

Synthesis and Characterization of a Salt-Resisting Superabsorbent Based on Poly(acrylic acid) with Sodium Tungstate as a Crosslinker

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ABSTRACT: A novel salt-resistant superabsorbent polymer was synthesized by solution polymerization from the monomer acrylic acid (AA) with potassium persulfate as the initiator. Sodium tungstate was first employed as a crosslinker in the preparation to achieve a better crosslinked polymer (WPAA). In addition to the xerogel WPAA, sodium hydroxide and tris(2-hydroxyethyl)amine (TEA) were introduced for the preparation of WPAA–sodium and WPAA–TEA hydrogels, respectively. The effect on the water absorbency of factors such as the reaction temperature, degree of neutralization of AA, and amounts of the crosslinker sodium tungstate and the initiator were investigated. The crosslinked xerogels were characterized with infrared spectroscopy. These crosslinked superabsorbent composites with sodium tungstate were characterized with thermogravimetric analysis and scanning electron microscopy. The water absorbency

of these superabsorbent composites in water and saline solutions were investigated. Results obtained from this study showed that under the same synthesis conditions, in comparison with superabsorbent composites with an aluminum salt as a crosslinker and styrene as a graft copolymer, the salt resistance of the superabsorbent composite synthesized with sodium tungstate as a crosslinker was obviously enhanced. Moreover, the WPAA–TEA xerogel had absorbency values of 223.6 and 81.9 g/g for distilled water and a 0.9 wt % NaCl solution, respectively, and it showed better salt resistance and a better water-absorbing rate than the WPAA–sodium xerogel because of the modification with triethanolamine. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2440–2445, 2008

Key words: initiators; networks; resins

INTRODUCTION

Superabsorbent polymers constitute a class of three-dimensional, loosely crosslinked polymeric materials that can absorb huge quantities of water or aqueous solutions and swell at the same time. In particular, the absorbed water can be hardly removed even under some pressure. Because of these excellent characteristics, superabsorbents are used in a variety of valuable applications, such as disposable diapers, feminine napkins, water reservation in agriculture and horticulture, drug delivery systems, gel actuators, water-blocking tapes, and absorbent pads.^{1–4} For the last 2 decades, there has been remarkable interest in designing and manufacturing new compounds of these kinds of polymers because of their outstanding utility in comparison with traditional water-absorbing materials.

Qualities such as low production costs and a high degree of swelling in water and a considerable range of applications in many fields have made superabsorbent objects of much of attention. However,

there are some insurmountable limitations to the applications of superabsorbent polymers because they have poor resistance to salts, as demonstrated by their notably high dehydration in electrolytic solutions such as 0.9 wt % NaCl solutions. The applications in which superabsorbents are used always include salts, such as disposable pads, sheets, and towels for surgery, products for adult incontinence, and feminine hygiene products. Therefore, it is important to improve the salt resistance of superabsorbents. On the basis of previous studies,^{5–7} Liu et al.⁸ reported a salt-resistant hydrogel compound of a polymer gel and an inorganic gel. It was a superabsorbent with water absorbency in a 0.9 wt % NaCl aqueous solution under atmospheric and applied pressure ($\approx 2 \times 10^3$ Pa) of 55 and 20 g/g, respectively. We intend to make some modifications of the chemical and space structure of the hydrogel to make it employable as a superabsorbent for various applications.

In this study, we conducted the polymerization of acrylic acid (AA) with potassium persulfate ($K_2S_2O_8$) as the initiator and for the first time employed sodium tungstate (Na_2WO_4) as a crosslinker in the preparation to achieve a better crosslinked polymer (WPAA). In addition to the WPAA xerogel, sodium hydroxide (NaOH) and $N(CH_2CH_2OH)_3$ [tris(2-

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hydroxyethyl)amine (TEA)] were introduced for the preparation of WPAA-Na and WPAA-TEA hydrogels, respectively. The effects on the water absorbency of factors such as the reaction temperature, degree of neutralization of AA, and amounts of the crosslinker Na_2WO_4 and the initiator were investigated. In addition, we determined the water absorbency and salt resistance of the superabsorbent composite with Na_2WO_4 for comparison with that of superabsorbent composites with aluminum ions as crosslinkers and styrene as a graft copolymer.

