

# Synthesis and Swelling Behavior of Crosslinked Copolymers of Neutralized Maleic Anhydride with Other Monomers

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**ABSTRACT:** A series of novel copolymer superabsorbents based on maleic anhydride (MLN), acrylamide (AAM), hydroxyethyl methacrylate (HEMA), and *N,N'*-methylenebisacrylamide (NMBA) were prepared by inverse-suspension polymerization. The influence of the reaction parameters on the water absorption was investigated to improve the understanding and to identify the optimum reaction conditions. The water absorbencies or swelling behaviors for these absorbents in various salt solutions and various alcohol solutions were studied. The tendency of the absorbency for

these absorbents in salt and alcohol solutions is in the order  $\text{Na}^+ > \text{Ca}^{2+} > \text{Al}^{3+}$  for NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  aqueous solutions and a glycerol > glycol > methanol > ethanol solution, respectively. This article also explains the IR and SEM characterization of the water-absorbing copolymers and their practical use in soil for water retention. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2725–2731, 2003

**Key words:** adsorption; copolymerization; crosslinking; swelling; hydrophilic polymers

## INTRODUCTION

With their high water absorbency and water retention, superabsorbent compositions are widely used in various areas, such as in disposable diapers, feminine napkins, soil for agriculture and horticulture, medicine for drug-delivery systems, and other advanced technologies.<sup>1–4</sup> Since Fanta et al.<sup>5</sup> succeeded, more than two decades ago, in grafting monomers onto starch to yield products with an absorbency of several hundred to thousand times its dried weight, research of superabsorbents from starch-based polymers to petrochemical-based polymers has been carried out. In this article, we report on copolymer superabsorbents prepared from maleic anhydride (MLN), acrylamide (AAM), hydroxyethyl methacrylate (HEMA), and *N,N'*-methylenebisacrylamide (NMBA) by inverse-suspension polymerization with potassium persulfate (KPS) as the initiator. The monomer ratio, neutralization degree of MLN, concentrations of the crosslinking agent and initiator, and bead size of the products were investigated to explain the swelling behavior of the copolymer superabsorbents. This article also deals with the water-retaining capacity of the obtained copolymer in soil.

## EXPERIMENTAL

### Materials

MLN (analytical pure), AAM (chemical pure), HEMA (commercial grade), NMBA (chemical pure), KPS (chemical pure), potassium hydroxide (analytical pure), and Span-40, Span-60, and Span-80 (chemical pure) were used as purchased. Methanol and cyclohexane were of analytical grade. Distilled water was used in the reaction system and water-adsorption measurements.

### Synthesis procedure

A series of the copolymer superabsorbents were prepared by the following procedure:

#### Preparation of the continuous phase

The continuous phase was prepared with 80 cm<sup>3</sup> cyclohexane and 0.8 g of a suspending agent (Span-40, Span-60, or Span-80) in a 250-cm<sup>3</sup>, three-necked, round-bottom flask fitted with a mechanical stirrer, a spiral reflux condenser, and a thermometer. The organic phase containing the suspending agent was stirred and heated using a water bath until the suspending agent was dissolved. To obtain suitable reaction conditions, the continuous phase was cooled to room temperature while stirring.

#### Preparation of the dispersed phase

A predetermined amount of MLN was dissolved in 5 cm<sup>3</sup> distilled water and neutralized carefully by a 10

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mol/L aqueous potassium hydroxide solution, which was thermally controlled not to be heated above 40°C to avoid polymerization and to obtain an MLN solution with a certain neutralization degree. Exact amounts of a thermal initiator (KPS), a crosslinking agent (NMBA), and other monomers (AAM, HEMA) were dissolved in the above-mentioned MLN solution in various molar ratios and stirred until a homogeneous monomer solution was obtained.

### Copolymerization

The mixed monomer solution was added into the continuous phase while being agitated at room temperature and stirred for a 10-min period. The mixture was heated to 70 + 1°C using a water bath and the reaction was allowed to proceed for 2 h to ensure complete consumption of the monomers. The reaction was then stopped, and water was removed from the copolymer by adding, dropwise, 100 cm<sup>3</sup> methanol while stirring. The mixture was stirred with a mechanical stirrer for over 3 h and then was filtered, washed with methanol, and dried in an oven at 50°C for 24 h. The dried reaction mass was ground and a white powdered product was obtained.

