

Synthesis of AA-Based Superabsorbent Interpenetrated with Sodium PVA Sulfate

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ABSTRACT: An interpenetrating network of acrylic acid (AA)-based superabsorbents and sodium PVA sulfate (SPS) were prepared by copolymerizing AA and *N,N'*-methylene bisacrylamide as a crosslinking monomer in a solution of SPS with KPS, a radical initiator. The SPS was prepared through the sulfation of the hydroxyl groups of PVA with DMF-SO₃ complex in DMSO. The AA-based superabsorbent interpenetrated with SPS (SA-IP-SPS) showed superior properties such as higher water and saline absorbency, absorbency under load (AUL), and water retention value (WRV) compared with AA-based superabsorbent due to the interpenetrated SPS. The maximum water and saline absorbency of SA-IP-SPS was 1753 and 125.6 g/g, respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2525–2532, 2000

Key words: AA; *N,N'*-methylene bisacrylamide; DMF-SO₃ complex; sodium PVA sulfate; superabsorbent; absorbency

INTRODUCTION

Superabsorbents can absorb tremendous amounts of water without dissolving in water, because superabsorbents have three-dimensional structures with considerable amount of hydrophilic groups.¹ They are used in various areas such as agriculture, hygiene, food, and cosmetics. Among the recently developed superabsorbents, acrylic acid (AA)-based superabsorbents have been extensively studied because AA is cheap and easily polymerized to a high molecular weight polymer. Various methods for the preparation of AA-based superabsorbents have been reported in the literature.^{2–8}

Philippova et al.⁹ synthesized polyacrylamide hydrogels with trapped polyelectrolyte rods. The incorporation of polyelectrolyte rods in the poly-

acrylamide network imparted useful properties to the hydrogel. They reported that it enhanced the swelling and mechanical properties of the hydrogel. However, as the polyelectrolyte rods were merely physically entrapped in the hydrogel network, diffusion of polyelectrolyte rods into the surrounding solution was possible, resulting in decreased absorbency. It appears that their idea can be applied in the preparation of superabsorbent if the loss of polyelectrolyte rods can be reduced. The immobilization of the polyelectrolyte can be achieved by increasing the crosslinking density or by using a long-chain polyelectrolyte, in which case entanglements with the superabsorbent network can inhibit its diffusion. The latter was considered more promising, because the entangled long-chain polyelectrolyte should also increase the absorbency by enhancing the degree of swelling, while increasing the crosslinking density will decrease its absorbency.

In this work, we prepared AA-based superabsorbents interpenetrated with high molecular

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weight sodium PVA sulfate (SA-IP-SPS) by solution polymerization. The polymerization conditions, absorbency, and other properties of SA-IP-SPSs were investigated.

EXPERIMENTAL

Materials

Acrylic acid (AA, Aldrich Chemical Co., Inc., Milwaukee, WI) was distilled twice in vacuum and stored in a refrigerator. Potassium persulfate (KPS, Kanto Chemical Co., Inc., Tokyo, Japan) was recrystallized from water and *N,N'*-methylene bisacrylamide (MBA, Kanto Chemical Co., Inc., Tokyo, Japan) was recrystallized from methanol. PVA (Aldrich Chemical Co., Inc., Milwaukee, WI), dimethylformamide (DMF, Duksan Pharmaceutical Co., Ltd., KyongKido, Korea), dimethylsulfoxide (DMSO, Duksan Pharmaceutical Co., Ltd., KyongKido, Korea), sulfuric acid fuming 65% SO₃ (Merck, Darmstadt, Germany), and other reagents were used as received without further purification.

Preparation of Sodium PVA Sulfate (SPS)

A DMF-SO₃ complex was prepared according to Schweiger's method.¹⁰ A γ -type sulfur trioxide, obtained by heating sulfuric acid fuming 65% SO₃ at 45°C, was dissolved in cold DMF to prepare a DMF-SO₃ complex, whose composition was 1 g SO₃/10 mL DMF-SO₃ complex. The prepared DMF-SO₃ complex was stored in a refrigerator.