EXPERIMENTAL

Materials

AA (Beijing Dongfang Chemical Factory, Beijing, China), styrene (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China), NaOH (Tianjin Chemical Regent Co., Tianjin, China), $\text{K}_2\text{S}_2\text{O}_8$ (Shanghai Aijian Co., Shanghai, China), Na_2WO_4 (Beijing Beihua Fine Chemicals Co., Ltd., Beijing, China), TEA (Tianjin Chemical Reagent No. 1 Plant, Tianjin, China), and sodium aluminate (Na_3AlO_3 ; Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) were directly used without further purification.

Preparation of the superabsorbent composites with Na_2WO_4 as a crosslinker

The sample was prepared with the following procedure. In a typical polymerization, AA (10 mL) dissolved in distilled water (40 mL), Na_2WO_4 (0.25 g), and $\text{K}_2\text{S}_2\text{O}_8$ (0.1 g) were added sequentially to a 250-mL, three-necked flask equipped with a condenser, a thermometer, a drop funnel, and a nitrogen line. The mixed solution was stirred in an oil bath with a preset temperature at 110°C under nitrogen. After 30 min of refluxing, more $\text{K}_2\text{S}_2\text{O}_8$ (0.1 g), dissolved in distilled water (10 mL), was charged to the mixed solution through the drop funnel. There was an additional hour of refluxing until the reaction mixture became a viscous hydrogel. After that, the resulting polymer was washed several times with distilled water, dried in a vacuum oven at 60°C to a constant weight, and then milled with a grinder. A weighed quantity (0.2 g) of the xerogel was added both to a 100-mL beaker with NaOH (0.02 g) dissolved in distilled water (10 mL) to make WPAA-Na and to a 100-mL beaker with TEA (0.1 g) dissolved in distilled water (10 mL) to make WPAA-TEA. This reaction process needed about 1 h, and the result was dried in a vacuum oven at 60°C to a constant weight. Thus, the superabsorbent composites WPAA, WPAA-Na, and WPAA-TEA were characterized with infrared spectroscopy and thermo-

gravimetric analysis and observed with scanning electron microscopy (SEM).

Preparation of the superabsorbent composites with Na_3AlO_3 as a crosslinker (AISPAA-Na)⁹

Na_3AlO_3 (1.2 g) and NaOH (0.6 g) dissolved in distilled water (6 mL) and AA (5.0 g) were added sequentially to a 50-mL, three-necked flask equipped with a condenser, a stirrer, a thermometer, and a nitrogen line. After 10 min of stirring, $\text{K}_2\text{S}_2\text{O}_8$ (0.1 g) was added to the mixed solution. The mixed solution was stirred in an oil bath with a preset temperature of 110°C . There was an additional hour of refluxing until the reaction mixture became a viscous hydrogel. After that, the resulting polymer was washed several times with distilled water, dried in a vacuum oven at 60°C to a constant weight, and then milled with a grinder.

Preparation of the superabsorbent composites with styrene as a graft copolymer (SPAA-Na)⁹

The preparation procedure of SPAA-Na was similar to that of AISPAA-Na, except with diatomite rather than Na_3AlO_3 as the crosslinker.

Water absorbency measurements

The different kinds of hydrogels were immersed in distilled water and 0.9 wt % NaCl solutions at room temperature and reached swelling equilibrium in about 8 h. Swollen samples were then separated from free liquid by filtration over a 100-mesh screen. The water absorbency of the superabsorbent was determined through the weighing of the swollen samples, and the water absorbency of the samples was calculated with the following equation:

$$\text{Water absorbency} = (m_2 - m_1)/m_1$$

where m_1 and m_2 are the weights of the dry xerogel sample and the water-swollen sample, respectively. The water absorbency was calculated as grams of water per gram of sample.

Characterization

Infrared spectra

Fourier transform infrared spectra were recorded from pressed KBr pellets with a Bio-Rad (California) FTS3000MX spectrophotometer (Palo Alto, CA).

Thermal stability

The dried specimens were studied on a ZRY-2P thermogravimetric analyzer (Hui-Juan Kang, Shanghai,

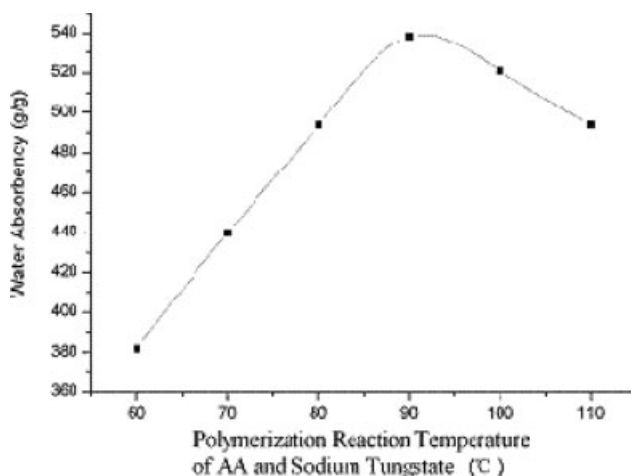


Figure 1 Effect of the reaction temperature on the water absorbency of the superabsorbent composite in distilled water (neutralization degree = 83%; concentration of acrylic acid (C_A) = 45.5 wt %; weight ratio of the crosslinker in the feed = 0.2; weight ratio of the initiator in the feed = 1.0).