### Characterization of the copolymers

The synthesized copolymers were investigated for their properties as follows:

#### Identification of functional groups of the copolymers

The functional groups of the copolymers were identified using a Fourier transform infrared (FTIR) spectrophotometer (Bio-Rad FTS 135) by the KBr-disc method.

#### Determination of surface morphology of the copolymers

The surface morphology of the copolymers was investigated using a scanning electron microscope (SEM: Model Hitachi S-3500N). The SEM was operated with a 20-kV accelerating voltage.

### Water absorbency of the copolymers

#### In distilled water

An amount of the dry copolymer, 0.1 g ( $W_0$ ), was immersed in 150 g distilled water ( $W_1$ ) at room temperature and allowed to swell sufficiently for 30 min. The completely swollen copolymer was filtered through a 160-mesh nylon screen for 10 min, and the nonabsorbed water ( $W_2$ ) was weighted. The water

absorbency ( $Q$ ) of the copolymer was calculated by the equation shown below:

$$Q(\text{g/g}) = \frac{W_1 - W_2}{W_0}$$

This will henceforth be called the base procedure of absorption.

#### In salt solution

To measure the water absorbency of the copolymers in the salt solution, the base procedure of absorption was carried out, replacing distilled water with a series of salt solutions, including sodium chloride, calcium chloride, and aluminum chloride solutions of various concentrations.

#### In alcohol solution

To measure the absorbency of the copolymers in alcohol solutions, the base procedure of absorption was carried out, replacing distilled water with a series of alcohol solutions, including methanol, ethanol, glycol, and glycerol solutions of various concentrations.

### Water retention of the copolymers

#### In air

The water retention of the copolymers in air was determined by a heating oven test at 40, 60, and 80°C. The swollen copolymer was weighted per hour at each fixed temperature.

#### In soil

The water retention of the copolymers in soil was determined by weighting the soil with the synthesized copolymers per day at 30°C. The soil contained 60.9 wt % of SiO<sub>2</sub>, 21.8 wt % of Al<sub>2</sub>O<sub>3</sub>, 9.6 wt % of Fe<sub>2</sub>O<sub>3</sub>, 0.02 wt % of CaO, and 0.16 wt % of MgO.

## RESULTS AND DISCUSSION

The influence of a series of reaction parameters on the water absorbency of the synthesized copolymers is discussed and explained as follows:

### Molar ratios of the monomers

Table I shows the results of the water-absorbency test of the copolymers synthesized by inverse-suspension polymerization with various molar ratios of the monomers. The crosslinked copolymers of MLN and AAM are swollen in water due to the hydrophilic groups (amide and carboxylate) in their structure<sup>6</sup> and the

electrostatic repulsion of the ionic charges of their networks.<sup>7</sup> The swelling increase is due to an increase of the ionic units, especially  $-\text{CO}_2\text{K}$ , but an excess of ionic units leads to an increase of the soluble portions of the network.<sup>7</sup> Among A1–A6 samples, the synthesized copolymer with a 20:80 molar ratio of MLN:AAM gave the highest water-absorbency value of 760 times its dry weight in distilled water and 170 times its dry weight in a 0.9% NaCl solution.

Table I also shows that the water absorbency of the superabsorbents was greatly enhanced by adding an amount of HEMA into the MLN–AAM reaction system, in which the molar ratio of MLN:AAM was about 20:80. Synergetic effects of ionic units and nonionic units, such as  $-\text{OH}$ ,  $-\text{CONH}_2$ , and  $-\text{CO}_2\text{K}$ , provide a strong force to improve the water absorbency and antisalt capacity of the superabsorbents. On the other hand, ionic units have a higher hydrophilic capacity than that of nonionic units, so the water absorbency decreases drastically with an excess of HEMA, which contains nonionic groups ( $-\text{OH}$ ). When the molar ratio of MLN:AAM:HEMA is 19.0:79.6:1.4, the copolymer with the highest water absorbency was produced, whose absorbency for distilled water and the 0.9% NaCl solution were 1140 and 320 g/g, respectively.