PVA of four different molecular weights were used in the preparation of SPS. Their average molecular weights were 19,000, 42,000, 90,000, and 152,000, respectively. A PVA solution prepared by dissolving 4-g PVA in 100 mL DMSO at 50°C was placed in a four-neck flask equipped with a mechanical stirrer, dropping funnel, thermometer, and a calcium chloride tube. The PVA solution was then cooled to 5°C in an ice bath. To prepare PVA sulfate, 290 mL of DMF-SO₃ complex (4 mol of SO₃ per OH of PVA) was then added to the PVA solution and stirred for 2 h at 5°C. The product was precipitated in acetone, then dissolved in distilled water and neutralized with NaOH solution to prepare SPS. The prepared SPS was dewatered with methanol, milled with a grinder, and dried in vacuum at 50°C for 2 days. The degree of substitution (DS) was 0.45–0.47 in all SPSs.

Preparation of Superabsorbent

Copolymerization of AA and MBA was carried out in a solution of SPS with KPS, a radical initiator. The reaction mixture was prepared by pouring a mixture of 5 g of AA (6.94×10^{-2} mol) and 20 mL of a SPS solution (prepared from 90,000 *M_w* PVA, unless otherwise specified) into a 50-mL vial and partially neutralizing with NaOH solution in an ice bath to a degree of neutralization of 40%. The reactant mixture was stirred with a magnetic stirrer during neutralization. KPS and MBA were then added to the mixture, and purged with a slow stream of nitrogen for 30 min to remove dissolved oxygen. The vial was sealed, and immersed in a oil bath fixed at a temperature in the range 50–100°C for the series of samples in which the effect of polymerization temperature was studied, and at 70°C for the series in which the effect of amount of initiator and crosslinking monomer were studied. Stirring was continued with the magnetic stirrer until the reaction mixture became viscous and gelled. The gel point was taken to be the time at which the stirrer stopped. The reaction product was immersed in methanol and stirred for 3 h to remove water. The dewatered product was then stirred in 70 vol % aqueous methanol solution for 24 h to remove water-soluble materials and then stirred in methanol for 3 h to remove water. It was milled with a grinder and dried in vacuum at 65°C for 2 days.

For the purpose of comparison, the AA-based superabsorbent without interpenetrated SPS (SA) was prepared under similar conditions but without SPS.

Water Absorbency Using Filtration Method

Approximately 20–30 mg of dried superabsorbents with average particle sizes of 215 μ m were dispersed in 60 mL of distilled water for 30 min. Then, excess water was allowed to drain through a 300-mesh wire gauze. The weight of the superabsorbent containing absorbed water was measured after draining for 1 h, and the water absorbency was calculated according to the following equation.

$$\text{Absorbency (g/g)} = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W_1 and W_2 are the weight of dry and swollen superabsorbent, respectively.

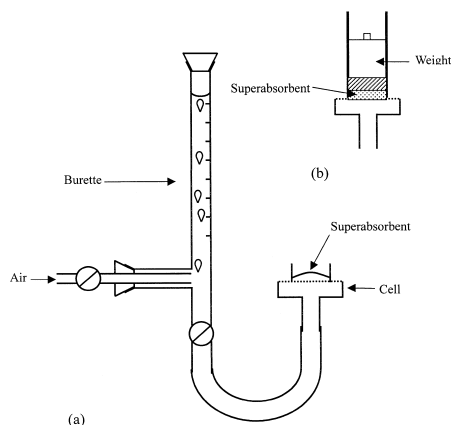


Figure 1 Demand wettability test apparatus and piston assembly.

Saline Absorbency Using Filtration Method

Approximately 30–40 mg of dried superabsorbents with average particle sizes of 215 μm were dispersed in 40 mL of 0.9 wt % NaCl solution for 30 min. Then, excess solution was allowed to drain through a 300-mesh wire gauze. The weight of the superabsorbent containing absorbed saline solution was measured after draining for 1 h, and the saline absorbency was calculated according to the above eq. (1).

Water Retention Value (WRV)

Approximately 20–30 mg of dried superabsorbents with average particle sizes of 215 μm were dispersed in 60 mL of distilled water for 30 min. The swollen particles were placed on a 300-mesh wire gauze fixed in centrifuge tubes, then centrifuged for 30 min at 700 G, unless otherwise specified, weighed, and WRV was calculated using the above eq. (1).

Absorbency and Absorbency under Load (AUL) by Demand Wettability (DW) Method

Absorbency using DW method was measured by DW test apparatus.¹¹ A graduated burette with an air inlet at the bottom was linked by a flexible tube to a cell covered with a metallic grid (250 mesh). After filling with water, the burette was sealed at the top and air was introduced while the superabsorbent absorbed water. Approximately 50–60 mg of dried superabsorbents with average particle sizes of 215 μm was placed on the grid, and the amount of absorbed water was measured

at intervals of 5 s. The apparatus of DW test is shown in Figure 1(a).

