# Ultraviolet-Induced Decomposition of Acrylic Acid-Based Superabsorbent Hydrogels Crosslinked with *N,N*-Methylenebisacrylamide

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**ABSTRACT:** Most acrylic acid-based superabsorbent hydrogels, which have been widely used in many applications, are crosslinked with water-solvable crosslinker *N,N*-methylenebisacrylamide (NMBA), which is easy to hydrolyze when radiated by ultraviolet, leading to decomposition of the superabsorbent hydrogels. In this article, ultraviolet-induced decomposition of acrylic acid-based superabsorbent hydrogels crosslinked with NMBA was investigated by weight loss method under ultraviolet radiation. The results showed that the decomposition rate of the superabsorbent hydrogels was controlled by ultraviolet-induced activation of amide groups on the networks when the intensity of ultraviolet radiation was low, whereas it was controlled by hydrolysis of amide groups on NMBA molecules when the intensity of ultraviolet radiation was high. The ultraviolet stability of acrylic acid-based superabsorbent hydrogels crosslinked with NMBA can be improved by increasing the neutralization degree of acrylic acid, increasing the dosage of crosslinker NMBA, or introducing acrylamide as comonomer. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3435–3441, 2008

**Key words:** superabsorbent hydrogels; ultraviolet stability; acrylic acid; acrylamide; decomposition; *N,N*-methylenebisacrylamide

## INTRODUCTION

Superabsorbent hydrogels are three-dimensional crosslinked polymers which can absorb large amount of water compared with general absorbing materials, and the absorbed water is hardly removable even under pressure.[1,2] Because of their excellent properties such as hydrophilicity, high swelling capacity, lack of toxicity, and biocompatibility, they can be used for many applications including soil conditioners for agriculture and horticulture, disposable diapers, absorbent pads, water blocking tapes, gel actuators, drilling fluid additives, polymer cracks blocking materials, feminine napkins, firefighting, extraction of precious metals, extraction of solvents, release of agrochemicals, adsorption of some cationic dyes, uranyl ions, and serum albumin, etc.[3–7] The use of superabsorbent hydrogels for agricultural applications has shown encouraging results, as they have been observed to help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in the soil, and increase plant growth rate. The use of superabsorbent hydrogels for additional applications, such as communication cables, industrial absorbents, anti-redecomposition agents for detergent formulations, artificial snow for winter sports, absorption-release of humidity, toys, cosmetics, and prevention of moisture ingress into walls and ceilings is in the experimental stage.[8,9] In all the aforementioned applications, the amount of water absorption and retention property is the most important. Meanwhile, to reduce the cost of the product, it is expected that the superabsorbent hydrogels have longer life.

Superabsorbent hydrogels have been synthesized by modification of natural resources such as starch, cellulose, proteins, chitin/chitosan, gum, etc., or by polymerization/copolymerization of petroleum-based water-solvable monomers such as acrylic acid (AA).[10–15] Superabsorbent hydrogels based on AA have been widely investigated by many researchers, and they have been successfully used in many applications.[16–21] *N,N*-methylenebisacrylamide (NMBA), a water-solvable monomer, which has two vinyl groups on its molecule, is the most popular crosslinker for AA-based superabsorbent hydrogels.[22–28]

It has been found that AA-based superabsorbent hydrogels crosslinked by NMBA are easy to lose their water absorption and retention property when used under sunlight, because crosslinker NMBA will hydrolyze under ultraviolet radiation, leading to disassembly of the three-dimensional crosslinked structure of the superabsorbent hydrogels.[29] Our essential idea in this article is to design a kinetics model of ultraviolet-induced decomposition of AA-based superabsorbent hydrogels crosslinked with NMBA, and evaluate the factors which influence ultraviolet-induced decomposition of AA-based superabsorbent hydrogels crosslinked with NMBA.