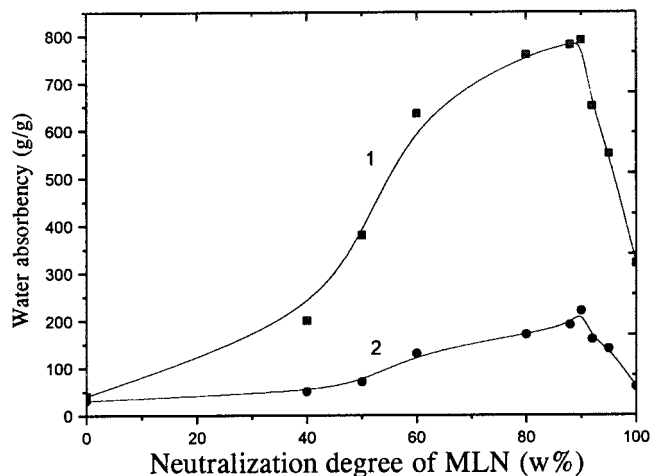
### Neutralization degree of MLN

Figure 1 shows the water-absorbing capacity of the crosslinked copolymers synthesized with a 20:80 molar ratio of MLN:AAM by 0.048 g of KPS (1.2 wt % of total monomers), 0.008 g of NMBA (0.2 wt % of total monomers), and 0.1 g of Span-60 at various MLN

**TABLE I**  
Influence of the Molar Ratios of the Monomers on the Water Absorbency of Crosslinked Copolymers

No.	Monomer in the feed (mol%)			Water absorbency (g/g)	
	MLN	AAM	HEMA	Distilled water	0.9% NaCl solution
A1	5	95	—	300	30
A2	15	85	—	350	40
A3	20	80	—	760	170
A4	25	75	—	400	80
A5	40	60	—	20	10
A6	50	50	—	10	5
B1	19.1	80.2	0.7	450	90
B2	19.0	79.9	1.1	980	250
B3	19.0	79.6	1.4	1140	320
B4	18.9	79.5	1.6	1100	300
B5	18.8	78.9	2.3	700	180
B6	18.7	78.5	2.8	200	40

Reaction conditions: NMBA, 0.2 wt % of total monomers; KPS, 1.2 wt % of total monomers; neutralization degree of MLN, 90 %; 0.1 g suspending agent; 10 cm<sup>3</sup> comonomer solution; 80 cm<sup>3</sup> cyclohexane; at 70°C; 2 h.



**Figure 1** Effect of neutralization degree of MLN on water absorbency of crosslinked poly(MLN–AAM): (a) in distilled water; (2) in 0.9% NaCl solution.

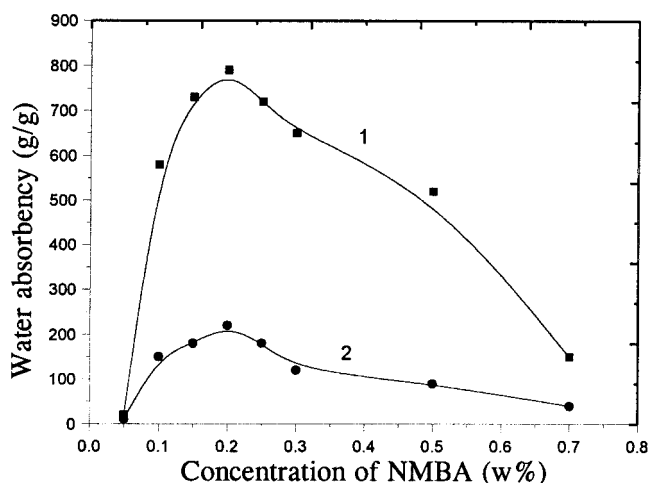
neutralization degrees. The crosslinked copolymer of neutralized MLN and AAM gave the optimum result at a neutralization degree of 90% with a water-absorbency value of 790 g/g in distilled water and 220 g/g in a 0.9% NaCl solution. Like neutralized poly(acrylic acid), the low neutralized poly(MLN–AAM) has many free, nonneutralized carboxylic functionalities and causes autocrosslinking through hydrogen abstraction from the polymer backbone.<sup>8</sup> On the other hand, higher degrees of neutralization increase the solubility of the synthesized copolymer and decrease the water-absorbing capacity.

