

Synthesis of acrylic acid-based superabsorbent interpenetrated with sodium PVA sulfate using inverse-emulsion polymerization

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Abstract

Acrylic acid (AA)-based superabsorbent interpenetrated with sodium poly(vinyl alcohol) (PVA) sulfate (SPS) was prepared by inverse-emulsion polymerization. The disperse phase was prepared by dissolving AA and crosslinking monomer in aqueous SPS solution. Toluene was used as the continuous phase in which oil-soluble initiator and emulsifiers were dissolved. Sorbitan monooleate and ethyl cellulose were used as emulsifiers. The maximum water and saline absorbencies were 5041 and 211.4 g/g, respectively. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

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. Many investigators prepared modified AA-based superabsorbents to enhance absorbency [1–6]. In our previous studies, AA-based superabsorbent interpenetrated with sodium poly(vinyl alcohol) (PVA) sulfate (SA-IP-SPS) prepared by solution polymerization method showed higher water and saline absorbency than AA-based superabsorbent due to higher ionic charge content and ionic strength.

Although the main method for synthesis of AA-based superabsorbent is solution polymerization, the method has some disadvantages when it is applied to the preparation of SA-IP-SPS. The extreme solution viscosity generated by the high molecular weight SPS

leads to problems such as the difficulties in stirring and heat transfer. These problems may be overcome by inverse-suspension or -emulsion polymerization [7–9]. An important advantage of the inverse-emulsion polymerization of AA-based superabsorbent is the easier heat dissipation and lower viscosity. Moreover, the polymerization may occur at a higher rate to yield a high molecular weight polymer.

In this article, AA-based superabsorbent interpenetrated with SPS was prepared by inverse-emulsion polymerization technique using sorbitan monooleate as the microstructure emulsifier and ethyl cellulose as the polymeric emulsifier. The polymerization conditions and their effects on the absorbency of the synthesized superabsorbents were investigated.

2. Experimental

2.1. Materials

Acrylic acid (AA, Aldrich Chemical Co., Inc.) was distilled twice in vacuum and stored in a refrigerator.

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Azobisisobutyronitrile (AIBN, Junsei Chemical Co., Ltd.) and *N,N'*-methylene bisacrylamide (MBA, Kanto Chemical Co., Inc.) were recrystallized from methanol. Toluene was distilled and purged with nitrogen to remove oxygen. Deionized water was boiled under nitrogen atmosphere and then cooled. Sorbitan monooleate (Span 80, Aldrich Chemical Co., Inc.), ethyl cellulose (Aldrich Chemical Co., Inc.), poly(vinyl alcohol) (PVA, Aldrich Chemical Co., Inc.), dimethylformamide (DMF, Duksan Pharmaceutical Co., Ltd.), dimethylsulfoxide (DMSO, Duksan Pharmaceutical Co., Ltd.), 65% SO₃ fuming sulfuric acid (Merck), and other reagents were used as received without further purification.

2.2. Preparation of sodium PVA sulfate

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

Four PVAs of 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-necked 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 moles 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 sodium PVA sulfate (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 calculated from the sulfur content which was measured by the combustion flask method [11]. The DS was 0.45–0.47 in all SPSs.

2.3. Preparation of superabsorbents

A predetermined amount of 7.5 N NaOH solution was added dropwise to the stirred aqueous AA solution in a 50 ml beaker cooled with an ice bath for partial neutralization. The crosslinking monomer, MBA, was dissolved in the above AA solution. The monomer solution was then added to the SPS solution in a 50 ml vial with nitrogen bubbling until a clear mixture was obtained which was used as the disperse phase. Toluene used as the continuous phase, in which a mixture of the emulsifier Span 80 and ethyl cellulose (weight ratio 10:1) was dissolved, was poured into a four-necked flask fitted