AUL was measured using a DW test apparatus with a piston assembly allowing addition of weights on top of the superabsorbent sample. The method is similar to the DW test, but measures the absorptive property under load. The piston assembly is shown in Figure 1(b).

The absorbency and absorbency under load by demand wettability method were calculated according to eq. (1)

IR Analysis

MIDAC M series FTIR spectrometer (MIDAC Co.) was used for IR analysis of KBr pellets.

Thermogravimetric Analysis

Thermogravimetric analysis was conducted with a Seiko Thermal Analysis System SSC 5200.

Degree of Substitution (DS) from Sulfur Content Analysis

The sulfur content of SPS was determined by the combustion flask method.¹² The DS of SPS was calculated from the sulfur content using the following equation.

$$DS = \frac{44 \times S}{3200 - 102 \times S} \quad (2)$$

where S is sulfur content (%) of SPS.

Absorbency of Solutions of Various pH

Absorbency of solutions of various pH was measured using the filtration method. The pH values of the solution to be absorbed were adjusted by adding HCl or NaOH solutions in water.

Absorbency of Aqueous Methanol Solution

The absorbency of aqueous methanol solution of different concentrations was measured using the filtration method.

RESULTS AND DISCUSSION

Preparation of SA-IP-SPS

The copolymerization of AA and crosslinking monomer was performed in a solution of SPS to incorporate SPS in a polyacrylic acid (PAA) net-

Table I The Polymerization Conditions and Conversions of AA Monomers

Reaction No.	Reaction Temp. (°C)	KPS ($\times 10^{-5}$ mol)	MBA ($\times 10^{-5}$ mol)	Conversion (%)
1	50	6.94	6.48	74.2
2	60	6.94	6.48	79.5
3	70	6.94	6.48	88.4
4	80	6.94	6.48	84.5
5	90	6.94	6.48	81.2
6	100	6.94	6.48	76.4
7	70	1.38	6.48	69.8
8	70	4.16	6.48	78.2
9	70	6.94	6.48	88.4
10	70	10.41	6.48	84.9
11	70	13.80	6.48	82.0
12	70	17.35	6.48	78.2
13	70	6.94	1.29	85.4
14	70	6.94	3.88	87.8
15	70	6.94	6.48	88.4
16	70	6.94	9.72	88.1
17	70	6.94	12.96	87.7

The other polymerization conditions: AA, 5 g; SPS 0.1 g.

work. As a result, an interpenetrating network in which SPS chains are entangled with the crosslinked PAA could be obtained. The conversion of AA ranged from 70 to 88% within the range of experimental conditions studied (Table I). Because 0.1 g SPS and 5 g AA was employed in the polymerization, the weight % of SPS in the final superabsorbent was approximately 2.2–2.8%.

In the IR spectra of SPS and SA-IP-SPS shown in Figures 2 and 3, respectively, a band due to S=O stretching can be observed at 1247 cm^{-1} , verifying the synthesis of SPS and the existence of SPS in the superabsorbent network. This S=O stretching peak did not appear in PVA and SA.

The thermal degradation behaviors of SPS, SA, SA-IP-SPS, and a physical mixture of SA and SPS were investigated by thermogravimetric analysis. In the thermograms illustrated in Figure 4, SPS shows significant weight loss at around 150°C and this behavior is reflected in the thermogram of the physical mixture of SA and SPS in the range of $150\text{--}400^\circ\text{C}$. However, the thermogram of SA-IP-SPS showed less weight loss compared with SA in the range of $150\text{--}400^\circ\text{C}$. This may be attributed to interaction between SPS and PAA network in the case of SA-IP-SPS.

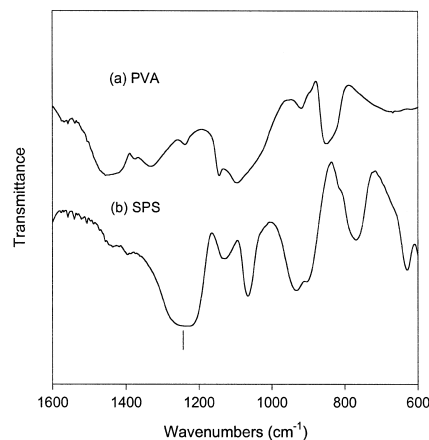


Figure 2 IR spectra of PVA and SPS. PVA: average $M_w = 90,000$. SPS: prepared from M_w 90,000 PVA, DS = 0.46.

