Theoretical and Experimental Investigation of the Swelling Behavior of Sodium Polyacrylate Superabsorbent Particles

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ABSTRACT: Sodium polyacrylate superabsorbent polymers were prepared in particle forms by the inverse suspension technique. The surfactant concentration effect on the polymer particle size was analyzed with molecular sieves and an optical microscope. Water absorption and desorption characteristics were analyzed by the gravimetric method. The equilibrium water uptake in sodium polyacrylate particles was strongly dependent on both the salt concentration of the aqueous media and the crosslinking density of the polymers. The polymer crosslinking density was determined from the measurement of Young's modulus and the polymer–solvent interaction parameter from the equilibrium swelling experiment. The degree of ionization was predicted from experimental measurements, and theoretical analysis was performed on the effects of the salt concentration and polymer crosslinking density on the equilibrium water swelling ratio. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 252–257, 2003

Key words: hydrogels; crosslinking; swelling

INTRODUCTION

Superabsorbent polymers (SAPs) are hydrogels that absorb water at a hundred times their own volume. They are not dissolved but are swollen in water, as they are three-dimensionally crosslinked with hydrophilic functional groups such as alcohol, carboxylic acid, amine, and sulfuric acid.

Because starch-*g*-polyacrylate resins were reported by Weaver et al. in the 1980s to absorb a considerable amount of water, many researches have conducted studies on the preparation, characterization, and applications of acrylic polymers because they have been thought of as one of the most prospective materials in view of synthetic cost and properties.[1]

Hydrophilic polymers prepared in particle forms may have many applications because their large surface area imparts not only good dispersing efficiency in polymer compounding but also a high water absorption rate and content in polymer properties. Although SAPs have been abundantly used in the disposable diaper industry for the past 30 years, their applications are still being expanded to many fields including water-swellable rubbers, water-blocking tapes, soil additives, and so on.[2,3] The applications of SAPs for soil or artificial media have benefits in high water-holding capacity, soil nutrient reserves, and low soil compaction.[4,5]

In this study, sodium polyacrylate SAP particles, especially for soil-enriching applications, were prepared by the inverse suspension polymerization technique. Thermal, mechanical, and water absorption/desorption properties were characterized. Polymer crosslinking density (*n*), particle size, and saline concentration are major parameters of the dynamic and equilibrium water sorption behavior of SAP particles.[3,6–10] The polymer–solvent interaction parameter (χ) and the degree of ionization (*i*) were determined from equilibrium swelling behavior.

EXPERIMENTAL

Preparation of sodium polyacrylate particles

Sodium polyacrylate particles were prepared by the inverse suspension polymerization technique.[11–14] Acrylic acid (20.8 g) was mixed with distilled water (5.2 g), and then the mixture was neutralized with 35 g of 25.4 wt % sodium hydroxide aqueous solution so that the pH of neutralized polymer gels was 5.7.[2,13] After neutralization, *N,N'*-methylene bisacrylamide (Aldrich, St. Louis, MO) and potassium persulfate (Duksan Chemical, Hwasung, Korea) as the crosslinking agent and initiator, respectively, were added and completely dissolved to produce a homogeneous aqueous solution. The concentrations of crosslinking agent were 0.025, 0.04, 0.06, 0.08, and 0.1 wt %, respectively, and that of the initiator was 0.7 wt % monomer

solution. Amounts ranging from 0.83 to 3.14 g of surfactant composed of the same amounts of SPAN 60 (Daejung Chemical, Daegu, Korea) and ethyl cellulose (Junsei Chemical, Japan) were dissolved in 220 mL of cyclohexane (Daejung Chemical) at 60°C under mechanical agitation at 250 rpm. The aqueous solution prepared was poured in a cyclohexane solution with a dropping funnel. A free-radical polymerization reaction was conducted at 60°C for 2 h with mechanical agitation at the same rate under a nitrogen gas environment. The precipitated sodium polyacrylate particles were washed several times with methanol. The products were filtered and then dried in a vacuum oven at 60°C for at least 2 days.