## EXPERIMENTAL

### Materials

AA, acrylamide (AAm), NMBA, NaOH, $K_2S_2O_8$, and $NaHSO_3$, AR grade, were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China) and used as received; UVB lamp, wavelength range is 280–400 nm, 250 W per lamp.

### Synthesis of superabsorbent hydrogels

Typically, in a 400-mL beaker, cooled with 20°C recycled water bath, 15.5 g distilled water was mixed with AA (the amount of AA was precalculated according to aimed composition of the superabsorbent hydrogels) under stirring, and then the stirred AA aqueous solution was neutralized by dropwise addition of sodium hydroxide aqueous solution (16.3 g sodium hydroxide and 36.1 g water). The neutralization was 0, 20, 40, 60, 80, and 100%, respectively, to obtain sample superabsorbent hydrogels with different composition. AAm was added to the solution and fully dissolved by stirring (the amount of AAm was precalculated according to aimed composition of the superabsorbent hydrogels), and the total monomers concentration was 43.6%. A weighed crosslinker NMBA was dissolved in the monomers mixture at ambient temperature while fully stirring. A weighed initiator $Na_2HSO_3$ (0.5 wt % of total amount of the monomers) was dissolved in 5 mL water and the solution was mixed with the monomers solution under stirring firstly, and then another weighed initiator $K_2S_2O_8$ (0.5 wt % of total amount of the monomers) was dissolved in 5 mL water and the solution was mixed with the monomers solution under stirring. The monomers solution was polymerized at room temperature. Each sample could reach its highest temperature within nearly 10 min and a polymeric gel was formed. The product was cut into small pieces and then dried in a vacuum at 105°C for 24 h. The dried xerogel was milled and particles between 60- and 80-mesh sieves were collected for ultraviolet-induced decomposition testing.
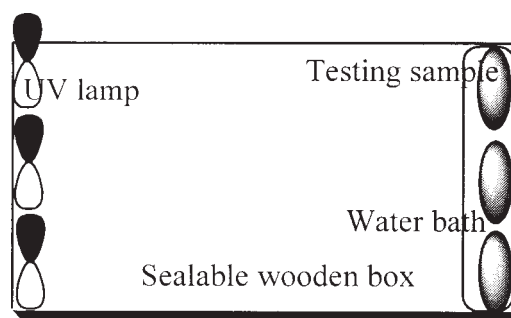


**Figure 1** Device for testing ultraviolet-induced decomposition of acrylic acid-based superabsorbent hydrogels crosslinked with NMBA.

### Ultraviolet-induced decomposition of superabsorbent hydrogels

The device for testing ultraviolet-induced decomposition of AA-based superabsorbent hydrogels crosslinked with NMBA is shown in Figure 1. The UV lamps were put on the left top of the sealable wooden box, while the water bath was put on the right bottom of the box. The preweighted xerogel was fully swollen in distilled water and put into transparent glass beakers. Put the hydrogels-containing beakers into water bath, seal the box and turn on the UV lamps when the temperature of superabsorbent hydrogels is stable. Turn off the UV lamps and take out the hydrogels after testing, wash the hydrogels with plenty of water to remove decomposed product which is water-solvable. The residual hydrogels were dried in a vacuum at 105°C for 24 h and weighted.

Weight loss of the superabsorbent hydrogels can be calculated as eq. (1):

$$WL = (W_1 - W_2)/W_1 \qquad (1)$$

where WL (%) is the weight loss of the superabsorbent hydrogels; $W_1$ (mg) is weight of the xerogel before testing; $W_2$ (mg) is weight of the xerogel after testing.

