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Inhomogeneous Swelling and Mechanical Properties of Polystyrene Bead-filled Poly(acrylic acid) Hydrogels

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ABSTRACT

Position-dependent swelling rates, storage moduli (G'), and damping factors (G''/G') of polystyrene bead-filled poly(acrylic acid) hydrogels (FPAGs) were investigated. FPAGs were synthesized via free radical crosslinking copolymerization of acrylic acid with methylene *bis*-acrylamide (MBAAm) weight fractions of 0.005 (FPAG5), 0.01 (FPAG10), and 0.02 (FPAG20), in the presence of polystyrene (PS) microemulsion. To study the position-dependency, two middle parts and two edge parts were cut out of a sample, and swelling and mechanical properties of those specimens were measured. The results showed that swelling rates in the middle (M) and edge (S) were similar in the first 2 h, but G' was decreased 1.8-2.5 times faster in S than in M. In unfilled-poly(acrylic acid) hydrogel prepared with MBAAm weight fraction of 0.01 (PAG10), G' was decreased 1.4 times faster in S than in M, but swelling rates were similar in both parts. These results suggested the crosslinking density was higher in M than in S, the incorporation of PS (36% volume fraction) increased the inhomogeneity, and G' about 40 times, and generated two-fold increase of damping factor at 15% swelling when compared FPAG10 and PAG10.

INTRODUCTION

Hydrogels with a crosslinked polymeric structure are water-swollen and behave mechanically in a manner similar to that of highly swollen elastomers. Hydrogels in particular have received significant attention because of their exceptional promise in biomedical applications, especially for being used as the substrates in cell cultures and tissue engineering.[1-3] End-use applications of hydrogels depend on the swelling rate and equilibrium swelling ratio, which are controlled by the ratio of monomer/comonomer, type of monomer,[4] and external stimuli such as pH,[5] and ionization,[6-8] salt,[9] and temperature.[10-13]

However, in most of these applications, hydrogels have two major drawbacks: inhomogeneity and mechanical weakness in swelling. Inhomogeneity may lead to inconsistent results, and mechanical weakness may limit the usefulness of the hydrogel.

The term inhomogeneity should be distinguished from heterogeneity. Inhomogeneity means the fluctuation of the crosslinking density in a unit volume, whereas heterogeneity indicates the phase separation between gel and solution.[14, 15] The phase separation is usually observed when the first gel formation appears, and this gel reabsorb the solution becoming the homogeneous gel for a course of crosslinking polymerization.[16] Moduli in heterogeneous gels are lower than in corresponding homogeneous and inhomogeneous gels.[17] Dynamic light scattering technique has been used to study the network inhomogeneity.[18-20] To improve the homogeneity of hydrogel, controlled radical

polymerization has been used for gel preparation. Kannurpatti el al. reported that radicals became entrapped in highly crosslinked region (microgel region) during the polymerization with conventional initiators,[21] and the formation of microgel where the segmental mobility was restricted, was the primary cause of inhomogeneity.[22-26] They prepared poly(ethyleneglycol) methacrylate hydrogel by living radical polymerization to reduce the formation of microgel region.[27-30] Grube el al. used thiol-ene polymerization to improve the homogeneity.[31] They reported that homogeneity could be improved due to the slow polymerization and the gel point observed at the high conversion in the controlled radical polymerization, but claimed that it was characterized only in macroscopic properties such as elasticity in most literatures,[32, 33] emphasizing that the microscopic property such as the density of active network chain by light scattering should be measured.

To overcome the mechanical weakness in swelling, several studies have suggested alternative procedures; e.g., incorporation of a filler into the network. Carbon black, silica,[34] and talc[35] have been used as fillers. For filler incorporation, the concentration, size, and dispersion are the most important parameters. As the size of the filler gets smaller, its reinforcing effect becomes more efficient.[36] Larger surface areas of fillers resulted from higher concentrations and smaller filler sizes may induce a greater reinforcing effect. However, if the concentration of filler is very large, the possibility that the filler will become coagulated increases. Filler dispersion is also a key factor regarding mechanical properties. Even if the filler particles are small, the coagulation between them can decrease the total surface area, and hence reduce the expected effectiveness. Nie el al. prepared poly(N-isopropylacrylamide)/clay nanocomposite hydrogel, and reported that shear modulus increased with clay and monomer concentration.[37] Their results inferred that clay particles acted as multi-functional crosslinks with an average effective functionality about 50.

A latex interpenetrating network (LIPN), which can be prepared by the crosslinking polymerization of comonomer on crosslinked polymer seed latex, is another useful tool to enhance the mechanical properties of a hydrogel by incorporating emulsion particles as fillers. When two homopolymers in an LIPN are miscible, a core-shell structure is formed.[38] However, if those two polymers are not miscible, the first polymer just forms layers on the surfaces of the second polymer particles produced by the emulsion polymerization.

In the present work, we introduced two new strategies to LIPN to promote the copolymerization of immiscible styrene and acrylic acid. First, we conducted the microemulsion polymerization instead of the conventional emulsion polymerization to reduce the particle size – the shape of particle was a little deformed.[39] Second, a crosslinking agent was not used in the preparation of the filler. In microemulsion polymerization, monomeric radical is escaped from a particle after the chain transfer reaction occurs in a particle.[40, 41] If the crosslinking agent is used, radicals will be more trapped between chains inside particles and increase of the number of particles will be slowed.

Therefore, we prepared PS filler by microemulsion polymerization up to 50% conversion first, and then used this emulsion as a reaction media instead of water in the crosslinking polymerization of acrylic acid. Swelling ratios, shear storage moduli, and damping factors were measured for 2 h swelling.