with a mechanical stirrer, thermometer, dropping funnel and a reflux condenser. The disperse phase containing the monomer and SPS was carefully added dropwise to the continuous phase while stirring with a propeller type stirrer at 500 rpm to form an emulsion. Purified nitrogen was bubbled at room temperature through the emulsion for about 20 min to eliminate oxygen. Temperature was equilibrated at 50–90°C in a thermal oil bath. AIBN initiator dissolved in toluene was then added and the reaction mass was stirred for 1 h. The product was then poured into methanol to remove water. The dewatered product was immersed in a methanol–toluene mixture (weight ratio 7:3) and stirred for 24 h to remove emulsifiers and initiator, and finally dispersed in methanol for 3 h. The product particles were filtered and dried in vacuum at 65°C for 2 days. The detailed polymerization conditions are shown in Table 1.

An FT-IR spectrometer (MIDAC Co.) was used for IR analysis, and morphology of superabsorbent particles was observed on a JEOL-JSM 35C scanning electron microscope (SEM) after gold coating.

2.4. Water absorbency using filtration method

Approximately 20–30 mg of dried superabsorbents with an average particle size of 215 μ m were dispersed in 60 ml of deionized 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 the dry and swollen superabsorbent, respectively.

Table 1
Polymerization conditions of SA-IP-SPS

AA concentration (wt.%) (based on the weight of the disperse phase)	25
DN (%)	20–100
SPS concentration (wt.%) (based on the weight of the disperse phase)	0.25–2.5
Initiator concentration (wt.%) (based on toluene)	0.19–0.44
Crosslinker concentration (wt.%) (based on the weight of the disperse phase)	0.2–0.6
Polymerization temperature (°C)	50–90
Emulsifier (Span 80/ethyl cellulose, 10:1 weight ratio) concentration (wt.%) (based on toluene)	0.63–6.25
Weight ratio of toluene and disperse phase	4:1

2.5. Saline absorbency using filtration method

Approximately 30–40 mg of dried superabsorbents with an average particle size 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 Eq. (1).

2.6. Water retention value

Approximately 20–30 mg of dried superabsorbents with an average particle size of 215 μm were dispersed in 60 ml of deionized 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 water retention value (WRV) was calculated using Eq. (1).

2.7. Absorbency under load

Absorbency under load (AUL) was measured using a demand wettability (DW) test apparatus with a piston assembly allowing addition of weights on top of the superabsorbent sample. The apparatus is shown in Fig. 1. The method is similar to the DW test but measures the absorptive property under load [12]. 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 under load, and the amount of absorbed water was measured at intervals of 5 s. AUL was calculated using Eq. (1).

3. Results and discussion

The copolymerization of AA and crosslinking monomer was performed in a solution of SPS to incorporate

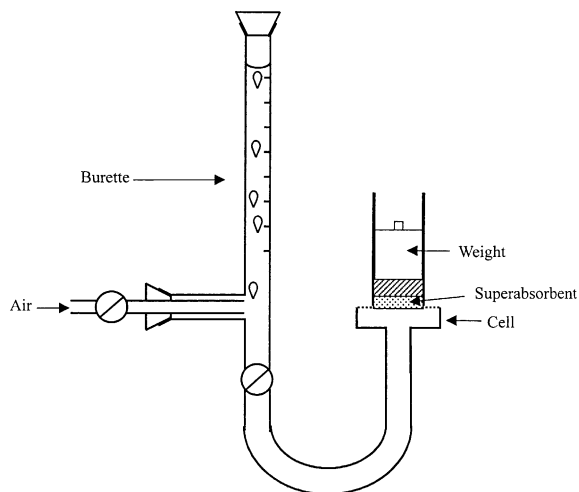


Fig. 1. AUL test apparatus.

SPS in a polyacrylic acid (PAA) network. As a result, an interpenetrating network in which SPS chains are entangled with the crosslinked PAA could be obtained. The interpenetrating network of SA-IP-SPS is illustrated in Fig. 2. The conversion of AA ranged from 90% to 93% within the range of experimental conditions studied.