## RESULTS AND DISCUSSION

### Development of the kinetics model

For AA-based superabsorbent polymer crosslinked with NMBA, it is stable under ultraviolet radiation when the polymer is dry (xerogel), while it is easy to decompose under ultraviolet radiation when the polymer is fully swollen (hydrogels). The decomposition product is water-solvable, and the amount of decomposition product is almost the same as xerogel. The reason is hydrolysis of crosslinker NMBA induced by ultraviolet radiation, leading to disassembly of the crosslinking structure of the hydrogels, as our previous study presented in ref. 29. The ultra-
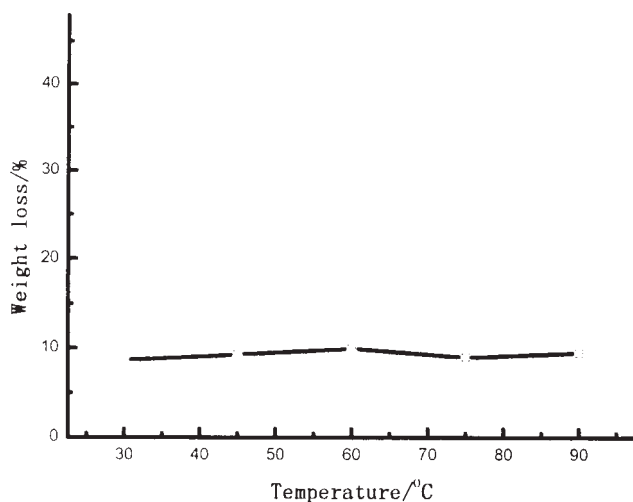
**Figure 2** Ultraviolet-induced decomposition of acrylic acid-based superabsorbent hydrogels crosslinked with NMBA.

violet-induced decomposition of acid-based superabsorbent polymer crosslinked with NMBA is illustrated in Figure 2.

The energy of C—N bond in amide groups is 288.9 kJ/mol, which corresponds to the energy of ultraviolet with the wavelength of 414 nm. When the AA-based superabsorbent hydrogels crosslinked with NMBA radiate with ultraviolet, C—N bond in amide group will absorb the UV energy, thus, the amide group on the networks will be activated by the ultraviolet radiation and become activated molecule (where $I_a$ is intensity of ultraviolet radiation):



$$\tag{2}$$

For ultraviolet-activated amide groups in the superabsorbent hydrogels, they can either lose their energy and become normal molecules, or combine with $H^+$ in the hydrogels, as shown in eqs. (3) and (4) (where $k_1$ and $k_2$ are rate constants):



$$\tag{3}$$



$$\tag{4}$$

For ultraviolet-activated amide groups combined with $H^+$, carbon atom can be attacked by $H_2O$ then the amide group hydrolyzed (where $k_3$ is rate constant):



$$\tag{5}$$

To make the system easier, above process can be described as follows:

$$A \xrightarrow{I_a} A^*$$

$$A^* \xrightarrow{k_1} A$$

$$A^* + H^+ \xrightarrow{k_2} B \tag{6}$$

$$B + H_2O \xrightarrow{k_3} C + D + H^+$$

where A is amide group in the superabsorbent hydrogels, $A^*$ is ultraviolet-activated amide group in the superabsorbent hydrogels, B is ultraviolet-activated amide group combined with $H^+$, C is —COOH group, and $D$ is —$NH_2$ group. For dried superabsorbent polymer containing no water (xerogel), only the reaction expressed in eq. (3) will happen while the reactions expressed in eqs. (4) and (5) would not happen, it is stable under ultraviolet radiation.

Before developing the kinetic model, proper postulations should be made to make the system easier. These postulations are as follows:

1. Water concentration [$H_2O$] is constant, because the amount of water in the superabsorbent hydrogels is much more than that of amide groups;
2. The concentration of either $A^*$ or B is constant;
3. Every amide group on either AAm or NMBA has the same chance to absorb ultraviolet radiation and to be activated, and every ultraviolet-activated amide group has the same chance to lose its energy or hydrolyze;
4. One of the two amide groups in NMBA molecule hydrolyzing will lead to disassembly of the crosslinking structure crosslinked with that NMBA molecule.