Effect of Polymerization Conditions on Absorbency

In this work, we carried out solution copolymerization of AA and MBA using a radical initiator KPS. Figure 5 shows the relationship between the reaction temperature and the absorbency of SA-IP-SPS. The optimal reaction temperature in our system was 70°C .

Figure 6 shows the relationship between the amount of initiator and the absorbency of SA-IP-SPS. The absorbency increased with initiator concentration up to 6.94×10^{-5} mol of KPS, then dropped, probably due to greater probability of termination reactions.

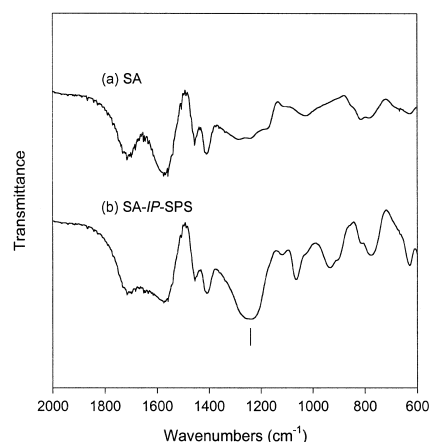


Figure 3 IR spectra of SA and SA-IP-SPS. SA polymerization conditions: AA, 5 g; MBA, 6.48×10^{-5} mol; KPS, 6.94×10^{-5} mol; reaction temperature, 70°C . SA-IP-SPS polymerization conditions: AA, 5 g; SPS, 0.1 g; MBA, 6.48×10^{-5} mol; KPS, 6.94×10^{-5} mol; reaction temperature, 70°C .

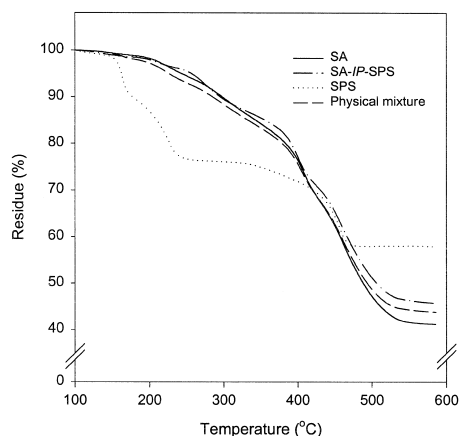


Figure 4 TGA curves of SPS, SA-IP-SPS, SA and a physical mixture of SA and SPS. SPS: same as in Figure 2. SA: same as in Figure 3. SA-IP-SPS: same as in Figure 3. Physical mixture of SA and SPS: weight ratio = 5 : 0.1.

Superabsorbents absorb water by the expansion of hydrophilic chains due to their charge repulsion. This expansion stops when the expansion force is equal to the elastic force of network.¹ This indicates that the absorbency is influenced by network structure as well as by hydrophilic groups. The amount of crosslinking monomer has a profound effect on network structure. Figure 7 shows the effect of the amount of crosslinking monomer on absorbency and WRV of SA-IP-SPS. As the amount of crosslinking monomer decreased, water absorbency increased due to a decrease in crosslinking density of the superabsorbent.

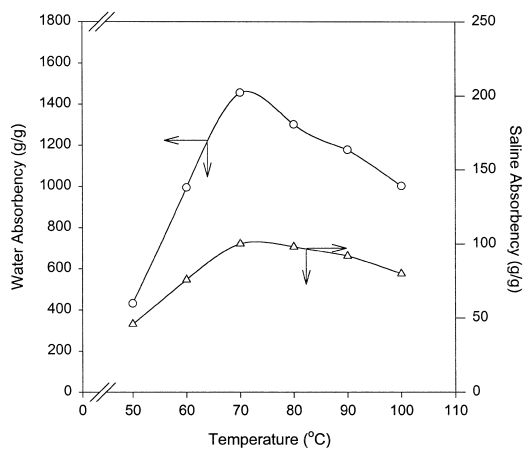


Figure 5 Relationship between the reaction temperature and absorbency. Polymerization conditions: AA, 5 g; MBA, 6.48×10^{-5} mol; SPS, 0.1 g; KPS, 6.94×10^{-5} mol.