China) with a temperature range of 30–800°C at a heating rate of 10°C/min.

Morphology

The dried specimens were examined for morphological details with SEM (model S-530, Hitachi, Tokyo, Japan) at an acceleration voltage of 20 kV. The specimens were coated with a gold-metal layer to provide proper surface conduction.

RESULTS AND DISCUSSION

Effect of the reaction temperature

Figure 1 shows that the water absorbency of the superabsorbent composite crosslinked with Na_2WO_4 increases as the reaction temperature increases from 60 to 90°C and decreases with further increases in the reaction temperature. When the temperature is below 90°C, as the reaction temperature increases, the rate of decomposition of the initiator in polymerization increases, and this results in a loss of crosslinking efficiency.¹⁰ With the same crosslinker content, the water absorbency increases with the reduction of the crosslinking efficiency according to Flory's network theory.¹¹ However, when the polymerization temperature is higher than 90°C, as the reaction temperature increases, the rate of polymerization reaction with chain transfer and chain termination increases, and the molecular weight decreases, so the water absorbency also decreases.

Effect of the crosslinker content

The effect of the crosslinker Na_2WO_4 content on the water absorbency is shown in Figure 2. The water

absorbency increases with the crosslinker content increasing from 0.2 to 0.4 wt %. Because a lower crosslinker content results in the generation of fewer crosslink points, the formation of an additional network is reduced, and the amount of soluble material increases. When the crosslinker content is higher than 0.4 wt %, the crosslinking density is greater, the additional network is dense growth, and the space left for water to enter decreases. The results are in agreement with Flory's network theory.¹¹

Effect of the initiator content

Figure 3 shows the effect of the initiator content on the water absorbency. The water absorbency increases as the $\text{K}_2\text{S}_2\text{O}_8$ content increases from 0.7 to 1.1 wt % and decreases with further increases in the content of $\text{K}_2\text{S}_2\text{O}_8$. The decomposition of $\text{K}_2\text{S}_2\text{O}_8$ belongs to a first-order reaction. The relation between the rate of decomposition (R_d) and the concentration of $\text{K}_2\text{S}_2\text{O}_8$ (II) is given by the following equation:

$$R_d = -d[I]/dt = k_d[I]$$

where k_d is the rate constant for decomposition and t is the time. According to the equation, the decomposition rate of the initiator in free-radical polymerization will increase with an increase in the initiator concentration, and this will result in an increase in the molecular weight in the free-radical polymerization and in the water absorbency. However, a further increase in the $\text{K}_2\text{S}_2\text{O}_8$ concentration leads to a decrease in the absorbency. This result may be caused by a further increase in the number of radi-

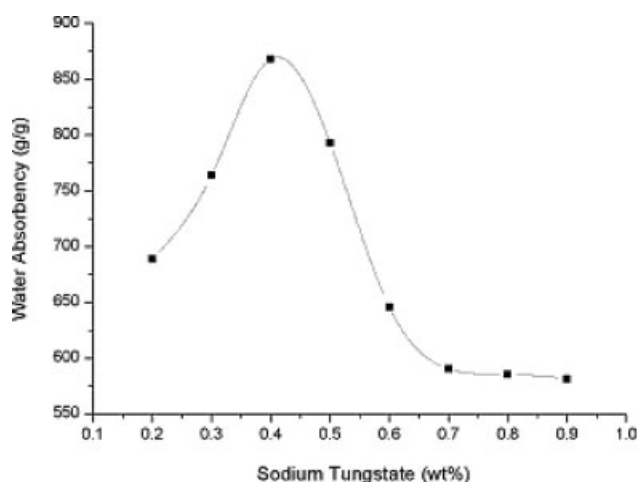


Figure 2 Effect of the content of Na_2WO_4 as the crosslinker on the water absorbency of the superabsorbent composite in distilled water (reaction temperature = 90°C; neutralization degree = 83%; C_A = 45.5 wt %; weight ratio of the initiator in the feed = 1.0).