IR spectra of PVA and SPS are shown in Fig. 3. A band due to S=O stretching can be observed at 1247 cm^{-1} , verifying the synthesis of SPS. This band can also be observed in IR spectrum of SA-IP-SPS shown in Fig. 4, verifying the existence of SPS in the superabsorbent network. This S=O stretching peak did not appear in PVA and AA-based superabsorbent without SPS (SA).

Fig. 5 represents the micrographs of the particles of SA-IP-SPS. Fig. 5(a) is the SEM micrograph of ground SA-IP-SPS prepared without the polymeric emulsifier, ethyl cellulose. Flocculation of the synthesized SA-IP-SPS can be observed. This flocculation could be prevented by using ethyl cellulose as a polymeric emulsifier, as can be seen in the SEM micrograph of SA-IP-SPS shown in Fig. 5(b). In our experiment, coemulsifiers of sorbitan monooleate and ethyl cellulose were used.

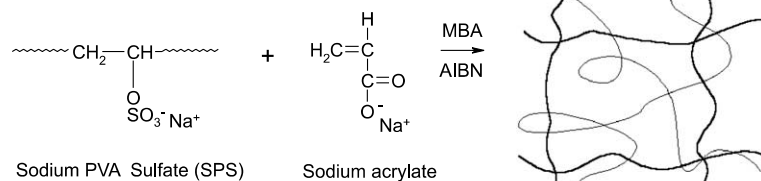


Fig. 2. The interpenetrating network of SA-IP-SPS.

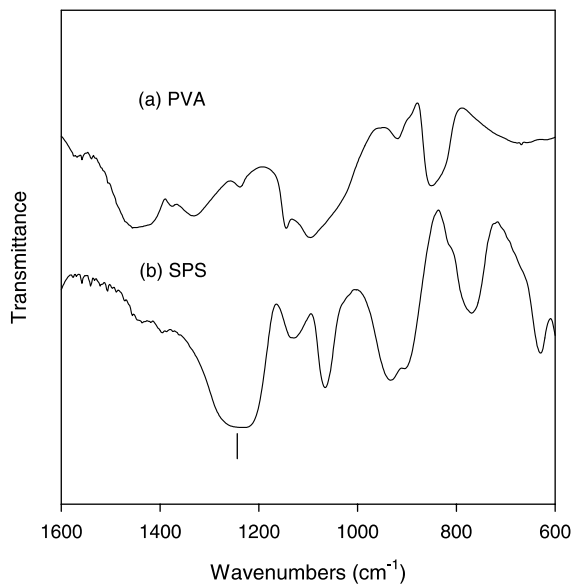


Fig. 3. IR spectra of PVA and SPS.

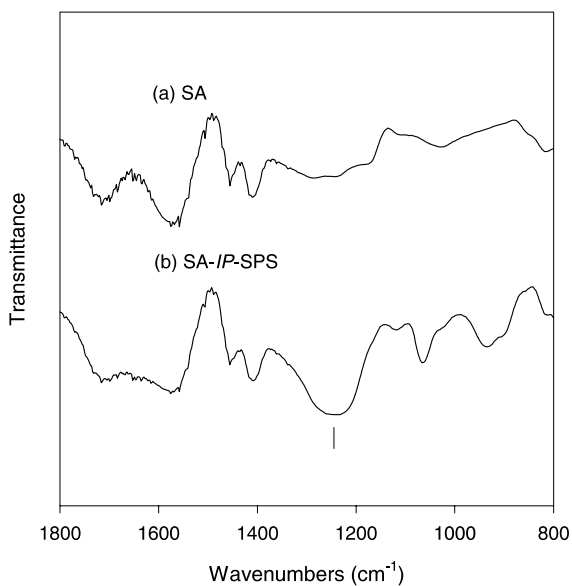


Fig. 4. IR spectra of SA and SA-IP-SPS.

3.1. Effect of polymerization conditions on absorbency

SPS prepared from PVA of molecular weight 90,000 was used in the experiments to investigate the effect of polymerization conditions on absorbency.