Characterization

The size distribution of the prepared sodium polyacrylate particles was analyzed with standard testing sieves (models 20, 25, 35, 40, 45, 50, 60, 70, 80, 120, 140; Chunggye, Seoul, Korea) and with optical microscopy. Inductively coupled plasma atomic emission spectrometry (ARL Fisons 35 ICP-AES; Thermo Jarrell Ash) was used to analyze the sodium ion content in the synthesized polymers.

Thermal stability was analyzed with a thermogravimetric analyzer (PerkinElmer, TGA7, Wellesley, MA). To estimate the absorption amount of environmental humidity in the prepared hydrophilic polymers, two types of polymer samples were prepared: samples stored in the atmosphere and those stored in a desiccator after being dried in a vacuum oven at 100°C. TGA measurements were performed at a scanning rate of 10°C/min in the presence of nitrogen gas.

We prepared sodium polyacrylates in cylindrical forms to measure the mechanical properties. Neutralized monomer, crosslinking agent, and water were mixed in cylindrical tubes with diameters of 5 mm, and the polymerization reaction was conducted with the same conditions as mentioned previously. The polymer products were cut into cylindrical shapes 10 mm in length.[15] A universal tensile machine (Lloyd, LR10K, Hampshire, UK) was used to measure the Young's moduli (E) of polymer samples with different amounts of crosslinking agent. Static tensile stress (σ)–strain (α) curves were obtained at room temperature. In this tensile experiment, the load was 0.2537 N/m^2.

We conducted dynamic swelling experiments to investigate the swelling kinetics of the prepared SAP in saline water with different NaCl concentrations of 0.09, 0.4, 0.9, and 1.5 wt %. The water uptake in sodium polyacrylate was measured with tea bags.[7] Superabsorbent particles were put in bags. Each tea bag including polymer particles was placed in 100 mL of saline aqueous solution with mild agitation. The weight of the polymer-loaded tea bag was periodically

measured until no weight change was observed. The water uptake ratio (Q) was determined as the water absorption amount divided by the initial polymer weight, as in shown eq. (1a):[2]

$$Q = \frac{W_t - W_0}{W_0} \tag{1a}$$

where W_t and W_0 are the weights of polymer samples at time t and at the initial time, respectively. We determined the weight of water-absorbing polymer samples by subtracting the weight of water-swollen tea bags initially measured from weight of the polymer-containing tea bags measured at an arbitrary time.

The water desorption kinetics from SAP particles was also measured. The SAP particles were dispersed in typical soil (perlite:peatmoss = 1:1) to have a final concentration of 0.5 wt %. The soil, with or without SAP particles, was initially saturated with excess water, and each was started to weigh after 10 min. The total weight was measured periodically at room temperature until no weight change was observed.

Being analogous to Q in eq. (1a), the water desorption ratio (Q') was determined as the water desorption amount divided by the initial sample weight as in eq. (1b):

$$Q' = \frac{W_t' - W_0'}{W_0'} \tag{1b}$$

where W_t' and W_0' are weights of the samples at time t and the initial time, respectively.

In these absorption and desorption experiments, the same measurements were repeated three times for each sample. The average value was taken for the determination of water absorption and desorption amounts.

RESULTS AND DISCUSSION

Characterization of sodium polyacrylate particles

The surfactant concentration effect on the average size of the prepared SAP particles is shown in Figure 1. Particle diameters were from 10s to 100s of μm. The mean particle diameters reduced from about 170 to 94 μm with increasing surfactant content from 0.83 to 3.14 g in 220 mL of cyclohexane. This occurred because more micelles were formed and stabilized in their dispersion when more surfactants were involved. The particles were well established in spherical forms, and the concentration of sodium ion in the polymer resin was about 14 wt % from the ICP-AES measurement.