EXPERIMENTAL

Materials

Styrene (purity > 90%) inhibited with stabilizer was purchased from J.T. Baker Chemical Co. The stabilizer was removed by an alkaline solution washing method: washing the styrene three times with an equal volume of 10-wt% NaOH solution, and then again three times with an equal volume of distilled de-ionized water (DI water). Potassium persulfate (purity > 99%, Aldrich Chemical Co.), acrylic acid (anhydrous, 99%, Aldrich Chemical Co.), ammonium persulfate (purity > 98%) (Sigma-Aldrich Co.), sodium dodecyl sulfate (SDS, purity 98%, OmniPur EMD Co.), 1-pentanol (purity > 99%, AlfaAesar Chemical Co.), *N*,*N'*-methylenebisacrylamide (MBAAm, Fluka), and ethylenediamine-tetraacetic acid (EDTA, Sigma) were all used as received.

Polymerization and Gelation

Recipe of PAG10 which was prepared with DI water instead of PS microemulsion, is in table 1. Oil-in-water microemulsion composed of water, SDS, 1-pentanol, and styrene was polymerized in 1000-mL kettle with four necks (Ingredients listed below Table 2). The reactor was immersed in a thermostatic water bath before the polymerization. A water-cooled condenser was connected to the reactor and nitrogen was bubbled continuously into the reactor liquid to remove dissolved oxygen. The reactor was heated to 70°C, and microemulsion was added and equilibrated for 20 min with stirring at 300 rpm. After equilibrating, with the addition of potassium persulfate initiator, 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 prelabeled 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 was measured with the assumption that monomers and polymers were dispersed uniformly in the solution. The equivalent amount of monomer could be calculated based on the weight of each sample and the weight % of monomer initially charged. Conversion rate could be obtained from eqn. (1).

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

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. $C_{initiator}$ 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.

Crosslinking copolymerization of acrylic acid and styrene was conducted at 60°C for 2 h. Before the polymerization, monomer solution was prepared by dissolving 16g of acrylic acid in 43ml of PS microemulsion solution with the addition of 0.08g (5mg/(g of acrylic acid), 0.16g, or 0.32g of MBAAm and 0.06g 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 0.38g of ammonium persulfate were added, and polymerization was conducted without stirring.
The obtained gel product was thoroughly washed with DI water to remove unreacted monomer and water-soluble fraction of the polymer. The gel product was washed five times for 2 days at room

temperature, and the equilibrium swollen ratios when the weight change of swollen was not observed were measured.

Swelling ratio and Density

The washed hydrogels (up to the equilibrium) were cut into four round pieces (25mm in diameter, two from M, and two from S) as shown in Fig. 1, and dried in a vacuum oven at 60°C. The dried weight and density was measured, and the volumetric swelling ratio (Q_v) of each hydrogel in DI water was monitored for the first 2 h at room temperature by using an electronic densimeter (SD-200L, ALFAMIRAGE Co. Ltd.). For the first 1 h, measurement interval was 1 min. For the last 1 h, it was 2 min. Swelling behavior was not affected by measurement intervals. It took about 15 sec in each measurement of weight and density.

Q_v was calculated from eqn. (2).

$$Q_v = \frac{(W_s/\rho_s) - (W_d/\rho_d)}{(W_d/\rho_d)} \qquad (2)$$

Where W_s is the weight of the hydrogel after swelling, W_d is the weight of dried hydrogel, ρ_s is the density of the hydrogel after swelling, ρ_d is the density of dried hydrogel.

Rheological measurements

To characterize the viscoelastic properties of the hydrogels, rheological measurements were performed with a rheometer (MCR 301, Physica, Anton Paar) using a plate-plate configuration (diameter: 25 mm). Hydrogel samples just after the measurement of Q_v were loaded onto the lower plate, then the upper fixture was lowered until the normal force was in the range 0.2–0.3 N, and the humidity chamber was placed around the sample to prevent dehydration during the data collection. After the measurement, hydrogel sample was place into the swelling medium again. This process was repeated 2 times at 15, 30, 45, and 60% Q_v for each specimen. The temperature, which was fixed at 20°C, was controlled using a water bath circulator (Julobo, F25). Rheological measurements were performed in the dynamic shear oscillation mode (frequency sweep), high to low frequency. The amplitude gamma was fixed at 0.1%, and the angular frequency (1/s) range was 0.2–300. In Figs 4 to 7, the range was reduced from 0.2 to 2.0 because G' and damping factors were almost constant when the angular frequency was over 20. G' was taken when the angular frequency was 19.3. Normal force was kept near 0.2-0.3N consistently. During the measurement, the Q_v and the density were not changed by more than 2%.

RESULTS AND DISCUSSION

Preparations of PS filler and FPAGs

To prepare the PS filler particles, microemulsion polymerization of styrene was conducted. The polymerization was stopped at 50% conversion, and the PS microemulsion was used as a medium in the crosslinking polymerization of acrylic acid with three different concentrations of the crosslinking agent. The polymerization parameters of the PS filler particles were calculated based on the conversion and the

particle size from transmission electron micrograph[39] using material balance (eqn. (3)), and two kinetic equations (eqn. (4) and (5)).

At 50% conversion (X_c = 0.5), the average diameter of particles (D_p) was 40 nm. The density of polystyrene (d_p) is 1.05 g/cm³.[42] $[M]_0$ is the initial monomer concentration. We could find the number of particles (N_p) which was 5.478×10¹⁴/cm³ from eqn. (3).