### Concentration of the crosslinking agent

A 20:80 molar ratio of MLN:AAM was selected to study the influence of various crosslinking agent concentrations on the water absorbency with 90% neutralization of MLN, 0.048 g of KPS (1.2 wt % of total monomers), and 0.1 g of Span-60 as the suspending agent. The result is shown in Figure 2. The optimum concentration of the crosslinking agent (NMBA) in the MLN–AAM polymerization system is 0.2 wt % of the total monomers. The water absorbency of the synthesized copolymers with a low crosslinking degree is low because the copolymers contain a high degree of noncrosslinked portions which dissolve in the water. However, higher percentages of the crosslinking agent increase the crosslinking density of the polymer network and decrease the space between each crosslinking point and minimize the soluble chains; thereby, the water absorbency decreased.<sup>9</sup>

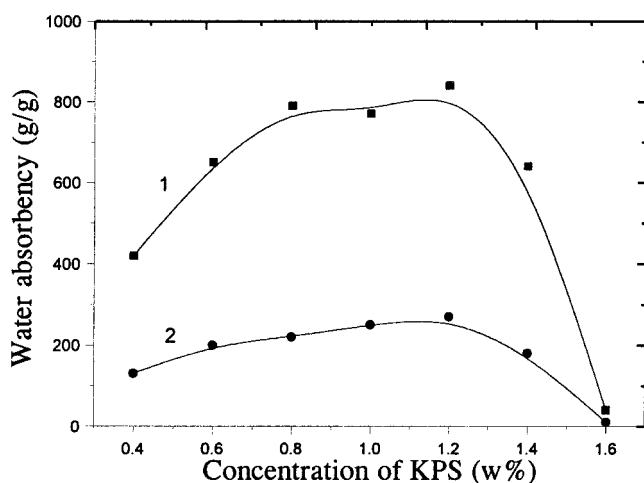
### Concentration of the initiator

In this section, the synthesized copolymers were produced using fixed conditions as in the early section,

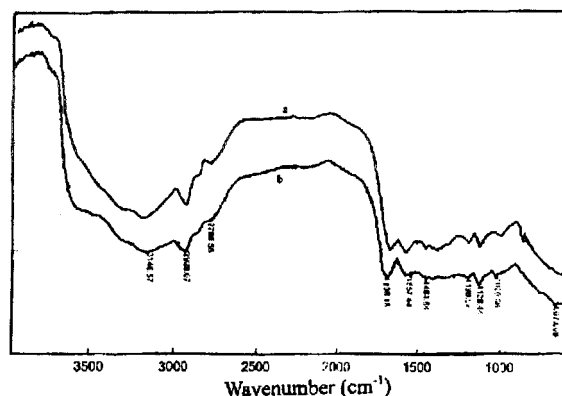


**Figure 2** Effect of concentration of the crosslinking agent on water absorbency of crosslinked poly(MLN-AAM): (a) in distilled water; (2) in 0.9% NaCl solution.

but with various concentrations of the initiator (KPS). Figure 3 shows the influence of the initiator concentration on the water absorbency of the obtained superabsorbents. The water-absorbing capacity of the copolymers increased with increasing initiator concentrations up to an optimum result at 1.2 wt % of the total monomers and then decreased with an increasing initiator concentration. At a low concentration of KPS, a low quantity of free radicals is produced and a small network is obtained, which affects the low water-absorbing capacity. At a high concentration of KPS, high quantities of the produced free radicals may cause a chain transfer to the polymers,<sup>10</sup> which leads to a high crosslinking density of the polymer network and a decreasing water absorbency.