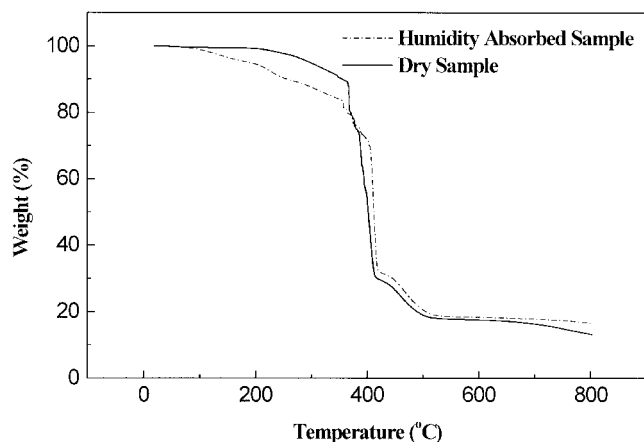Figure 2 shows the thermogravimetric analysis (TGA) of sodium polyacrylates. There was about 10%
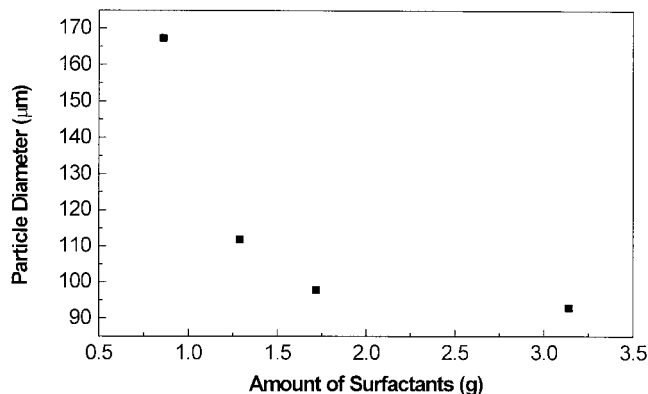
Figure 1 Effect of surfactant content on the average size of the prepared SAP particles.

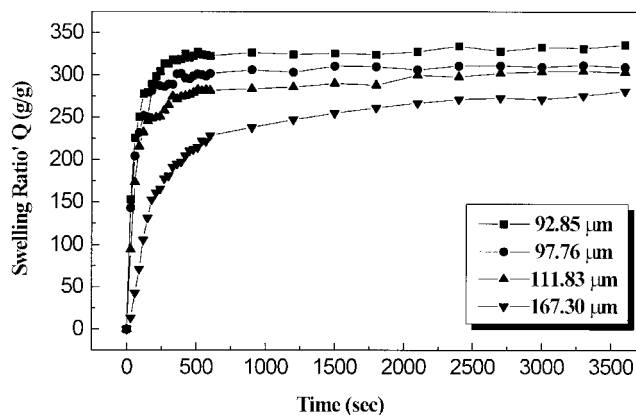**Figure 3** Particle-size dependence of the dynamic swelling behavior of sodium polyacrylate.

weight loss during heating to 200°C for the polymer samples stored in the atmosphere at room temperature. There was, however, no significant weight loss up to 200°C for those samples stored in the desiccator. Because of this result, the weight loss that occurred in the scan of the first samples was attributed to the presence of humidity absorbed or adsorbed in or on the polymer samples; there was no actual chemical degradation of polymer molecules up to 200°C.

Swelling properties of sodium polyacrylate particles

Figure 3 shows the particle-size dependence of the dynamic swelling behavior of sodium polyacrylate. The water absorption rate increased with decreasing particle size. Decreases in particle size led to increases in the surface area per unit of polymer mass, resulting in more rapid water adsorption on particle surfaces. As polymer particles were too fine to blot their surfaces dry, the particle size dependence of equilibrium water uptake showed a similar trend.