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

(3)

The polymerization rate (R_p) 2.22×10⁻⁶ mol/s was obtained in eqn. (4) after integrating the left hand side in terms of the reaction time, and the right hand side in terms of the conversion rate.

$$R_p = [M]_0 \frac{dX_c}{dt}$$

(4)

The average number of radicals per particle ($\bar{n}$) was found from eqn. (5).

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

(5)

N_A is Avogadro's number (6.02×10²³), and the propagation rate constant, k_p, is 3.29×10⁵ cm³/mol·s at 70°C.[43] Monomer concentration in particles ($[M]_p$) approximately equals to $[M]_0(1-X_c)$ which is estimated from the assumption that no more droplets exist over 4% conversion because all the monomers in the core of mixed micelles diffuse out, and those droplets become empty micelles in microemulsion polymerization of styrene.[40, 41] The solubility of PS in water is negligible (10⁻⁵g of styrene dissolves in g of water at 25°C). Based on the above parameters, $\bar{n}$ was 0.113 which was calculated from eqn. (5).

The structure of FPAG is similar to a block copolymer. One part is PS particle, and the other part consists of poly(acrylic acid) network and particles which had been formed when the poly(acrylic acid) radicals dispersed in the aqueous phase enter into micelles. Copolymerization could be achieved if these poly(acrylic acid) radicals enter into PS particles. At the initial condition of crosslinking polymerization, styrene is 0.86g, and acrylic acid is 16g. Molar ratio of these monomers is 1:27. Poly(acrylic acid) is water-soluble, but with a crosslinking, it can be precipitated, resided, and enter into the micelles or the particles.
Therefore, in FPAG product, there were three types of fillers – PS and poly(acrylic acid) particles, and empty micelles. If these fillers were chemically connected to network chains, the mechanical properties could be successfully enhanced. This was proved by SEM (Fig. 2), swelling and moduli tests.

Fig. 2 represents the surfaces of FPAGs and PAG10. The surfaces became smooth as the crosslinking degree increased as shown in Fig. 2, (a) for FPAG5 and (c) for FPAG20. The PS filler, poly(acrylic acid) particles, and empty micelles crowded near the periphery of each hole; this behavior was more significant in FPAG5. In other words, as the crosslinking degree lowered, the sizes of the holes became

bigger and the numbers of filler particles and micelles involved with each hole increased. This might be due to the coagulation of fillers even if the surface of filler was ionized with SO_4^-.

The surfaces were also rougher when the filler was incorporated at the fixed concentration of the crosslinking agent. Incorporation of the PS filler induced more structural inhomogeneity, as shown in Fig. 2 (b) and (d), which were for FPAG10 and PAG10. Energy dispersive X-ray analysis (EDX) was performed for the white area and the dark area in Fig. 2. In this process, the amount of the crosslinking agent is negligible compared to those of the monomers and surfactant. The ratio of elements in each ingredient is different. The ratio of carbon to oxide is 3:1 for SDS, 3:2 for acrylic acid, and 8:0 for styrene. This ratio was 2.7:1 in the white area and 5.9:1 in the dark area (Fig. 3 (a) and (b)). Based on these results, it can be inferred that the abundant molecules were acrylic acid and SDS in the white area, and styrene and acrylic acid in the dark area.

The dangled poly(acrylic acid) chains with radicals from the network could enter the micelles. The acrylic acid molecules were already in the cores of the micelles owing to the high miscibility with water. Therefore, it can be surmised that these dangling poly(acrylic acid) radicals from the network entered the micelles and formed poly(acrylic acid) particles that were chemically bonded to the network chains. Dangling chains are elastically inactive part of network structure, which do not contribute a stress.[44] Loose, dangling chain ends, attached to the network by only one end are regarded as defects which tend to decrease the retractive stress.[45-48] However, the incorporation of a microemulsion of PS could make these chains contribute, especially if more than two dangling chains were involved with one particle so that those chains could not be dangled, and would be part of a network.

Position-dependent Swelling and Mechanical Properties

Q_v of the hydrogels were measured for 2 h. Four dried parts of each hydrogel, FPAG5, FPAG10, FPAG20, and PAG10, were consecutively placed in DI water, and the weights and densities were measured to obtain Q_v. During the swelling, G' and damping factor were also measured at 15, 30, 45, and 60% of Q_vs. This process was conducted for M and S in each sample. Results from two M and two S were averaged with standard deviation, respectively.
Q_v and G' of FPAG5 were plotted in Fig. 4 (a) for M and (c) for S, and damping factors were presented in Fig. 4 (b) for M and (d) for S. The slope of G' was found to elucidate the effect of Q_v on G'. Decreasing rate of G' was about 2.5 times faster in S than in M. Q_v was also increased faster in S. Damping factors in S were generally lower than in M. As the swelling was progressed, damping factors became lower, but it's not significant over 30% of Q_v.

The different results of swelling and mechanical properties in M and S were due to the inhomogeneity of hydrogel. This inhomogeneity is intimately related to the process of crosslinking polymerization.

In free radical crosslinking polymerization, many kinds of radicals are generated, and those are correlated to produce the three dimensional network. These radicals can be generally classified into three types – water-soluble linear oligomeric radicals in a pre-gelation period, radicals from the one large network chain in a gelation period, and trapped radicals isolated between the chains after the gelation.