**Figure 3** Effect of concentration of the initiator on water absorbency of crosslinked poly(MLN-AAM): (a) in distilled water; (2) in 0.9% NaCl solution.



**Figure 4** IR spectra for samples A3 and B3: (a) A3; (b) B3.

### Characterization of the functional groups of the copolymers by FTIR

The functional groups of the synthesized copolymer were investigated by FTIR. In the spectra (Fig. 4), the absorbances at 1672 and 1698  $\text{cm}^{-1}$  confirm the existence of the amide group ( $-\text{CONH}_2$ ). The existence of the carboxylate group ( $-\text{CO}_2\text{K}$ ) is evidenced by the absorption peaks at 1454 and 1575  $\text{cm}^{-1}$  in the IR spectra.

### Type of the suspending agent

Table II shows the chemical and physical properties of suspending agents and the influence of the suspending agent type on the water absorbency of the synthesized copolymers, which were produced under the same reaction conditions as those of sample B3 mentioned above. The synthesized beads gave the optimum properties with the Span-80 surfactant as the suspending agent with a water-absorbency value of 1200 g/g in distilled water and 330 g/g in a 0.9% NaCl solution.

Figure 5 shows the SEM morphology of the crosslinked copolymer beads. It is apparent from the photographs that the copolymer beads synthesized by different suspending agents have different average particle sizes, that is, Span-80 (37  $\mu\text{m}$ ) < Span-60 (40  $\mu\text{m}$ ) < Span-40 (57  $\mu\text{m}$ ).

From Table II and Figure 5, a reasonable conclusion could be made that the chemical and physical properties of the suspending agents have great effects on the particle size of the polymer beads. When different suspending agents were used in the inverse-suspension polymerization, the particle size of the suspending beads varied with their stabilization efficiency, which is related to hydrophile-lipophile balance (HLB) values and the hydroxyl value of the suspending agents. The average particle size of the synthesized copolymer beads increased with increasing HLB values and the hydroxyl value of the suspending agents in the order of Span-80, Span-60, and Span-40. Thus,

**TABLE II**  
**Influence of the Type of Suspending Agent on the Water Absorbency of Crosslinked Copolymers**

No.	Suspending agent	Chemical and physical properties of suspending agent		Water absorbency of crosslinked copolymers (g/g)	
		HLB	Hydroxyl value	Distilled water	0.9% NaCl solution
C1	Span-40	6.7	275–305	920	250
C2	Span-60	4.7	235–260	1140	320
C3	Span-80	4.3	193–209	1200	330