Fig. 6 shows the effect of degree of neutralization (DN) of the PAA on absorbency. The water absorbency increased with the increase in DN when DN is less than 70%. The absorbency decreased with the increase in DN

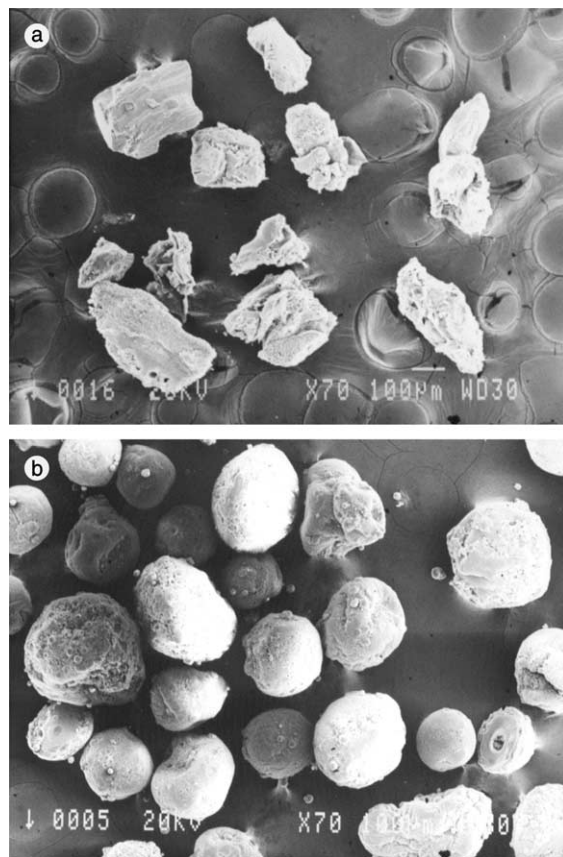


Fig. 5. Scanning electron micrograph of (a) ground SA-IP-SPS prepared without ethyl cellulose and (b) SA-IP-SPS prepared with ethyl cellulose.

when DN is higher than 70%. According to Flory [13], ionic networks swell extensively due to the ionic charges of networks. The neutralized PAA network has negatively charged carboxyl groups which tend to expand the network due to the electrostatic repulsion. The electrostatic repulsion increases with the increase in DN, then decreases. This may be attributed to the screening effect of carboxyl groups with excess sodium ions [14]. Therefore, there exists an optimum DN of PAA in the preparation of AA-based superabsorbents. In our system, a DN of 70% was optimal according to the absorbency results.

Chen and Zhao [14] reported that the increase of chain ends in AA-based superabsorbent is the reason for the increased absorbency with increasing initiator concentration and polymerization temperature. It is well known that the degree of polymerization decreases with increase in initiator concentration and polymerization temperature, due to the increase in termination and chain transfer rate [15]. The decrease in degree of polymerization brings about the increase in chain ends. The

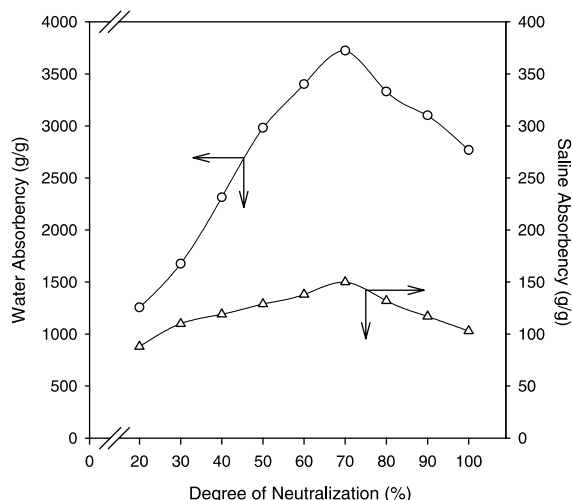


Fig. 6. Effect of DN on absorbency. Polymerization temperature: 70°C, crosslinker concentration: 0.4 wt.%, initiator concentration: 0.25 wt.%, SPS concentration: 1.0 wt.%, emulsifier concentration: 2.5 wt.%.