Of those radicals, the trapped radicals generate the inhomogeneity of the hydrogels. It takes more time for these radicals to react with other radicals or to double bond in the limited space in the network, and

they produce a denser region. Because of the difference in densities, the water-uptake rate in those two regions is different. Adnadjevic et al.[49] reported three different shapes of swelling curves for poly(acrylic acid) hydrogels and formulated this behavior with several kinetic models, diffusion, first-order, and second-order chemical reactions. Their results showed that the application of each model to the swelling curve was limited to a certain part of the curve, and that the swelling behavior was not dependent on the shape of the hydrogel, but on the movement rate of the interface between water and hydrogel. Kannurpatti et al.[21] reported that using living radical polymerization could remove the trapped carbon radicals and that the homogeneity could be improved. The formation of dense regions was generally proportional to the concentration of the crosslinking agent.

Interestingly, in our conventional free radical crosslinking polymerization, the denser regions were not dispersed, but crowded in S than in M. It was speculated that the formation of lower structural inhomogeneity in M might be related to the experimental gelation process. When the gel was formed, the gel would push water outside. Side and bottom faces of a reactor were blocked, and water could be discharged only to the middle and upward, to the interface of air and solution. Due to the relatively higher concentration of solution, the network chains might be more flexible, and could increase the probability of radicals reacting with unreacted monomers or each other, and reduce the structural inhomogeneity after gelation in M and upper regions. However, the radicals in the upper side of the reactor are more deactivated due to the contamination of oxygen in air. Therefore, the inhomogeneity in M could be minimized. Furthermore, the radical polymerization generates the heat, and M as the most isolated region could be hottest in a reactor. This could accelerate the polymerization in M than in any other regions.

Network is formed with an appearance of one gigantic molecule in a reactor. To form this infinite molecule, both ends of one molecule must meet sides or bottom of a reactor, and those ends would be fixed. Tobita and Hamielec reported that gelation was first occurred at the lower part of a reactor during the formation of poly(acrylamide) hydrogel.[50] The polymerization was faster in the presence of a crosslinking agent at the pre-gelation period than in the linear polymerization.[50, 51] In other words, polymerization between monomer or oligomer, and crosslinking agent was progressed before the gelation. The lower section of a reactor after gelation was more diluted than its upper section in the conventional free radical crosslinking polymerization of acrylamide.[16] Therefore, it could be inferred that the gelation started from the wall of reactor, and network chains in those sections would be more rigid and in more dilute state. It might induce the inefficiency of crosslinking agent, and the higher inhomogeneity.

Durmaz and Okay reported the position-dependent elastic properties of poly(acrylamide) gel.[16] In their report, a cylindrical gel was divided into five parts, from top to bottom. The specimen at the top, the first neighbor to the liquid phase, was inhomogeneous due to the low crosslinking efficiency and slow polymerization. The lowest G' was observed from the bottom – 3000 pa, and the highest G' was from the middle – 5300 pa. G' was high in the order of, middle > top > bottom.

Q_v in M and S of FPAG5 were not much different. After 2 h swelling, Q_v was 88% in M, and 77% in S. This gap was decreased in FPAG10 as the more crosslinked FPAG, 67% in M, and 64% in S. For FPAG20, 65% in M, and 67% in S. In case of PAG10, Q_v increased much faster than that of FPAGs. Q_v of PAG10 was 197% in M, and 168% in S.

When compared FPAG10 and PAG10, the differences of Q_v in M and in S were 3% and 29%. In both cases, Q_v in M increased faster than in S. However, G' was decreased faster in S. The relationship between Q_v and G' could not be pinpointed, but it was surmised that in the beginning of swelling, there must be the effect of inefficiency of a crosslinking agent.

Hariharan el al. suggested the model that the swelling process could be influenced by the phase transition from a glassy to a rubbery state.[52] It was explained by the network's shear deformation changes affected by the constant stress which was induced by the interaction between the molecules of swelling medium and molecules of network chains. Little and Jovanovic et al. reported that in the first stage of swelling when the dried gel started to swell, water molecules were bound on the chains of dried gel, i.e. solvation of dried gel.[53, 54] The energy released from the solvation of dried gel was a source of faster motion of chain segments – separation of chains (highly elastic state) and chain stretching (rubbery state). At this time, the activation energy was corresponded to the energy of water adsorption on the gel surface which contain free (or ionized) hydrophilic groups such as –OH, -COOH, and –SO_4. Increase of activation energy was a consequence that the entropy increase of solvation complex formed on the interface between the dried gel and water.

Thus, the surface property of gel could affect its swelling property. MBAAm as a crosslinking agent has two –C=O groups between –N-H and –C=C- groups, but less hydrophilic than acrylic acid. On the surfaces of M and S, M has more acrylic acid having -COOH than S due to the crosslinking efficiency. This was thought to increase Q_v faster in M. In case of FPAG20, Q_v in S increased 2% faster at 2 h swelling, but it was in the error range, and the gap was not much different.

Damping factors were decreased with Q_v, but it was not significant over 30%. When the angular frequency was over 2.0, damping factors were stabilized. Damping factors appeared in the range of 0.13 to 0.15 for FPAG5 (Fig. 4 (b) and (d)), 0.12 to 0.16 for FPAG10 (Fig. 5 (b) and (d)), 0.08 to 0.13 for FPAG20 (Fig. 6 (b) and (d)), and 0.04 to 0.08 for PAG10 (Fig. 7 (b) and (d)). The maximum and minimum values to the frequency at each Q_v were presented in table 3.

As the Q_v is increased, G' is decreased. Decreased damping factor means that the loss modulus (G'') is decreased faster than G'. However, this behavior was observed until 30% swelling except for M of FPAG5 which was almost constant from 45% swelling. In other words, in the beginning of swelling, G'' was more affected by water diffusion into a gel. We thought this was due to the activation energy generated by interaction between water molecules and the surface of gel. When the surface was sweat by water (over 30% swelling), G' and G'' were decreased at the same rate.