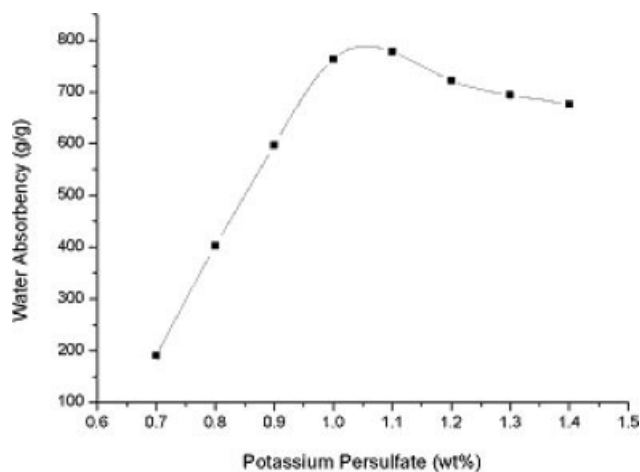


Figure 3 Effect of the initiator content on the water absorbency of the superabsorbent composite in distilled water (reaction temperature = 90°C; neutralization degree = 83%; C_A = 45.5 wt %; weight ratio of the crosslinker in the feed = 0.2).

calculated as the content of $K_2S_2O_8$ increases. The additional network is dense growth and results in a reduction of the water absorbency.

Effect of the neutralization degree

The effect of the neutralization degree on the water absorbency is shown in Figure 4. The water absorbency increases from 0.5 to 0.85 and decreases with further increases in the neutralization degree of poly(acrylic acid) (PAA). The decrease in the neutralization degree of PAA results in an increase in the number of carboxyl groups on the network, and the swelling ability of the network decreases. Therefore, the water absorbency of the superabsorbent compos-

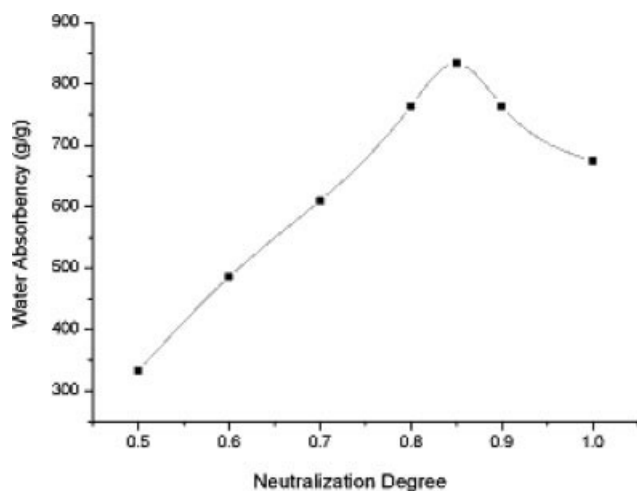


Figure 4 Effect of the neutralization degree on the water absorbency of the superabsorbent composite in distilled water (reaction temperature = 90°C; C_A = 45.5 wt %; weight ratio of the crosslinker in the feed = 0.2; weight ratio of the initiator in the feed = 1.0).

ite decreases. According to Flory's network theory,¹¹ with an increase in the neutralization degree, the fixed electronic charge density and the osmotic pressure increase in the network, and this results in an increase in the water absorbency. However, further higher neutralization increases the number of carboxylate group and water solubility of the superabsorbent composite. Therefore, the water absorbency decreases. Under our experimental conditions, WPAA with a neutralization degree of 0.85 possesses the highest water absorbency.

Infrared spectra

The infrared spectrum of the unneutralized superabsorbent composite WPAA can be compared with the spectra of neutralized superabsorbent composites with TEA and NaOH. The characteristic peaks at 1697, 885, and 774 cm^{-1} arise from the carbonyl group C=O of PAA and tungstate W—O of Na_2WO_4 ,¹² and this indicates a graft polymerization reaction between PAA and Na_2WO_4 . As far as a comparison of WPAA–Na and WPAA–TEA is concerned, the absorbency at 1697 cm^{-1} , decreasing in the spectra of WPAA–Na, provides evidence of a neutralization reaction between PAA and NaOH. The characteristic absorption peak of C—N asymmetric stretching of TEA appears at 1061 cm^{-1} in the spectra of WPAA–TEA.