increase in chain ends may be the reason for the increase in absorbency to the maximum value in Figs. 7 and 8. However, further increase in AIBN concentration and polymerization temperature above the optimum values is accompanied by a decrease in absorbency. This may be attributed to the decrease in the swelling capacity resulting from the decrease in molecular weight. Liu and Rempel [5] studied the effect of polymerization

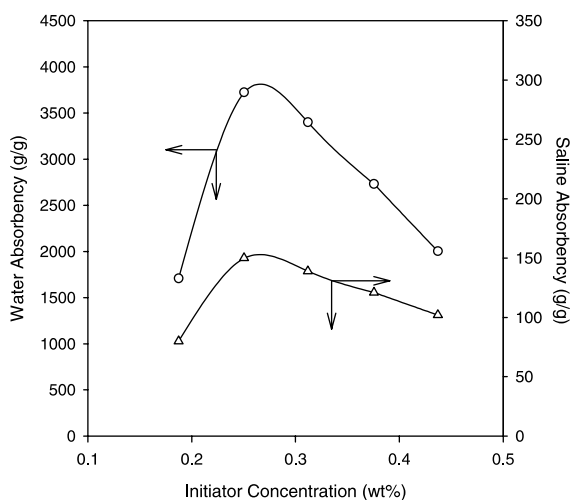


Fig. 7. Effect of initiator concentration on absorbency. DN: 70%, polymerization temperature: 70°C, crosslinker concentration: 0.4 wt.%, SPS concentration: 1.0 wt.%, emulsifier concentration: 2.5 wt.%.

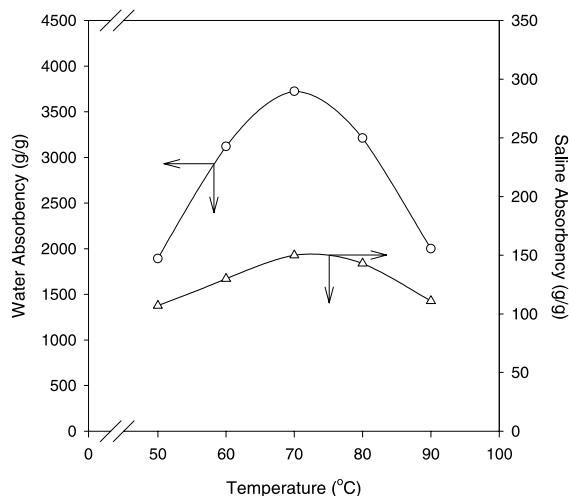


Fig. 8. Effect of polymerization temperature on absorbency. DN: 70%, crosslinker concentration: 0.4 wt.%, initiator concentration: 0.25 wt.%, SPS concentration: 1.0 wt.%, emulsifier concentration: 2.5 wt.%.

temperature on the absorbency of AA and acrylamide copolymer superabsorbent and found the absorbency to decrease with increasing polymerization temperature. They attributed it to the decrease in swelling capacity resulting from a decrease in molecular weight. The increase in chain ends may contribute to some extent but the excess number of chain ends does not contribute to absorbency because the decrease in molecular weight decreases the swelling capacity.