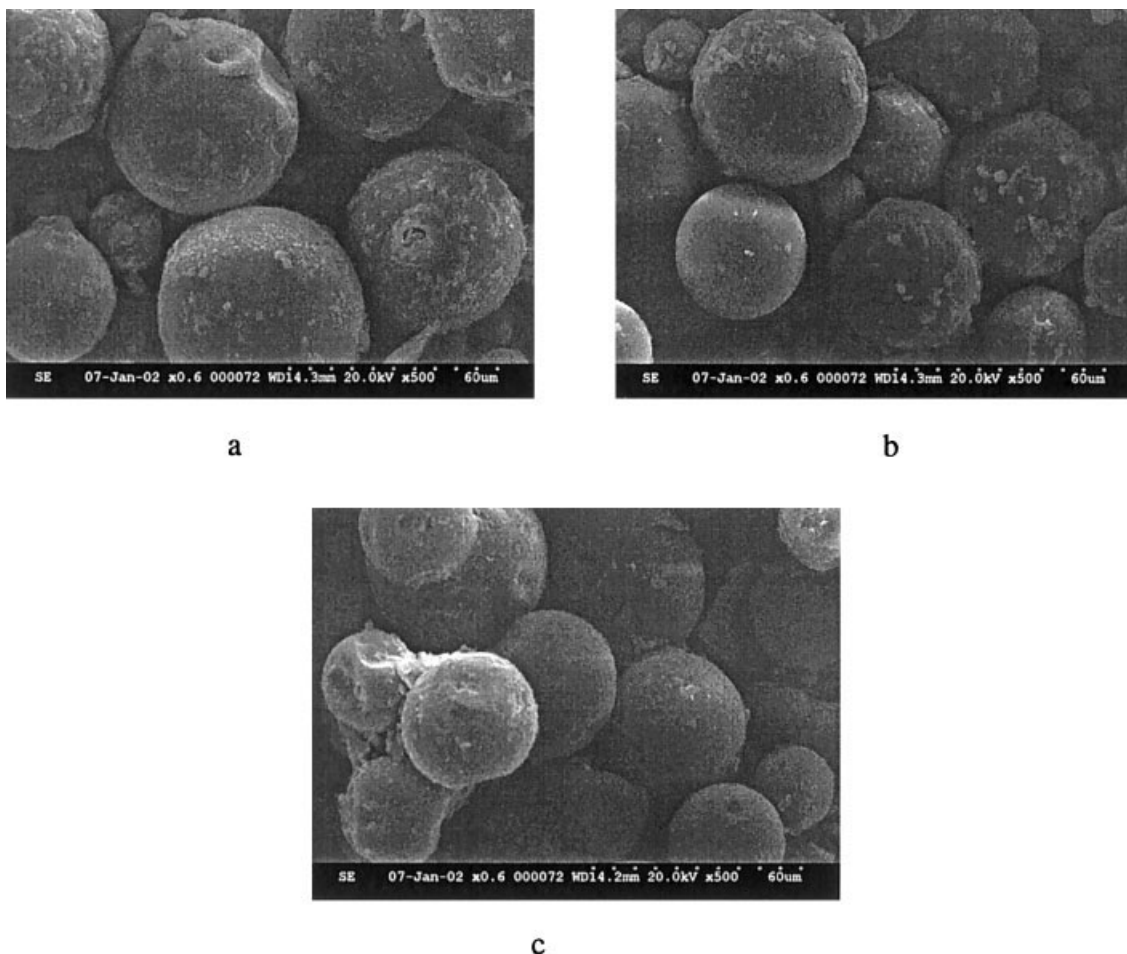
the average particle size of the copolymer beads by Span-80 is smaller than that of the copolymer beads by Span-40 and Span-60, giving more surface area and resulting in a higher water-absorbing capacity.<sup>6</sup>

#### Swelling behavior in salt solution

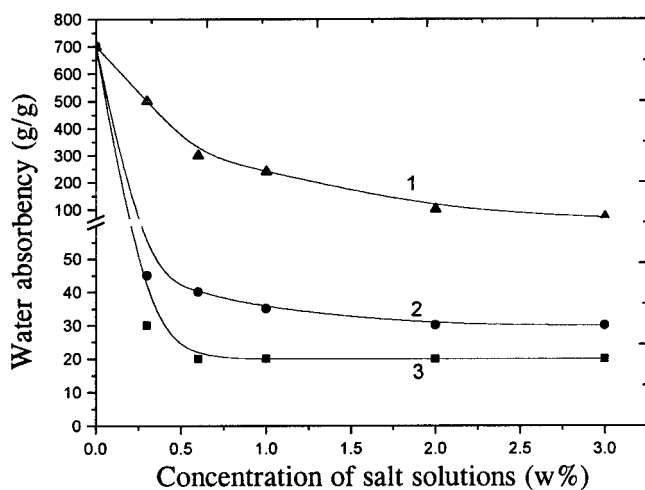
The synthesized copolymer obtained earlier with a water absorbency of 700 g/g in distilled water, which will, henceforth, be called the test sample, was selected to test the swelling behavior in various concentrations of NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub> solutions as shown in Figure 6. A water-absorbent system consists of a

quantity of a polymer network with a variable quantity of aqueous components. The osmotic pressure attributable to the polymer network is a driving force for the water absorption and greatly depends upon the salt effect, which leads to the pressure differential between the internal and external solutions of the copolymers due to the different ionic concentrations.<sup>11</sup>