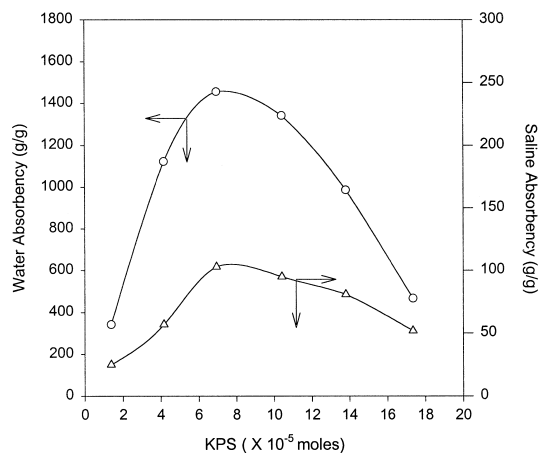


Figure 6 Relationship between the amount of initiator and absorbency. Polymerization conditions: AA, 5 g; MBA, 6.48×10^{-5} mol; SPS, 0.1 g; reaction temperature, 70°C.

However, in the lower range of the amount of crosslinking monomer, WRV decreased with a decrease in the amount of crosslinking monomer employed. The decrease in crosslinking points results in increased swelling capacity, allowing higher water absorption in the filtration method. But the highly swollen superabsorbent with lower crosslinking density may lose larger amounts of absorbed water due to the centrifugal force in WRV method. The large loss of absorbed water resulted in the decrease in WRV when less crosslinking monomer were used. Saline absorbency showed similar behavior with WRV.

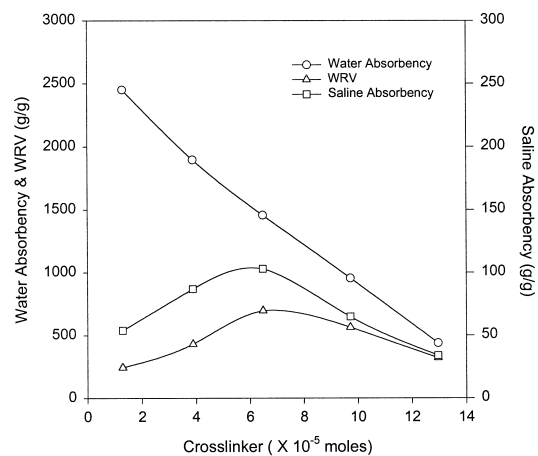


Figure 7 Effect of the amount of crosslinking monomer on absorbency and WRV. Polymerization conditions: AA, 5 g; KPS, 6.94×10^{-5} mol; SPS, 0.1 g; reaction temperature, 70°C.

Table II Absorbency of Superabsorbents Prepared from Different Molecular Weight SPS

Sample Code	Average M_w of PVA	SPS Used in Polymerization (g)	Conversion of AA (%)	SPS Content in Product (%) ^a	Water Absorbency (g/g)	Saline Absorbency (g/g)
SA	—	0	88.9	—	1192	78.0
SA-IP-SPS(1)	19,000	0.3	87.3	6.4	1243	105.0
SA-IP-SPS(4)	42,000	0.3	86.5	6.5	1345	115.2
SA-IP-SPS(9)-1	90,000	0.1	88.4	2.2	1457	100.3
SA-IP-SPS(9)-2	90,000	0.2	87.7	4.4	1621	118.1
SA-IP-SPS(9)-3	90,000	0.3	87.3	6.4	1753	125.6
SA-IP-SPS(9)-4	90,000	0.4	86.5	8.5	1671	120.0
SA-IP-SPS(9)-5	90,000	0.5	86.1	10.4	1590	119.0
SA-IP-SPS(9)-6	90,000	0.6	85.3	12.3	1271	115.2
SA-IP-SPS(9)-7	90,000	0.7	84.0	14.3	1010	112.7
SA-IP-SPS(15)	152,000	0.3	84.2	6.7	988	92.2

^a Calculated from conversion of AA.

Polymerization conditions: AA, 5 g; MBA, 6.48×10^{-5} mol; KPS, 6.94×10^{-5} mol; reaction temperature, 70°C.