The relationship between the absorbency and network structure parameters was investigated by Flory and given as the following equation [13]:

$$q_m^{5/3} = \frac{[(\frac{1}{2} \frac{i}{v_u} \frac{1}{S^{*1/2}})^2 + (\frac{1}{2} - x)/V_1]}{(v/V_0)} \quad (2)$$

where q_m is the equilibrium swelling ratio, v/V_0 is the number of effectively crosslinked chains in unit volume, S^* is the ionic strength of the swollen liquid, i/v_u is the concentration of fixed charge referred to the unswollen networks, x is the polymer–solvent thermodynamic interaction parameter, V_1 is the molar volume of water. This relationship may be applied to SA-IP-SPS, because the interpenetrating SPS may be considered as a part of the network. S^* , i/v_u , x , and V_1 is constant when the absorbed liquid is fixed. Therefore, v/V_0 is the only factor that can influence the absorbency. The factor (v/V_0) in Eq. (2) expresses the crosslinking density. Therefore, higher concentration of crosslinkers may result in a decrease in absorbency. Fig. 9 shows the relationship between the amount of MBA and absorbency.

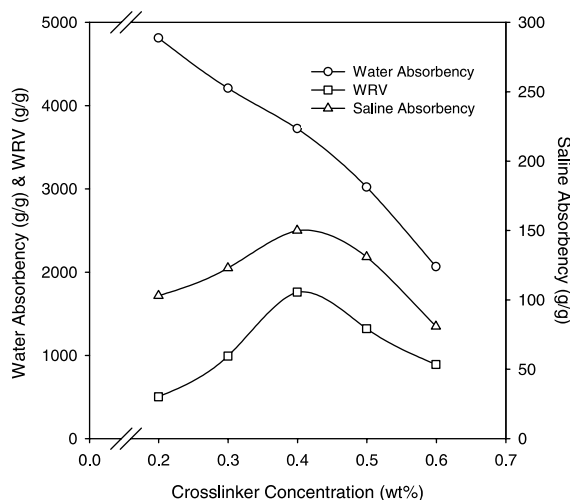


Fig. 9. Effect of crosslinker concentration on absorbency. DN: 70%, polymerization temperature: 70°C, initiator concentration: 0.25 wt.%, SPS concentration: 1.0 wt.%, emulsifier concentration: 2.5 wt.%.

As MBA concentration decreased, water absorbency increased due to a decrease in crosslinking density of the superabsorbent. However, in the lower range of the amount of introduced crosslinking monomer, WRV decreased with a decrease in the concentration of MBA. 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.

The relationship between emulsifier concentration and absorbency is shown in Fig. 10. The absorbency increased with an increase in emulsifiers concentration and reached a maximum at 5 wt.%.

3.2. Effect of SPS on absorbency

It is well known that the absorbency of superabsorbent is enhanced by the electrostatic repulsion of the ionic charges of its network [13]. The interpenetrated SPS in the PAA network can enhance the absorbency by increasing ionizability and the ionic charge content of the superabsorbent. The relationship between SPS (prepared from 90,000 M_w PVA) concentration and absorbency is shown in Fig. 11. The water and saline absorbency increased with increasing SPS concentration and reached a maximum at 2 wt.%. However, with further increase beyond 2 wt.%, absorbency decreased. This

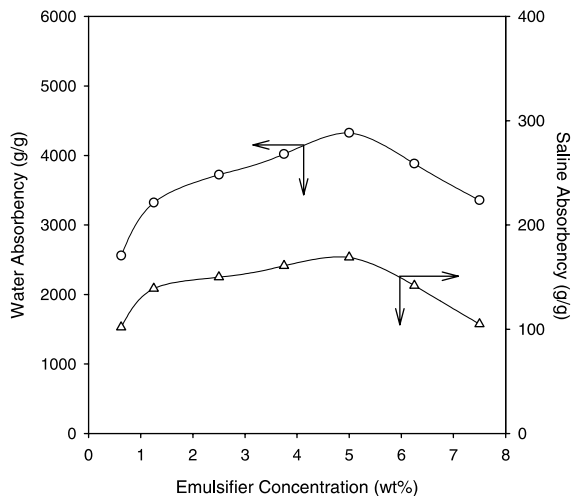


Fig. 10. Effect of emulsifier concentration on absorbency. DN: 70%, polymerization temperature: 70°C, crosslinker concentration: 0.4 wt.%, initiator concentration: 0.25 wt.%, SPS concentration: 1.0 wt.%.