G' of FPAG10 in Fig. 5 and PAG10 in Fig. 7 were compared to elucidate the effect of filler. To obtain the filler loading level, especially the volume fraction of PS in FPAG10, densities of equilibrium swollen gels were measured. With those densities, the density of dried gel was calculated from the equilibrium swollen ratio because the exact density value of dried gel could not be found experimentally. From the density of dried gel, PS fraction was obtained because the gel consisted of crosslinked poly(acrylic acid), PS, and SDS. Density of dried crosslinked poly(acrylic acid) was obtained from PAG10. For the density, PS was 1.05 g/cm^3, and SDS was 1.01g/cm^3.[55] It was assumed that the solubility of PS and SDS in water was negligible. This method could induce an overestimated value due to the existence of poly(acrylic acid) particles – the effect of lowering the density of gel. However, we derived the volume fraction of PS with the assumption that the conversion rate of acrylic acid was 100%, and the decreased monomer concentration to form the network due to the monomer consumption in particles could increase the density of gel. Density of PAG10 was higher than that of linear poly(acrylic acid). Thus, we thought those decreasing and increasing effects offset each other in a degree. When we followed above procedure, the volume fraction of PS was 35% in FPAG5, 36% in FPAG10, and 29% in FPAG20.

G' of FPAG10 was in the range of 23 kpa to 42 kpa (Fig. 5 (a) and (c)) up to 60% swelling. These values were about 40 times higher than those of PAG10 which were 710 pa to 1150 pa (Fig. 7 (a) and (c)). If filler particles were not chemically bonded to network chains, Q_v should be increased faster due to the sulfonic ions on the surface of fillers and also G' would not be higher.[39]

G' of FPAG5 was also in the range of 23 kpa to 43 kpa (Fig. 4 (a) and (c)) which was similar to that of FPAG10. In the crosslinking degree, FPAG10 was two times higher than FPAG5, but G' was not so different, whereas G' of FPAG20 which crosslinking degree was four times higher than FPAG5, was lower than G's of FPAG5 and FPAG10. G' of FPAG20 was observed in the range of 12 kpa to 28 kpa. The increasing effect of crosslinking degree on G' was insignificant in the filled samples at the early stage of swelling. Meanwhile, volume fraction of PS was more pronounced in the effect on G'.

The gap of G' in M and S was higher in FPAG5 than in FPAG10. At 15% swelling, it was 14 kpa for FPAG5, and 3 kpa for FPAG10. For M and S, decreasing slope of G' at 15 to 60% swelling was 2.5 times different in FPAG5, and 1.8 times different in FPAG10. Therefore, FPAG5 as the low crosslinked filled hydrogel was more inhomogeneous with the premise that volume fraction of PS was about 35%, same in both FPAG5 and FPAG10, and it was inferred that the large mesh size generated from the low concentration of a crosslinking agent induced the low dispersity of fillers.

From the results of analysis of swelling and G', it could be elucidated that a continuous poly(acrylic acid) hydrogel filled with PS was formed. The filler acted as a crystallite or a temporary crosslinking point where mechanically useless dangling chains were met, and increased effectively the mechanical properties of hydrogel.

CONCLUSIONS

Inhomogeneity of PS bead-filled poly(acrylic acid) hydrogel, and the reinforcement of mechanical properties by the incorporation of PS filler were studied. Microemulsion containing PS which polymerization was stop at 50% conversion was used as a media in the crosslinking polymerization of acrylic acid, in the presence of three different concentrations of a crosslinking agent. PS fillers including poly(acrylic acid) particles and empty micelles were successfully incorporated into the hydrogel and induced the enhanced mechanical properties, and the slowed swelling rates.

Our results indicated that in cases of FPAG10 and PAG10, the incorporation of PS filler successfully reinforced the mechanical properties, but the inhomogeneity was also increased. The higher inhomogeneity was observed in S than in M due to the inefficiency of a crosslinking agent and the rigidity of network chains in S and at the bottom of a reactor.

G' was decreased faster in S, and Q_v was increased faster in M, at the beginning of swelling. It was thought to be arisen from the higher inhomogeneity in S, and the more hydrophilic surface in M. Damping factors were decreased until Q_v reached to 30%. When Q_v was over 30%, damping factors were almost constant. Activation energy generated by the attractive interaction between water molecules and carboxyl groups of acrylic acid caused the faster decrease of G'' than G'. However, over 30% of Q_v, G'' and G' were decreased at the same rate, inducing the constant damping factors.
The degree of mechanical enforcement by the incorporation of PS filler was mainly determined by the volume fraction of PS. The effect of crosslinking degree on the mechanical properties in PS filled

hydrogel was insignificant. In the measurements of G' and Q_v for FPAG10 and PAG10, the incorporation of 36% PS filler resulted in the 40 times increase of G' at 15% of Q_v, and 33 times increase of G' at 30% Q_v.