Effect of SPS on the Absorbency and Other Properties of Superabsorbent

It is well known that the absorbency of superabsorbent is induced by the electrostatic repulsion of the ionic charges of its network.¹ The interpenetrating SPS in the PAA network can enhance the absorbency by increasing the ionic charge content of the superabsorbent. The relationship between the amount of SPS and the absorbency of SA-IP-SPSs is shown in Table II. The water and saline absorbency increased up to 0.3 g of SPS due to increased ionic charge content of the superabsorbent, then decreased. This may be attributed to the increase in the number of physical crosslinks, due to the entanglement between SPS and PAA network, which decreases the swelling capacity.¹³

It appears that there are two roles of SPS in the water absorption of SA-IP-SPS. The first role is to increase the ionic charge content of the superabsorbent, and the second role may possibly be chain expansion, which can promote the expansion of the PAA network. As the molecular weight of SPS increases, the second role may become more important as the degree of expansion of SPS will increase with its molecular weight. The effect of the molecular weight of PVA used in the preparation of SPS on the absorbency of SA-IP-SPSs is also shown in Table II. The water and saline absorbency increased with the molecular weight of PVA up to 90,000, probably due to the increase in the expansion of SPS, then decreased. The decrease may be attributed to the increase in interpolymer complexes between SPS and PAA

network, probably due to the entanglement effect.¹³

For the comparison of water retention power, we used WRV method. The WRV and weight of water lost by swollen superabsorbents on centrifuging at different centrifugal forces are shown in Figure 8. SA-IP-SPS(9)-3 showed larger WRV than SA, and similar behavior in weight loss of absorbed water. This indicates that SA-IP-SPS not only exhibits higher absorbency but also better water retention.

DW absorbency of SA and SA-IP-SPSs prepared with different molecular weight SPSs are shown in Figure 9. SA-IP-SPSs showed larger

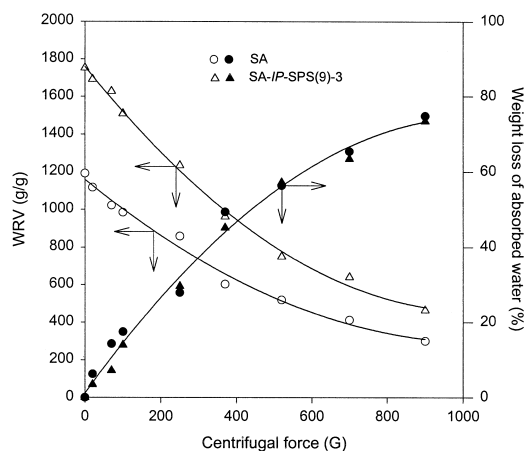


Figure 8 Variation in WRV and weight loss of absorbed water of SA-IP-SPS(9)-3 and SA with centrifugal force.

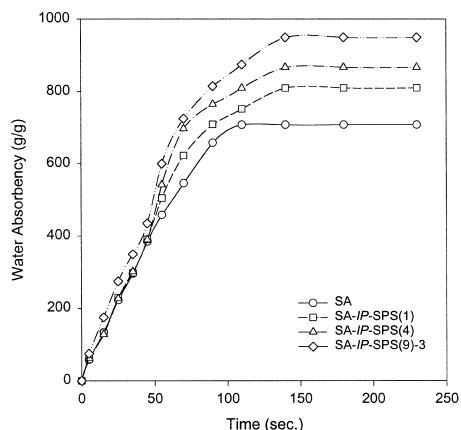


Figure 9 Absorbency of SA-IP-SPSs and SA using DW method.

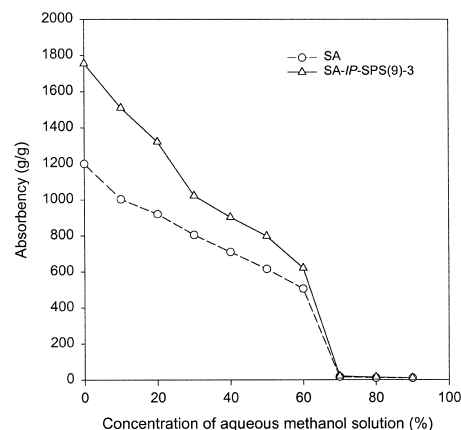


Figure 11 Gel phase-transition of SA-IP-SPS(9)-3 and SA with the concentration of methanol in water.

equilibrium absorbency than SA, and the equilibrium absorbency of SA-IP-SPSs increased with the molecular weight of SPS.

AUL is an important factor in the practical application of superabsorbents. The absorbencies measured under different loads are shown in Figure 10. The difference of AUL between SA-IP-SPS(9)-3 and SA became larger with increase in load. It appears that the interpenetrating SPS in SA-IP-SPS increases the swelling force.