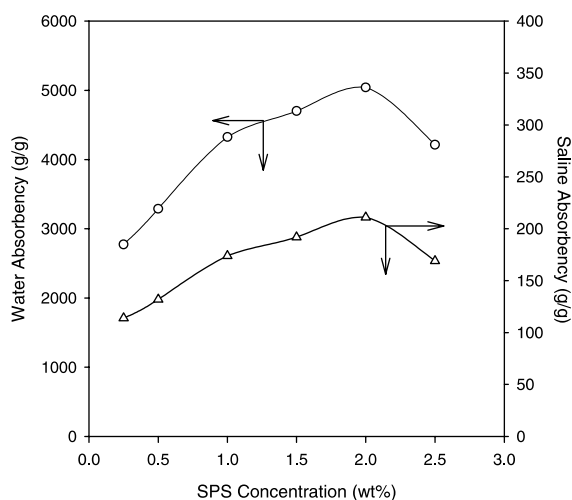


Fig. 11. Effect of SPS concentration on absorbency. DN: 70%, polymerization temperature: 70°C, crosslinker concentration: 0.4 wt.%, initiator concentration: 0.25 wt.%, emulsifier concentration: 5.0 wt.%.

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. Kayaman et al. [16] prepared polyacrylamide hydrogels interpenetrated with poly(itaconic acid), and observed the swelling ratio of hydrogels decreased with increasing content of poly(itaconic acid) above the optimal value. They suggest that the decrease in swelling ratio is caused by the increase in the number of junctions probably due to the entanglement effect.

Table 2
Relationship between the molecular weight of PVA and absorbency

Sample code	Average M_w of PVA	SPS concentration (wt.%)	Water absorbency (g/g)	Saline absorbency (g/g)
SA	–	0	1582	104.1
SA-IP-SPS(1)	19,000	2	2673	165.3
SA-IP-SPS(4)	42,000	2	2877	169.0
SA-IP-SPS(9)-1	90,000	0.5	3288	132.2
SA-IP-SPS(9)-2	90,000	1	4326	174.1
SA-IP-SPS(9)-3	90,000	1.5	4701	192.4
SA-IP-SPS(9)-4	90,000	2	5041	211.4
SA-IP-SPS(9)-5	90,000	2.5	4215	169.0
SA-IP-SPS(15)	150,000	2	3621	158.7

DN: 70%, polymerization temperature: 70°C, crosslinker concentration: 0.4 wt.%, initiator concentration: 0.25 wt.%, emulsifier concentration: 5.0 wt.%.

The effect of the molecular weight of PVA used in the preparation of SPS on the absorbency of SA-IP-SPS is also shown in Table 2. The water and saline absorbency increased with the molecular weight of PVA and reached a maximum at 90,000 M_w . The increase in absorbency may be attributed to the increase in the expansion length of SPS during swelling. However, with a further increase in molecular weight of PVA, absorbency decreased. This may be attributed to the decrease in swelling capacity resulting from entanglement effects.

For the comparison of water retention power, we used WRV method. The effect of centrifugal force on loss of absorbed water is shown in Fig. 12. The loss of absorbed water by SA-IP-SP(9)-4 with 5041 g/g water absorbency was slightly higher than that of SA with 1581 g/g water absorbency.

AUL is an important factor in the practical application of superabsorbents. AUL was measured using the apparatus described in Fig. 1. The measured AUL of SA and SA-IP-SPS are shown in Fig. 13. SA-IP-SPS showed higher AUL than SA. It shows that the interpenetrating SPS in SA-IP-SPS increases the swelling force.