According to the earlier mechanism, the kinetic equations can be written as follows:

$$\frac{dC}{dt} = k_3[B][H_2O] \tag{7}$$

$$\frac{dB}{dt} = k_2[A^*][H^+] - k_3[B][H_2O] \tag{8}$$

$$\frac{dA^*}{dt} = I_a - k_1[A^*] - k_2[A^*][H^+] \tag{9}$$

According to our postulations, eq. (7) can be described as in eq. (10), and eq. (9) can be described as in eq. (11), and eq. (12) can be obtained according to eqs. (10) and (11) as follows:

**Figure 3** Influence of temperature on weight loss of the superabsorbent hydrogels (power of UV lamp = 250 W).

$$\frac{dC}{dt} = k_2[A^*][H^+] \tag{10}$$

$$[A^*] = \frac{I_a}{k_1 + k_2[H^+]} \tag{11}$$

$$\frac{dC}{dt} = \frac{k_2 I_a[H^+]}{k_1 + k_2[H^+]} \tag{12}$$

According to the molecular weight of AAm (71) and NMBA (154), when the dosage of NMBA is $X_1$ (wt %), the dosage of AAm is $X_2$ (wt %), the proportion of ultraviolet-activated amide groups on NMBA molecules in total ultraviolet-activated amide groups can be described as in eq. (13) as follows:

$$71X_1/(71X_1 + 77X_2) \tag{13}$$

Thus, eq. (12) can be described as in eq. (14) as follows:

$$\frac{dC}{dt} = \frac{71X_1 k_2 I_a[H^+]}{(71X_1 + 77X_2)(k_1 + k_2[H^+])} \tag{14}$$

Because the crosslinking density of the superabsorbent hydrogels is changing with decomposition under ultraviolet radiation, and the decomposed product which is water-solvable was removed by water wash after testing, the weight loss is in proportion with $dC/dt$ and the proportion of hydrolyzed NMBA in total NMBA. Thus, the weight loss rate of the superabsorbent hydrogels can be described as in eq. (15) as follows:

$$-\frac{dW}{dt} = \frac{71X_1 k_4 k_5 k_2 I_a[H^+]}{(71X_1 + 77X_2)(k_1 + k_2[H^+])} \tag{15}$$
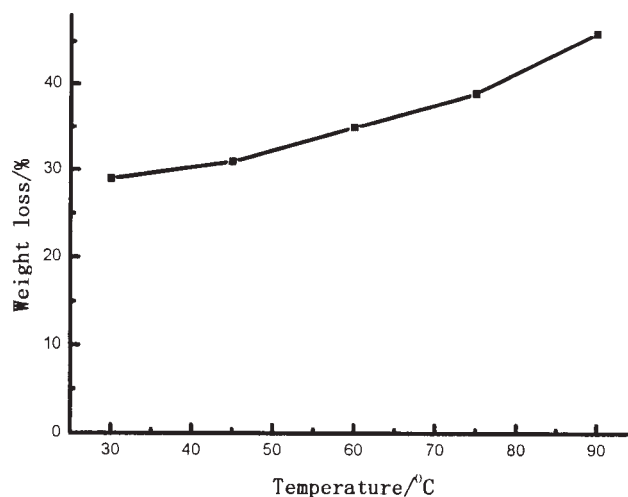
**Figure 4** Influence of temperature on weight loss of the superabsorbent hydrogels (power of UV lamp = 1500 W).

where $-dW/dt$ is weight loss rate of the superabsorbent hydrogels, $k_4$ is the proportion of hydrolyzed NMBA in total NMBA, and $k_5$ is the proportion constant of $-dW/dt$ to $dC/dt$.