Since Tanaka¹⁴ reported on the gel phase-transitions of saponified polyacrylamide gels caused by an acetone-water mixture and of saponified starch-*g*-polyacrylonitrile superabsorbent in a water-alcohol system, many scientists have studied the gel phase transition of hydrogels and superabsorbents. Figure 11 shows the gel phase transitions of SA and SA-IP-SPS brought about

by the change in the concentration of aqueous methanol. Gel phase transition behavior of SA-IP-SPS in aqueous methanol solution is similar to that of SA. Figure 12 shows the variation of absorbency as the pH of the solution varies from 1 to 13. In the pH region from 5 to 9, the absorbency of SA roughly maintained a constant. This may be attributed to the buffer action of the carboxylate groups with an acid or base.⁶ The absorbency decreased rapidly from pH 5 to 1 and from pH 9 to 13, implying that the buffer action has disappeared. However, the buffer action was not shown in SA-IP-SPS, probably due to the sulfate groups with high degree of ionization in SPS.

The possibility of loss of SPS chains from SA-IP-SPS by its diffusion in the dewatering process after polymerization or swelling was studied by comparing the sulfur contents of dried SA-IP-

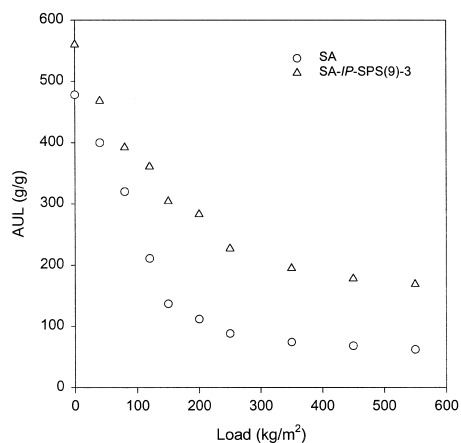


Figure 10 Absorbency under load (AUL) of SA and SA-IP-SPS(9)-3.

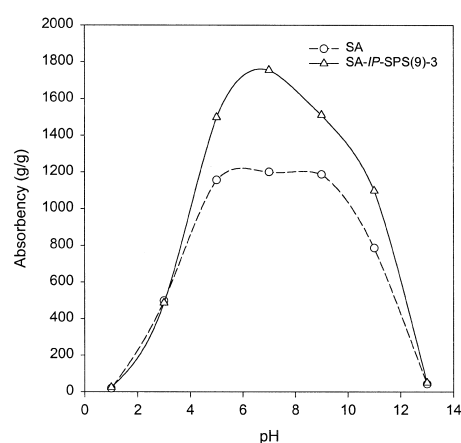


Figure 12 Absorbency of SA-IP-SPS(9)-3 and SA with the pH of external solution.

Table III Determination of SPS Loss from Sulfur Content Measurement

Sample Code	Theoretical Sulfur Content (%)	Experimental Sulfur Content (%)	
		Before Swelling ^a	After Swelling ^b
SA-IP-SPS(9)-1	0.6	0.6	0.7
SA-IP-SPS(9)-4	2.2	2.1	2.2
SA-IP-SPS(9)-6	3.7	3.6	3.5

^a Sulfur content was measured with the prepared SA-IP-SPS.

^b Swollen SA-IP-SPS was dewatered with methanol, dried, and its sulfur content was measured.

SPS. The possible release during dewatering process was investigated by measuring the sulfur content of prepared SA-IP-SPS. To investigate the possible release during swelling, swollen SA-IP-SPS was filtered, dewatered with methanol, and dried in vacuum at 50°C for 24 h, then its sulfur content was measured. The results are shown in Table III. Experimental values of sulfur content are similar to the theoretical values, indicating that SPS chains have been sufficiently immobilized by forming an interpenetrating network.

CONCLUSIONS

SA-IP-SPS was prepared by copolymerizing AA, and *N,N'*-methylene bisacrylamide in SPS solution with KPS and its polymerization conditions

and absorbency were investigated. The SA-IP-SPS showed larger water and saline absorbency, AUL, and WRV than SA, due to the SPS introduced in the superabsorbent network, and the release of interpenetrated SPS was negligible. The gel phase transition of SA-IP-SPS with the concentration of aqueous methanol solution was similar to SA. The absorbency of SA-IP-SPS in solutions of various pH did not show the buffer action due to the sulfate groups in SPS.

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