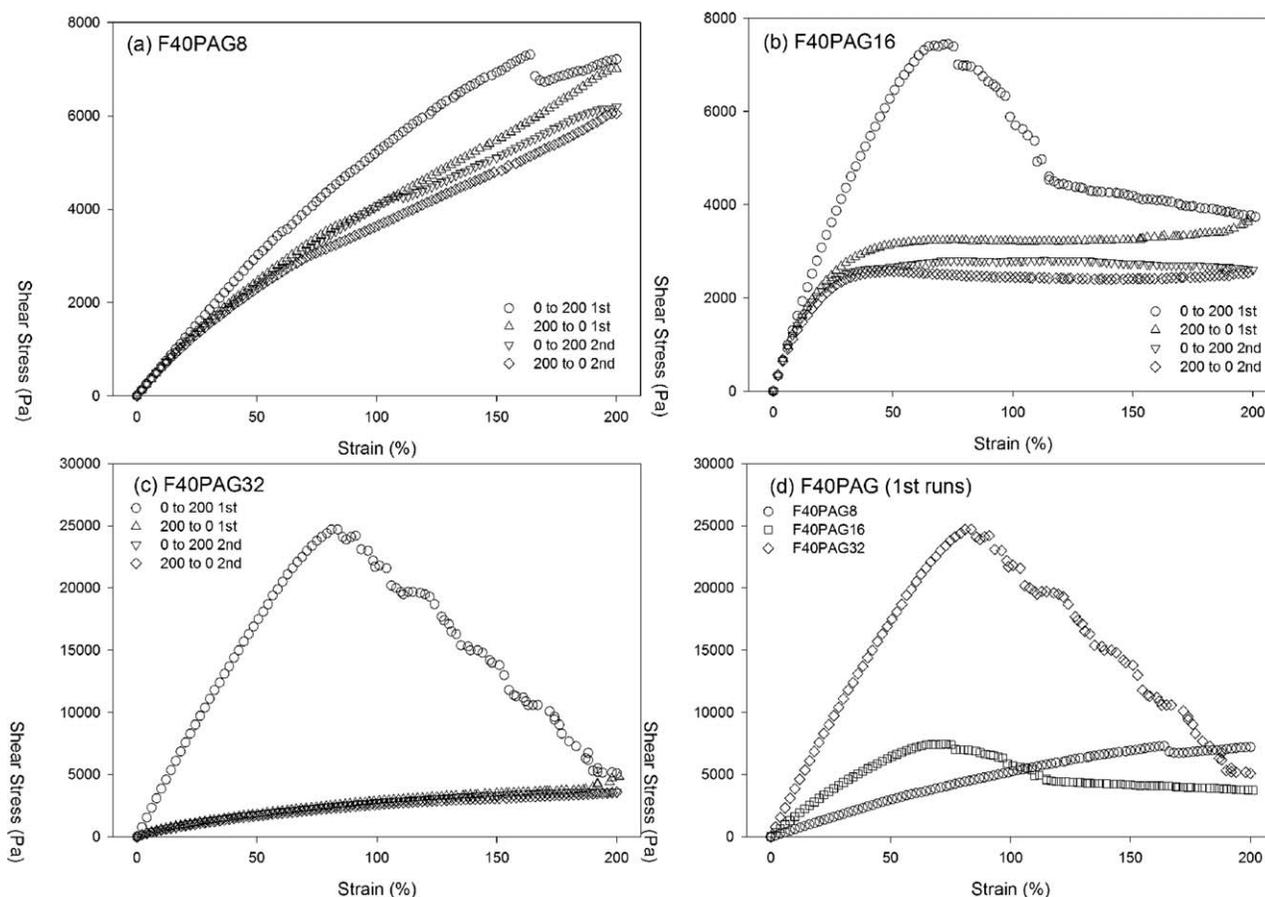


Figure 9. Shear stress to shear strain measured by the amplitude sweep mode (went up and down two times 0–200% strain) (a) F40PAG8, (b) F40PAG16, (c) F40PAG32, and (d) F40PAG one way from 0 to 200%.

measure of the rigidity of the material. The higher the shear modulus, the more resistant the material is to various shearing or twisting motions. The stress–strain curves of F40PAG are plotted in Figure 9 based on the results of the strain rate-controlled oscillation mode (amplitude sweep) experiments carried out at a fixed angular frequency of 10 rad/s. Yielding points were 164, 73, and 81%, yield strengths were 7310, 7440, and 24,700 Pa, and G -values were 44.57, 101.92, and 304.94 Pa for F40PAG8, F40PAG16, and F40PAG32, respectively. Within the range of elastic deformation, the polymer chains are considered to undergo only bending and straining and hence, they can be restored with time. Above the yielding point, however, it appears as if the polymer chains are uncoiling, slipping, or breaking off, and the deformed polymer chains cannot be recovered. On increasing and decreasing the strain from 0 to 200% twice, yield strength could not be observed but at the first increasing.

In Figure 9(d), the first runs of the three samples are compared. F40PAG8 was most the flexible and showed the highest yielding point. Above the yielding point, is the elongation increased despite a small decrease in the shear stress at the yielding point. However, shear stresses of F40PAG16 and F40PAG32 dropped significantly at the yielding point and did not increase again.

Increased drop in the shear stress from the peak value and the highest yield strength were observed for F40PAG32.

From the results of the analysis of swelling, it could be understood that a continuous network consisting of PAAc chains and fillers was formed in the filled compound. Hence, the filler acted as a temporary crosslinking point or a crystallite and the frictional resistance to the movement of the polymer chains was enhanced by the higher crosslinking density or loading levels of the filler with the dispersity. A similar mechanism was also reported for hydrocarbon rubbers filled with carbon black, in which a dominant filler–matrix interaction occurs.⁵⁴

CONCLUSIONS

PAAc hydrogels (PAG) crosslinked by different concentrations of methylenebisacrylamide (MBAAm) and filled with nanosized PS beads were successfully prepared. Swelling tests and rheological measurements were conducted to demonstrate that the swelling rate, equilibrium swelling ratio, and rheological properties of the hydrogels could be controlled by the concentrations of the crosslinking agent, addition of filler, and pH of the system.

Stabilizing the PS in PAG and forming the good bonding between PAG and PS surfaces were challenging. Two different

schemes for introducing PS beads into PAG were investigated. The PAGPS series was prepared by first completing the PAG reaction and then the mixture used for the microemulsion reaction for preparing nanosized PS was introduced into the swollen PAG at equilibrium. The microemulsion reaction was allowed to be complete. The F40PAG series was prepared by mixing the PAG reaction mixture and PS microemulsion reaction mixture (with 50% conversion) in the reactor and both reactions were allowed to proceed simultaneously.

When compared with the other two hydrogels, that is, PAG and PAGPS, F40PAG showed the slowest swelling rate, lowest equilibrium swollen ratio, highest pH sensitivity of equilibrium swelling ratio, highest storage shear modulus, CV, and yield strength. These differences were most pronounced for samples with low concentration of the crosslinking agent. However, differences between the characteristics of PAG and PAGPS samples were insignificant. Our data suggest that a strong bonding exists between PS and PAG. However, more research is needed to clearly define and describe the nature of the bonding.

In conclusion, we have successfully demonstrated a reaction strategy to reinforce PAG by incorporating nanosized PS, which will provide an useful approach for tailor-making hydrogels with desirable swelling, rheological, and mechanical properties.

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