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Table 1 Recipe of PAG10

	Water (g)	Acrylic acid (g)	MBAAm (g)	EDTA (g)	Ammonium persulfate (g)
PAG10	53	16	0.16	0.06	0.38

Table 2 Recipe of FPAGs

	Micro-emulsion[a](g)	Acrylic acid (g)	MBAAm (g)	EDTA (g)	Ammonium persulfate (g)
FPAG5	53	16	0.08	0.06	0.38
FPAG10	53	16	0.16	0.06	0.38
FPAG20	53	16	0.32	0.06	0.38

a) Microemulsion includes: water 44g, styrene 0.8g, polystyrene 0.8g, sodium dodecyl sulfate 4.9g, and 1-pentanol 2.1g

Table 3 Damping factors at high frequency (ω = 48.2, min) and low frequency (ω = 0.2, max) to Q_v

Q_v	FPAG5		FPAG10		FPAG20		PAG10	
	M	S	M	S	M	S	M	S
15% (Max)	0.28	0.18	0.19	0.18	0.17	0.15	0.17	0.11
15% (Min)	0.24	0.13	0.15	0.14	0.12	0.10	0.09	0.08
30% (Max)	0.21	0.17	0.16	0.17	0.13	0.12	0.11	0.11
30% (Min)	0.13	0.12	0.11	0.12	0.09	0.09	0.06	0.08
45% (Max)	0.19	0.16	0.18	0.15	0.12	0.11	0.09	0.10
45% (Min)	0.12	0.11	0.11	0.10	0.09	0.09	0.07	0.09
60% (Max)	0.19	0.16	0.16	0.15	0.11	0.11	0.09	0.06
60% (Min)	0.12	0.11	0.11	0.11	0.09	0.09	0.07	0.04

Fig. 1 Schematic illustration: measurements of swelling and shear modulus. Four specimen in a sample were cut and swollen in DI water. M1 and M2 were cut from the middle, and S1 and S2 were cut from the side of a hydrogel. At 15%, 30%, 45%, and 60% of Q_v, G' and damping factor were obtained with standard deviations.

Fig. 2 Field emission scanning electron micrographs (FE-SEM) of (a) FPAG5, (b) FPAG10, (c) FPAG20, and (d) PAG10.
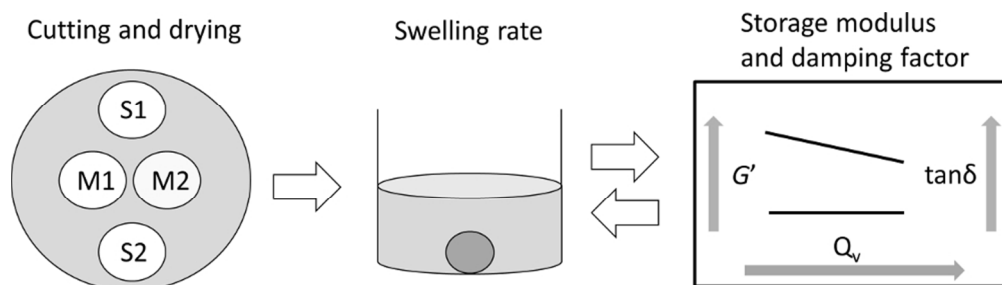
Fig. 3 Energy dispersive X-ray analysis (EDX) of (a) white region-rod element and (b) dark region-background in Fig. 2.

Fig. 4 Swelling and mechanical properties of FPAG5, (a) Q_v and G' in M, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in M, (c) Q_v and G' in S, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in S.
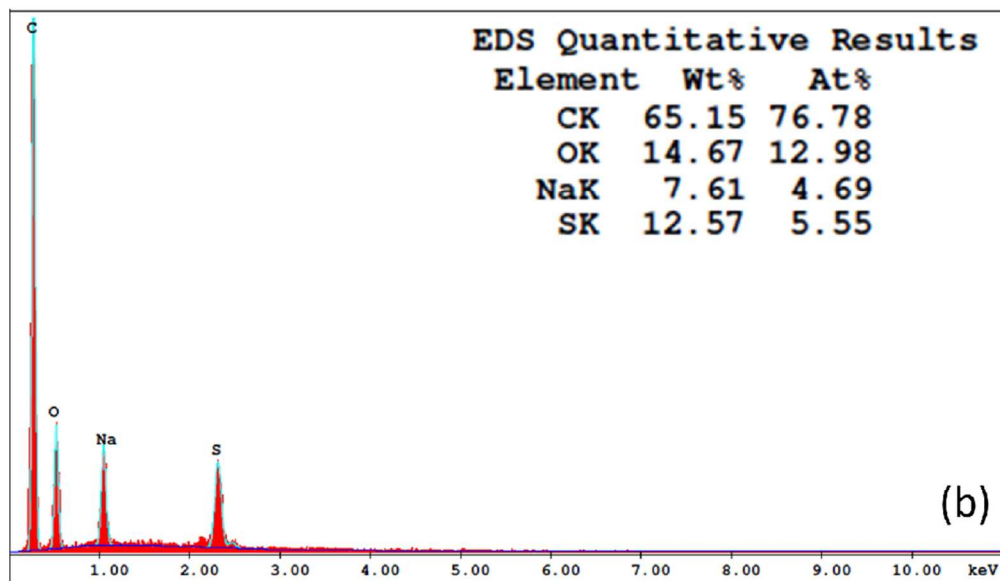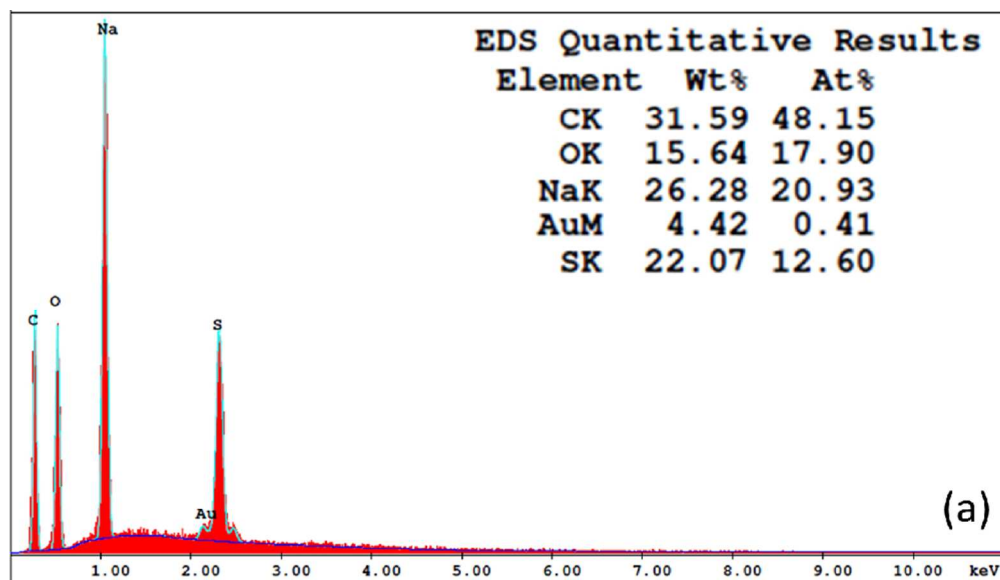
Fig. 5 Swelling and mechanical properties of FPAG10, (a) Q_v and G' in M, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in M, (c) Q_v and G' in S, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in S.