### Influence of temperature and UV power on weight loss of the superabsorbent hydrogels

According to Figures 3–6, for the same testing sample (the content of AM was 30 wt %, the content of crosslinker was 0.073 wt %, the neutralization degree of AA was 80%), effect of temperature on weight loss of the superabsorbent hydrogels is different when intensity of ultraviolet radiation is different. When intensity of ultraviolet radiation is low (the power of UV lamps is 250 W), temperature had no apparent influence on weight loss of the superabsorbent hydrogels; whereas, when intensity of ultraviolet radiation is high (the power of UV lamps is 1500 W), weight loss
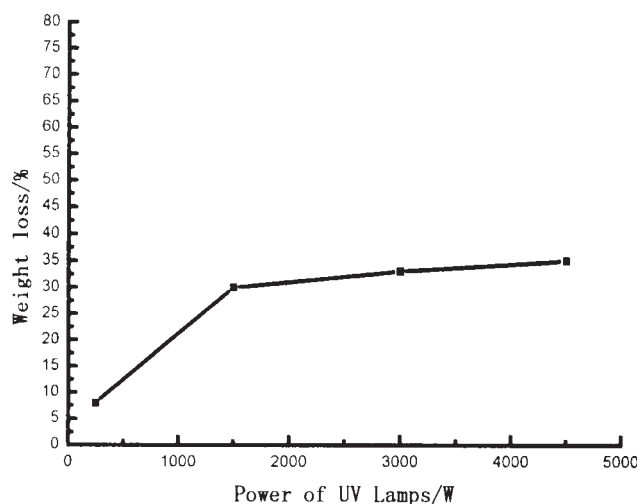


**Figure 5** Influence of intensity of ultraviolet radiation on weight loss of the superabsorbent hydrogels (30°C).
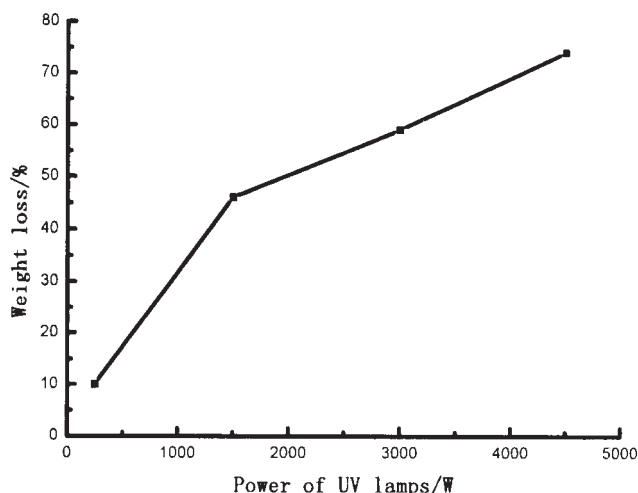
**Figure 6** Influence of intensity of ultraviolet radiation on weight loss of the superabsorbent hydrogels (90°C).

of the superabsorbent hydrogels increased with increasing temperature. In the same way, intensity of ultraviolet radiation affects weight loss of the superabsorbent hydrogels too. When the temperature is 30°C, weight loss of the superabsorbent hydrogels did not change much with increasing of ultraviolet radiation intensity; whereas, when the temperature is 90°C, weight loss of the superabsorbent hydrogels increased rapidly with increasing ultraviolet radiation intensity. The results showed that decomposition rate of the superabsorbent hydrogels was controlled by ultraviolet-induced activation of amide groups on the networks when the intensity of ultraviolet radiation was low, whereas it was controlled by hydrolysis of amide groups on NMBA molecules when the intensity of ultraviolet radiation was high. When intensity of ultraviolet radiation was low, activation rate of amide groups in the superabsorbent hydrogels was lower than their hydrolysis rate, activated amide groups were not easy to lose their energy while they were easy to hydrolyze; thus, $k_2$ is much bigger than $k_1$ in eq. (15). In this instance, eq. (15) can be described by eq. (16) as follows:

$$-\frac{dW}{dt} = \frac{71X_1k_4k_5I_a}{72X_1 + 77X_2} \quad (16)$$

When intensity of ultraviolet radiation was high, hydrolysis rate of amide groups in the superabsorbent hydrogels were lower than their activation rate, activated amide groups were easy to lose their energy and become normal amide groups; thus, $k_1$ is much bigger than $k_2$ in eq. (15). In this instance, eq. (15) can be described by eq. (17) as follows:

$$-\frac{dW}{dt} = \frac{71X_1k_4k_5k_2I_a[\mathrm{H^+}]}{k_1(71X_1 + 67X_2)} \quad (17)$$

Because amide groups on the networks of superabsorbent hydrogels activated by ultraviolet radiation either lose their energy and become normal or hydrolyze, the results can be used to describe rivalrousness of the two reactions.