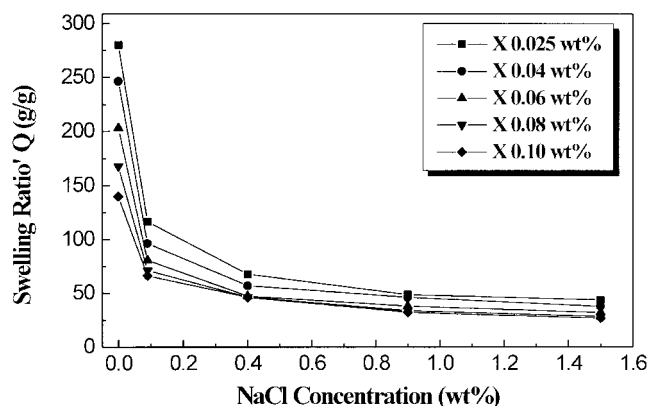Figure 4 shows the equilibrium swelling ratio of sodium polyacrylate particles in saline water. The equilibrium water uptake decreased for higher polymer crosslinking densities due to tighter network structures. The fixed charges on sodium polyacrylate polyelecrolyte gels led to an unequal distribution of mobile ion concentrations between the gel and solution phases, and this generated an ionic swelling pressure. Thus, the equilibrium water uptake decreased with increasing concentration in the external solution phase due to the decrease in the ionic swelling pressure.

Water desorption behavior of sap particles

Figure 5 shows the water desorption kinetics of SAP particles premixed with soil. The net amount of water initially absorbed in polymer-dispersed soil was 1.5–2 times higher than that in pure soil. A slightly higher initial water sorption was observed for soils with smaller SAP particles. The time to vaporize all water from soil was significantly affected by the presence of

Figure 2 TGA of sodium polyacrylates.

Figure 4 n effect on the equilibrium swelling ratio of sodium polyacrylate particles in saline water.
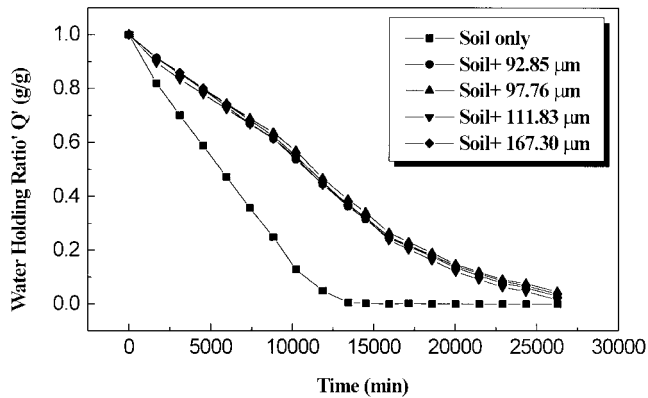
Figure 5 Water desorption kinetics of SAP particles pre-mixed with soil.

SAP particles. About 27,000 min were required for SAP-incorporated soils, but only 12,500 min were required for pure soil. The particle-size effect on the water-releasing kinetics from SAP-loaded soils was negligible compared with the water-releasing kinetics from pure soil.

Mechanical properties and molecular weight between crosslinks ($\overline{M}_c$)

Figure 6 shows the E of sodium polyacrylates with different amounts of crosslinking agent. E increased from 0.21 to 0.88 MPa with increasing crosslinking agent concentration (X) from 0.025 to 0.1 wt %.