Fig. 6 Swelling and mechanical properties of FPAG20, (a) Q_v and G' in M, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in M, (c) Q_v and G' in S, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in S.

Fig. 7 Swelling and mechanical properties of PAG10, (a) Q_v and G' in M, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in M, (c) Q_v and G' in S, (b) Damping factors at (●) 15%, (□) 30%, (▲) 45%, and (▽) 60% of Q_v in S.

Cutting and drying

Swelling rate

Storage modulus
and damping factor

S1

M1 M2

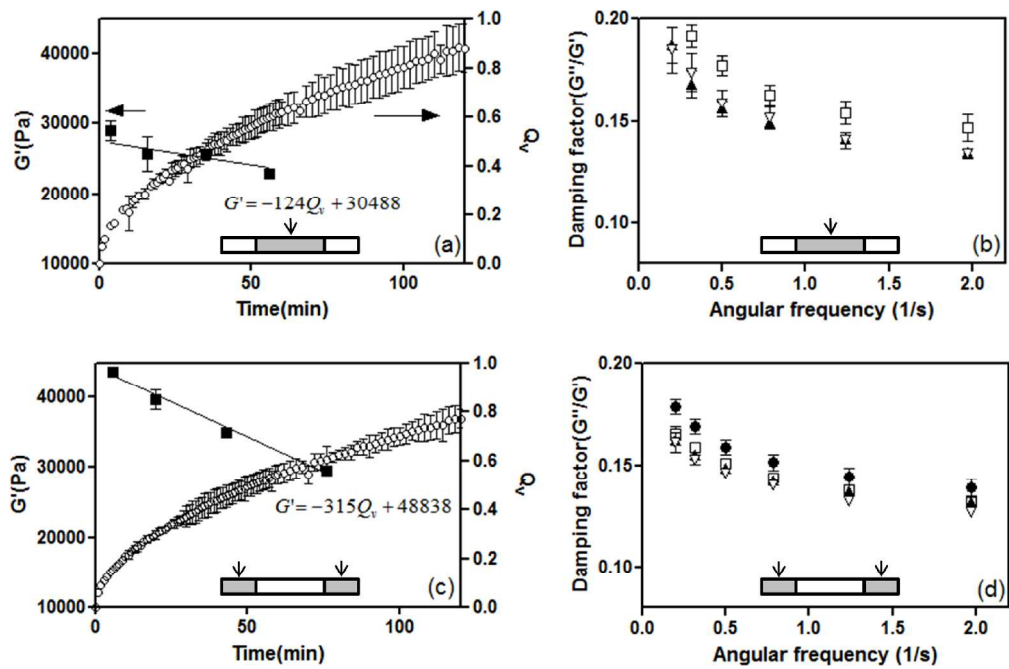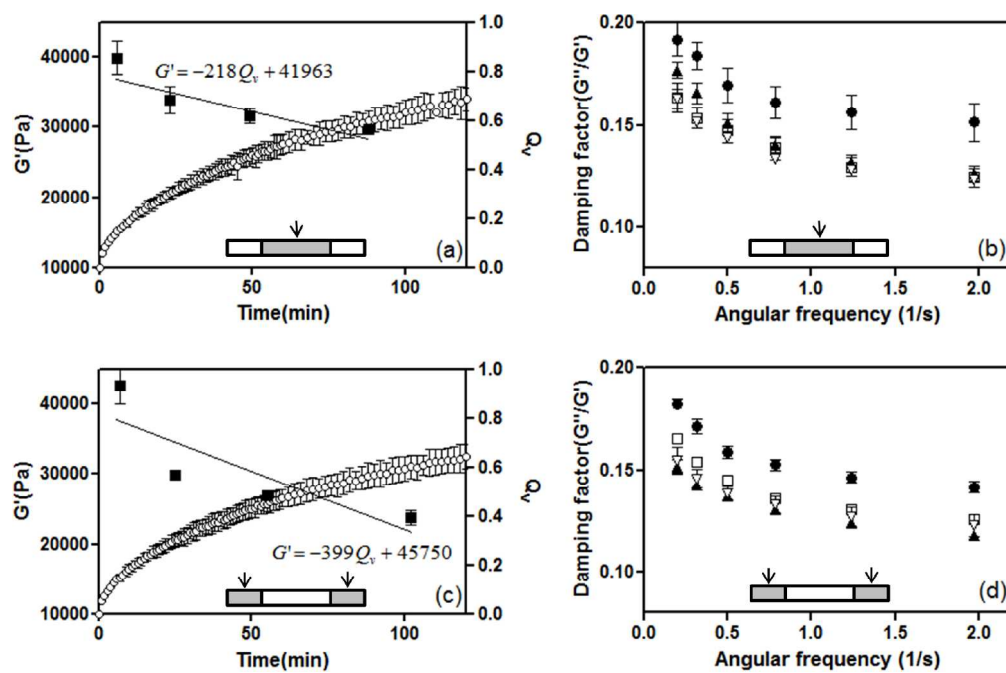S2