Thermal stability¹³

Thermogravimetric analysis curves of crosslinked WPAA, WPAA–Na, and WPAA–TEA with Na_2WO_4 are shown in Figure 5(a–c), respectively. The three

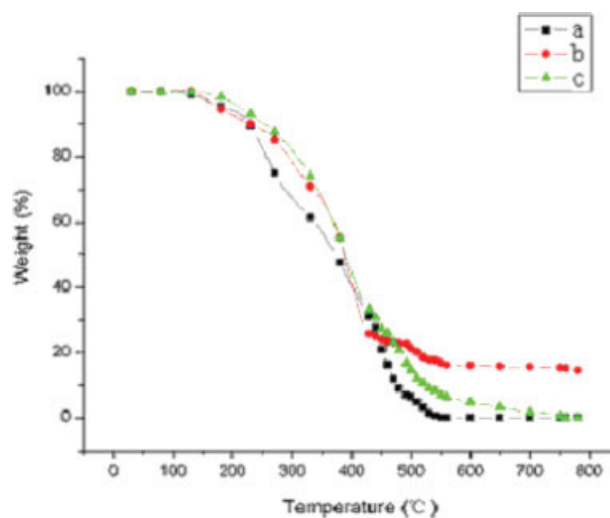


Figure 5 Thermogravimetric analysis curves of (a) WPAA, (b) WPAA–Na, and (c) WPAA–TEA at a heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

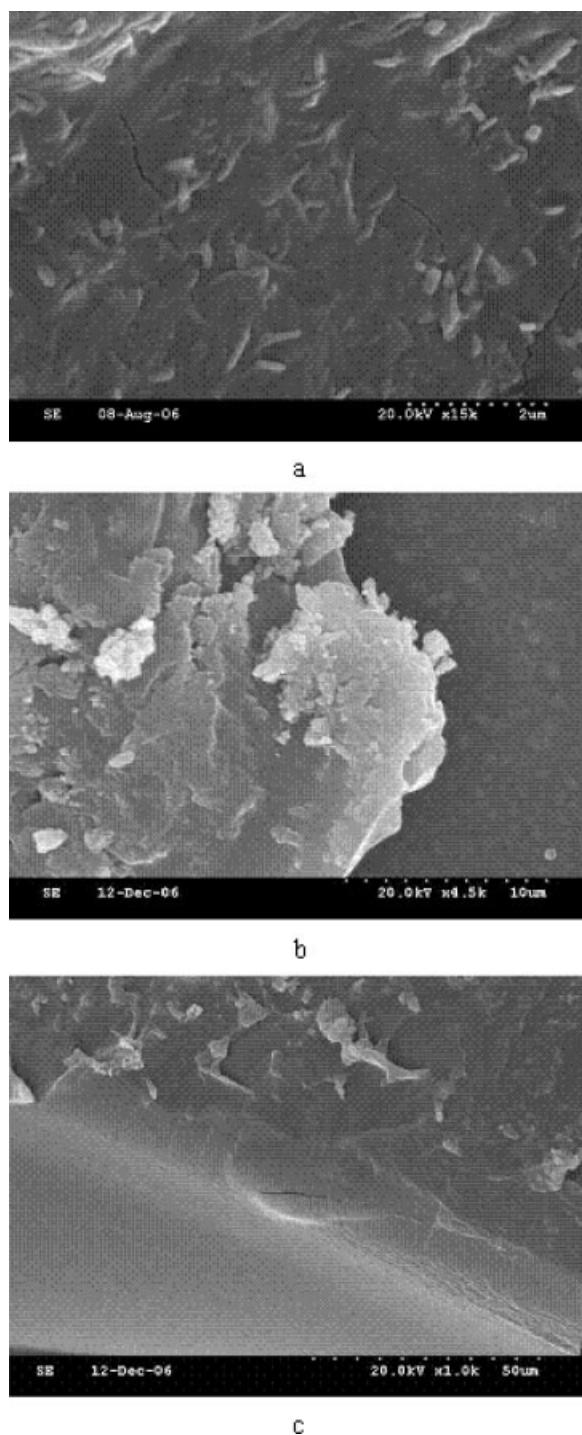


Figure 6 SEM micrographs of (a) WPAA, (b) WPAA-Na, and (c) WPAA-TEA.

kinds of superabsorbent composites show a very small weight loss below 130°C that implies a loss of moisture. Around 230°C, WPAA and WPAA-Na have similar significant weight losses of about 10%, and WPAA-TEA loses about 7% of its weight. After this, the three kinds of superabsorbent composites have a major weight loss, and WPAA has a more marked reduction in weight than WPAA-Na and WPAA-TEA. When the temperature rises to about

560°C, WPAA completely decomposes. The complete decomposition temperature of WPAA-TEA is about 780°C, whereas when the temperature increases from 560 to 800°C, WPAA-Na hardly decomposes. The results indicate that neutralization with NaOH and the introduction of TEA into the polymer network result in an increase in the thermal stability.