The theory of rubber elasticity gives the following relationship between the polymer n and E. The relationship between σ and α ($= L/L_0$) for the swollen polymer sample is given by eq. (2):[16,17]
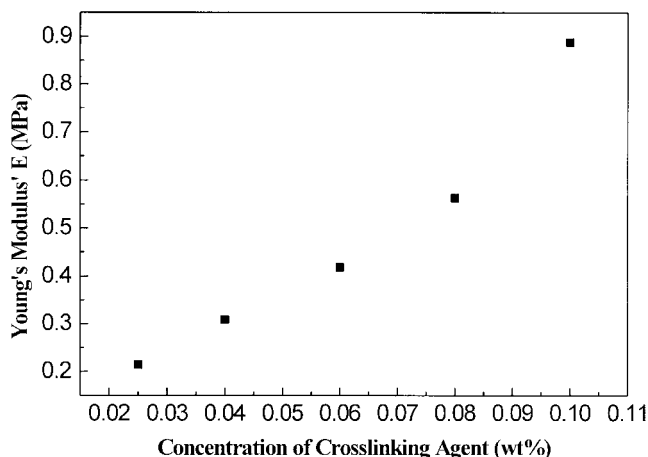
Figure 6 E of sodium polyacrylates with different amounts of crosslinking agent.

TABLE I
Crosslinking Density and Molecular Weight Between Crosslinks for the Prepared Sodium Polyacrylate Polymers

X (wt %)	n (gmol/cm^3) $\times 10^{-4}$	$\overline{M}_c$ (g/gmol) $\times 10^4$
0.025	0.257	3.925
0.04	0.442	2.728
0.06	0.498	2.012
0.08	0.807	1.493
0.10	1.269	0.946

$$\sigma = \left(\frac{\partial F}{\partial \alpha}\right)_{T.V} = n'RT\,\frac{\overline{r_i^2}}{\overline{r_0^2}}\left(\alpha - \frac{1}{\alpha^2}\right) \quad (2)$$

where F is Gibbs free energy; L and L_0 are the sample lengths at the extension and initial states, respectively; R is the gas constant; T is the temperature; and n' is the effective number of moles in the network (v_e) per unit volume of the polymer in the initial state (V_i).

For small σ ($\alpha \cong 1$), E is given by eq. (3):

$$E = L\left(\frac{\partial \sigma}{\partial L}\right)_{T.V} = n'RT\,\frac{\overline{r_i^2}}{\overline{r_0^2}}\left(2\alpha^2 + \frac{1}{\alpha}\right) \cong 3n'\,\frac{\overline{r_i^2}}{\overline{r_0^2}}RT \quad (3)$$

The front factor ($\overline{r_i^2}/\overline{r_0^2}$) in eq. (3) indicates the ratio of the mean square radius of gyration of swollen to dry polymers, and thus, its value is the same as $(V_i/V_0)^{2/3}$. In this case, eq. (3) can be described in terms of the effective moles of moles in the network per unit volume of the dry polymer, n ($= \rho/\overline{M}_c = v_e/V_0$) and the polymer volume fraction of the initially swollen sample ($v_2^0 = V_0/V_i$). ρ indicates the density of polymer sample.

n ($= v_e/V_0$) and $\overline{M}_c$ of each polymer sample were determined from the E data in Figure 6 and eq. (3). The resulting values of n and $\overline{M}_c$ are represented in Table I. The value of $\overline{M}_c$ decreased from 3.925×10^4 to 0.946×10^4 g/gmol with increasing X from 0.025 to 0.1 wt %.

χ and i

At equilibrium, the chemical potentials of water (μ_1) in the gel and solution phases are the same , and thus, the total osmotic pressure (π), the summation of all osmotic pressures contributing to the system, is zero as in eq. (5):[17–22]

$$\Delta\mu_1^g = \Delta\mu_1^s \quad (4)$$

$$\pi = \pi_{\mathrm{mix}} + \pi_{\mathrm{el}} + \pi_{\mathrm{ion}} = \frac{-\Delta\mu_1^g + \Delta\mu_1^s}{V_1} = 0 \quad (5)$$

where V_1 is the molar volume of the solvent. The osmotic pressures associated with mixing, elastic, and ionic contributions (π_{mix}, π_{el}, and π_{ion}, respectively) are given by eqs. (6), (7), and (8), respectively:

$$\pi_{mix} = -\frac{RT}{V_1}(\ln(1 - v_2) + v_2 + x_1 v_2^2) \quad (6)$$

$$\pi_{el} = -RT(\nu_e/V_0)\left(v_2^{1/3} v_2^{0\,2/3} - \frac{v_2}{2}\right) \quad (7)$$

$$\pi_{ion} = RT \sum_i (c_i^g - c_i^s) = RT[ic_2/z_+ - \nu(c_s^* - c_s)] \quad (8)$$

where v_2 is the volume fraction of the polymer; c_i^g and c_i^s are the mobile ion concentrations inside the gel and bulk solution, respectively; i is the degree of ionization multiplied by the valency of the anionic group attached to the polymer chain; c_2 is the polymer concentration ($= v_2/V_u$, where V_u is the molar volume of the polymer); $c_s^* - c_s$ is the difference in mobile electrolyte concentrations between inside and outside the gel; ν ($= \nu^+ + \nu^-$) is the number of total ions into which the given electrolyte dissociates; and z_+ is the valency of the cation.

When c_s^* is much smaller than ic_2, as for this experiment, substitution of eqs. (6), (7), and (8) in eq. (5) results in eq. (9):

$$\ln(1 - v_2) + v_2 + x_1 v_2^2 + V_1(\nu_e/V_0)\left(v_2^{1/3} v_2^{0\,2/3} - \frac{v_2}{2}\right)$$
$$- V_1(iv_2/z_+ V_u) = 0 \quad (9)$$

In a very dilute solution concentration, a very large ionic osmotic pressure develops, causing a very small v_2.

The χ was determined from the equilibrium swelling behavior of nonionized poly(acrylic acid). In this case, the relationship between the equilibrium swelling ratio and n is described by eq. (10), where no ionic term is present:

$$\ln(1 - v_2) + v_2 + x_1 v_2^2 + V_1(\nu_e/V_0)\left(v_2^{1/3} v_2^{0\,2/3} - \frac{v_2}{2}\right) = 0$$
$$(10)$$

The equilibrium volume fraction of poly(acrylic acid) in distilled water was measured and illustrated in Table II. Incorporation of the values of n from Table I and v_2 in eq. (10) led to the determination of χ, as shown in Table II. The resulting value was around 0.6,

TABLE II
Polymer Solvent Interaction Parameter and Degree of Ionization for the Prepared Sodium Polyacrylate Polymers

X (wt %)	χ	i
0.025	0.586	0.108
0.04	0.589	0.142
0.06	0.600	0.169
0.08	0.607	0.207
0.10	0.620	0.280

and the value slightly increased with increasing polymer n.

By introducing all parameters, n ($= v_e/V_0$), χ, v_2, and so on, determined so far to eq. (9), we obtained i for each sample. Its value increased from 0.1 to 0.3 with increasing polymer n, as shown in Table II. In its calculation, ρ was 1.22 g/cm^3, and V_u and V_1 were 72.06 and 18 g/gmol, respectively.[23] The value of v_2^0 was set to be 1, as no water was present in the initial swelling experiment.

CONCLUSIONS

Sodium polyacrylate SAPs were synthesized in particle forms with the inverse suspension polymerization method. The mean diameter of the prepared polymer particles decreased from 170 to 94 μm as the surfactant amount increased from 0.83 to 3.14 g in 220 mL of cyclohexane. The equilibrium swelling ratio of polymer particles in water decreased not only with saline concentration but also with polymer n. The equilibrium swelling ratio of polymers increased with decreasing particle sizes due to increasing polymer surface areas. The water desorption rate increased slightly with decreasing particle size for the same reason. n was obtained from Es of polyacrylate gels. χ was determined from equilibrium sorption data, and its value was around 0.6. From all calculated parameters, i was determined. Its value increased from 0.1 to 0.3 with increasing polymer n.

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