Figure 6 shows the tendency that the water absorbency decreases with an increasing salt concentration in the same salt solution. A low salt concentration causes the polymer network to expand and minimize the repulsion free energy. As the salt concentration increases, repulsion is shielded.<sup>11</sup> Figure 6 also sug-



**Figure 5** SEM of synthesized copolymer beads with (a) Span-40, (b) Span-60, and (c) Span-80 as the suspending agents.

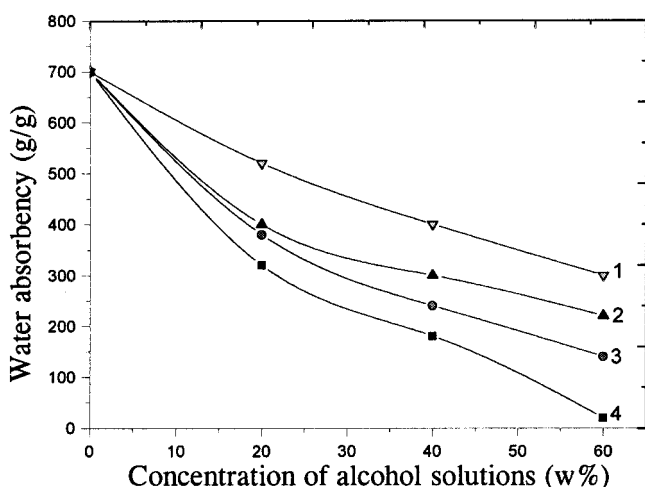


**Figure 6** Effect of various salt solutions at various concentrations on the water absorbency of the synthesized copolymers: (1) NaCl; (2) CaCl<sub>2</sub>; (3) AlCl<sub>3</sub>.

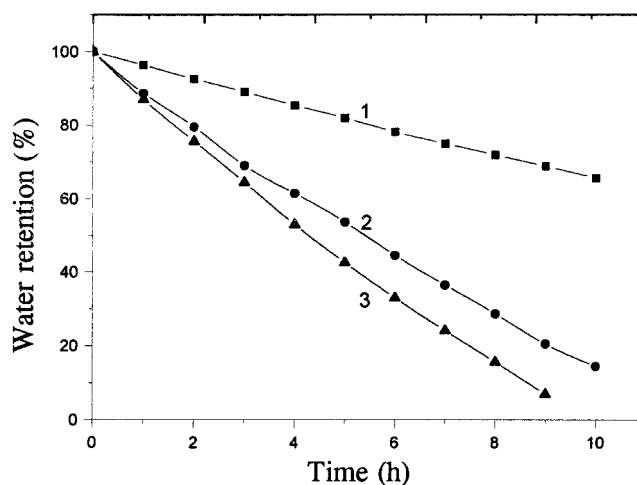
gests that the water absorbency of the synthesized copolymers decreases in various salt solutions at the same concentration in the order of NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub>. The result showed the influence of the salt effect upon the osmotic pressure of the polymer network. Obviously, at a fixed concentration, the ionic concentration of the AlCl<sub>3</sub> solution is the highest, followed by the CaCl<sub>2</sub> and NaCl solutions. The water-absorbing tendency is just in contrast with that of the ionic concentration.

#### Swelling behavior in alcohol solution

The test sample mentioned above was used to investigate the swelling behavior in various concentrations of alcohol solutions as shown in Figure 7. Compared with the swelling in salt solutions, the water absor-



**Figure 7** Effect of various alcohol solutions at different concentrations on the water absorbency of the synthesized copolymers: (1) glycerol; (2) glycol; (3) methanol; (4) ethanol.



**Figure 8** Water retention of the synthesized copolymer (B3) in air: (1) 40°C; (2) 60°C; (3) 80°C.

bency of the synthesized copolymers in the alcohol solutions greatly depends upon hydrophilic groups (—OH) of the organic alcohol. At the same concentration, the water absorbency of the superabsorbents in various alcohol solutions increases in the order of ethanol, methanol, glycol, and glycerol. On the other hand, the absorbing capacity of the superabsorbents in distilled water is much higher than that of the superabsorbents in all organic alcohol solutions. Consequently, the water absorbency of the synthesized copolymers in the alcohol solutions decreases as the concentration increases in the same alcohol solution.