SEM observations

Microphotographs of crosslinked WPAA, WPAA-Na, and WPAA-TEA with Na_2WO_4 are shown in Figure 6(a–c), respectively. The SEM micrograph of unneutralized WPAA shows irregularly shaped particles and ravine-shaped breaks in the particles, whereas the SEM micrographs of WPAA-Na and WPAA-TEA show obvious sea-island-shaped structures; their particles are smaller and the breaks in their particles are larger than those shown in the SEM micrograph of WPAA. Therefore, WPAA-Na and WPAA-TEA have good water absorbency.

Water absorbency

Crosslinked polymer WPAA with Na_2WO_4 can be regarded as a dried complex of the polymeric superabsorbent and tungsten hydrogel. Na_2WO_4 , employed as a crosslinker and serving as an ionic hydrophilic group in the resin, results in increased water absorbency of the superabsorbent. The larger surface spaces between WPAA particles can wrap more water molecules and lead to greater water absorbency. Moreover, the tungsten hydrogel, which serves as an inorganic hydrogel, has greater salt resistance. Crosslinking between the tungsten hydrogel and polymeric superabsorbent can strengthen the salt resistance of the superabsorbent. The test results for distilled water and 0.9 wt % NaCl solution absorbency of WPAA-Na and WPAA-TEA show

TABLE I
Decomposing Stages of WPAA, WPAA-Na, and WPAA-TEA with Respect to the Temperature

Temperature (°C)	Weight (%)		
	WPAA	WPAA-Na	WPAA-TEA
30.1	100	100	100
79.5	100	100	100
230.3	89.36	90.02	92.88
330.3	61.41	70.87	74.04
429.8	31.06	25.82	32.99
450.8	21.17	23.99	27.33
470.1	11.99	23.05	23.06
500.1	6.38	21.38	14.73
530.39	1.47	17.77	9.19
560.6	0	16.24	6.45
700.1	0	15.65	1.81
780.2	0	14.54	0

TABLE II
Water Absorbency of Several Kinds of Superabsorbent Composites

Sample	Water absorbency (g/g)	
	Distilled water	0.9 wt % NaCl
WPAA-Na	220.5	62.8
WPAA-TEA	223.6	81.9
AlPAA-Na	201.8	42.7
SPAA-Na	195.7	57.8

The reaction conditions were as follows: reaction temperature = 110°C; neutralization degree = 23%; concentration of the crosslinker in the feed = 19%; concentration of the initiator in the feed = 2%.

that there is little difference between their water absorbencies, but the NaCl solution absorbency of the latter is 20 g/g more than that of the former (Table I). The triethanolamine of WPAA-TEA is a larger hydrophilic group with hydroxyls, whose water absorbency is less influenced by salt. Hence, the salt resistance of the superabsorbent increases significantly. Under the same synthesis conditions, in comparison with that of AISPAA-Na and SPAA-Na, the water absorbency of the superabsorbent composite synthesized with Na₂WO₄ as crosslinker slightly increases, but its salt resistance is obviously enhanced (Table II).

CONCLUSIONS

In this study, for the first time Na₂WO₄ was employed as a crosslinker in the preparation of water-absorptive resins. These crosslinked superabsorbent composites with Na₂WO₄ were characterized with infrared spectroscopy, thermogravimetric analysis, and SEM. The effects of the reaction temperature, degree of neutralization, and amounts of the cross-

linker and initiator were investigated. The test of distilled water and 0.9 wt % NaCl solution absorbency of WPAA-Na and WPAA-TEA suggested that they had better water absorbency and salt resistance than AISPAA-Na and SPAA-Na. In comparison with WPAA-Na, WPAA-TEA had a slight and obvious increase in the absorbency for distilled water and 0.9 wt % NaCl solutions, and the NaCl solution absorbency of the latter was more than that of the former. Under our experimental conditions, a crosslinked PAA superabsorbent composite with Na₂WO₄ with a water absorbency of about 870 g of H₂O/g was synthesized, and it had a composition of 0.4 wt % crosslinker and 1.0 wt % initiator, a neutralization degree of 83%, and a reaction temperature of 90°C. This excellent water absorbency may be especially useful in agricultural and horticultural applications.

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