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 SPS contents calculated from the sulfur content of dried SA-IP-SPS. The possible release during dewatering process was investigated by measuring the sulfur content of prepared SA-IP-SPS. To investigate the possible release

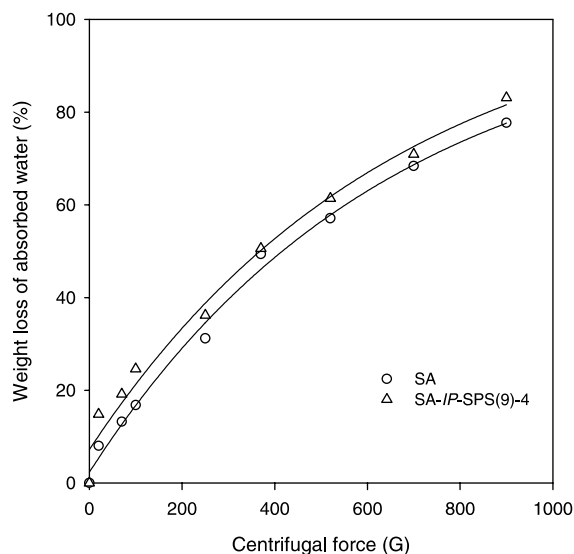


Fig. 12. Weight loss from absorbed sample on centrifuging under different conditions. Polymerization conditions are the same as in Table 2.

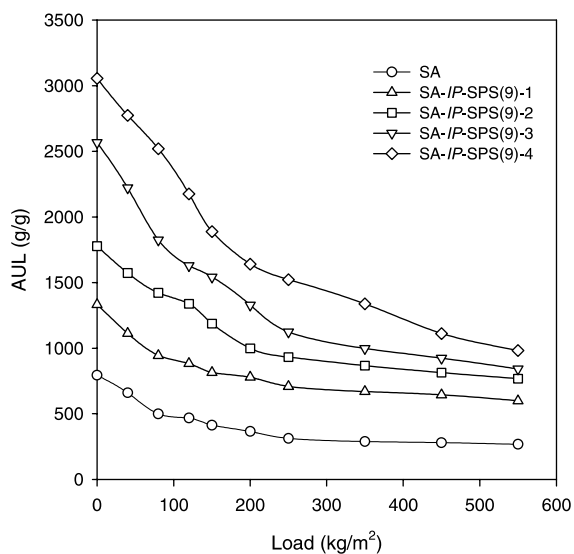


Fig. 13. Absorbency under load. Polymerization conditions are the same as in Table 2.

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 to determine SPS content. The results are shown in Table 3. Experimental values of SPS content are similar to the theoretical values indicating that SPS chains have been sufficiently immobilized by forming an interpenetrating network.

Table 3
Determination of SPS loss from sulfur content measurement

Sample code	Theoretical SPS content (%)	Experimental SPS content (%)	
		Before swelling ^a	After swelling ^b
SA-IP-SPS(9)-1	2.1	2.0	2.0
SA-IP-SPS(9)-3	6.1	6.0	5.9
SA-IP-SPS(9)-5	9.9	9.8	9.7

^aSPS content was determined through the sulfur content measurement of the prepared SA-IP-SPS.

^bSwollen SA-IP-SPS was dewatered with methanol, dried, and its sulfur content was measured to determine SPS content.

4. Conclusion

SA-IP-SPS was prepared via inverse-emulsion polymerization method to enhance absorbency. The effects of polymerization conditions on absorbency were investigated. The absorbency was affected by polymerization conditions such as DN of AA monomer, temperature, molecular weight of PVA used in the preparation of SPS, concentrations of initiator, crosslinker, emulsifier and SPS. An optimum condition for highest absorbency existed with respect to DN, temperature, molecular weight of PVA used for SPS, and the concentrations of initiator, emulsifier and SPS. Whereas the water absorbency using filtration method decreased with increasing crosslinker concentration, the saline absorbency using the filtration method and WRV showed a maximum value at a specific concentration.

The weight loss of absorbed water in SA-IP-SPS on centrifuging was similar to that in SA in spite of the significantly higher absorbency of SA-IP-SPS. The SA-IP-SPS showed higher absorbencies and AUL than those of SA due to the introduced SPS in the super-absorbent network.

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