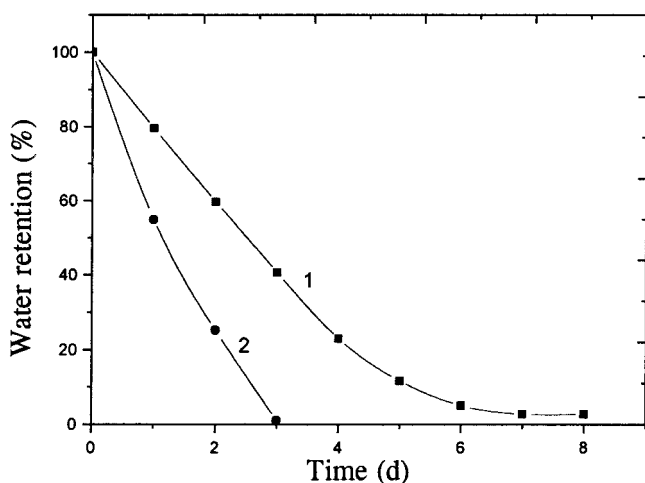
#### Water retention in air and soil

Figure 8 shows the water retention of sample B3 in air at 40, 60, and 80°C. The result suggests that the synthesized copolymers have a good water-retaining capacity in air even at high temperature. The swollen superabsorbents give a higher water retention at low temperature than that at high temperature in air.

Figure 9 shows that the water retention of soil was enhanced using the poly(MLN-AAM-HEMA) superabsorbent (sample B3). The water in the soil without superabsorbents was almost completely lost at 30°C after 3 days, while the soil with sample B3 (2 wt % of the soil) held 5% of the total water after 6 days under an atmosphere of 30°C. The water-retention test suggests valuable potentials of the synthesized superabsorbents in practical applications such as in agriculture and horticulture.

#### CONCLUSIONS

The novel copolymer superabsorbents of crosslinked poly(MLN-AAM) and crosslinked poly(MLN-AAM-HEMA) were synthesized by inverse-suspension polymerization with MLN, AAM, and HEMA as the



**Figure 9** Water retention of the synthesized copolymers in soil at 30°C, B3 content: (1) 2 wt % of soil; (2) 0%.

comonomers, KPS as the initiator, NMBA as the crosslinking agent, Span as the suspending agent, and cyclohexane as the continuous phase. The synthesized beads were collected by precipitation with excess methanol. The influence of the reaction parameters on the water absorbency of the synthesized copolymers was investigated. The optimum conditions are as follows: the molar ratio of MLN:AAM:HEMA, 19.0:79.6:1.4; the neutralization of MLN, 90%; the concentration of the initiator (KPS), 1.2 wt % of the total monomers; the concentration of the crosslinking agent (NMBA), 0.2 wt % of the total monomers; the suspending agent (Span-80), 0.1 g; cyclohexane, 80 cm<sup>3</sup>; and the volume ratio of the aqueous phase to the organic phase, 1:8. The optimum superabsorbent obtained (sample C3) gives a high water absorbency value of 1200 g/g in distilled water and 330 g/g in a 0.9% NaCl solution. It was found that the osmotic pressure attributable to the

polymer network and the hydrophilic functional groups of the synthesized copolymers are the vital driving forces for the water absorbency and water retention. The water absorbency of the synthesized copolymers depended highly on the type of suspending agents due to the different particle sizes of the obtained copolymer beads by different suspending agents. The water absorbency of the synthesized copolymers decreases with an increasing concentration of the salt and alcohol solutions. At the same concentration, the superabsorbents have a tendency to absorb water in the salt and alcohol solutions in the order NaCl > CaCl<sub>2</sub> > AlCl<sub>3</sub> and glycerol > glycol > methanol > ethanol, respectively. The synthesized copolymers show good water retention in air and soil at a high temperature. The water retention of the soil was greatly enhanced by using the superabsorbent (sample B3).

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