G'

$\tan\delta$

Q_v

84x23mm (300 x 300 DPI)
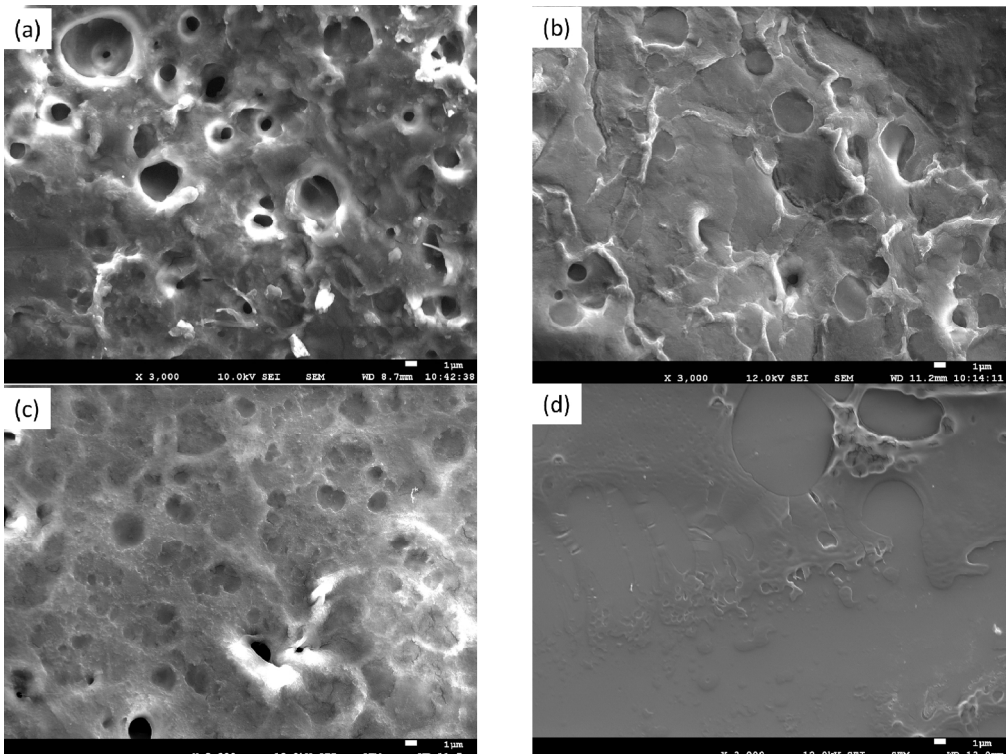
177x133mm (300 x 300 DPI)

84x101mm (300 x 300 DPI)

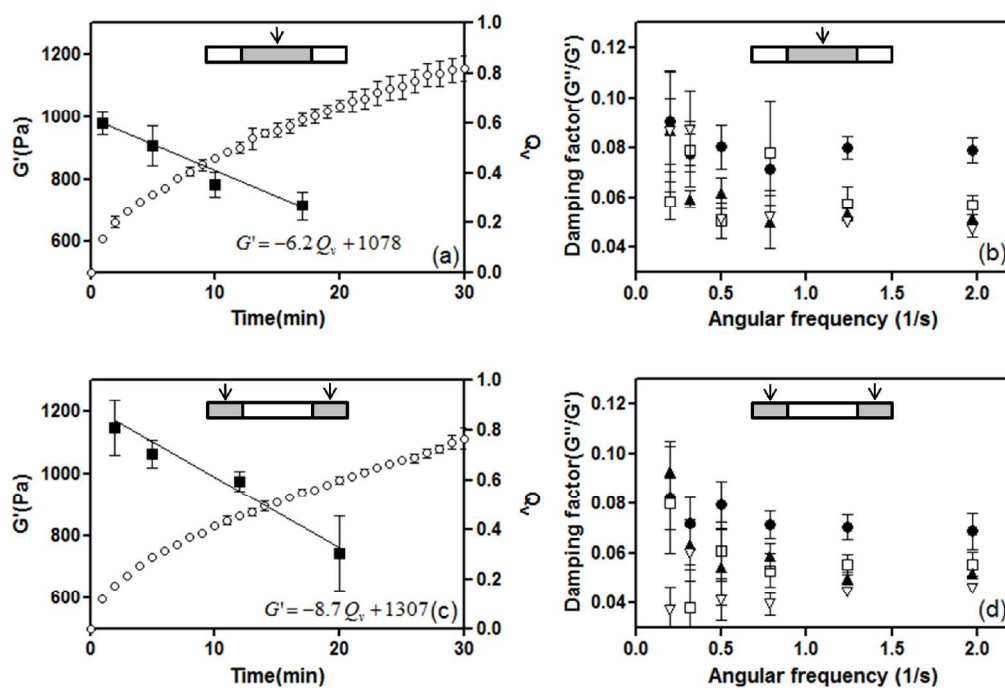177x116mm (300 x 300 DPI)

$G' = -218Q_v + 41963$

$G' = -399Q_v + 45750$

177x116mm (300 x 300 DPI)

177x119mm (300 x 300 DPI)

177x119mm (300 x 300 DPI)