### Influence of crosslinker dosage

Since the reason of ultraviolet-induced decomposition of AA-based superabsorbent hydrogels crosslinked with NMBA is hydrolysis of crosslinker NMBA, the ultraviolet stability of the superabsorbent hydrogels can be significantly improved by increasing NMBA dosage, as shown in Figure 7 (the content of AM was 30 wt %, the neutralization degree of AA was 80%). When the dosage of NMBA increased from 0.032% to 0.139%, the weight loss decreased from 100% to 9.3%. Although $X_1$ in eq. (15) increased as the dosage of NMBA increased, more ultraviolet energy was needed to fully decompose the crosslinker, because $k_4$ in eq. (15) (proportion of decomposed NMBA in total NMBA) decreased more.

### Influence of neutralization degree of acrylic acid

It has been reported that neutralization degree of AA had influence on water absorption property of AA-based superabsorbent hydrogels,[30] but it was found that neutralization degree of AA also had significant influence on their ultraviolet stability. Figure 8 shows effect of neutralization degree of AA on weight loss of the superabsorbent hydrogel (the content of AM was 30 wt %, the content of crosslinker was 0.073 wt %). From Figure 8 one can find ultraviolet stability of AA-based superabsorbent hydrogels crosslinked by NMBA was significantly improved by increasing neutralization degree of AA;
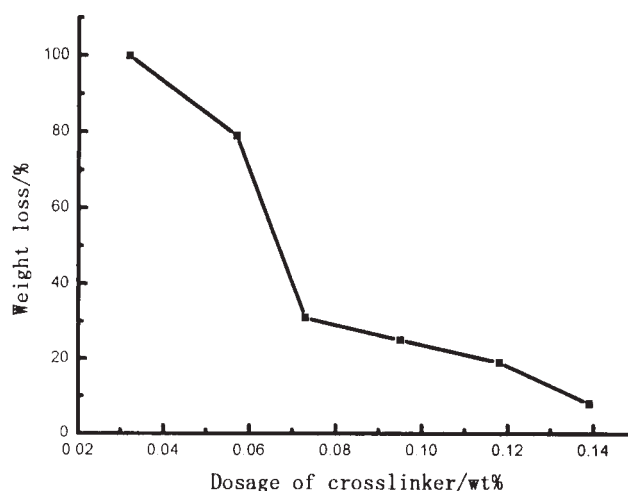


**Figure 7** Influence of crosslinker on weight loss of the superabsorbent hydrogels (the content of AM was 30 wt %, the neutralization degree of acrylic acid was 80%).

the weight loss decreased from 42.0% to 30.4% as the neutralization degree of AA increased from 0 to 100%. Hydrolysis of amide group in the superabsorbent hydrogels can be catalyzed by either $H^+$ or $OH^-$; and the concentration of $H^+$ or $OH^-$ was very low when the neutralization degree was 100%. Additionally, weight loss of the superabsorbent hydrogels will decrease as the concentration of $H^+$ decrease according to eq. (15).

### Influence of acrylamide

Because both AAm and NMBA have amide group on their molecular structures, AAm was introduced as comonomer to copolymerize with partially neutralized AA (sodium acrylate) and NMBA, to obtain NMBA-crosslinked poly(sodium acrylate-*co*-acrylamide) copolymer superabsorbent hydrogels, and we hope the copolymer superabsorbent hydrogels will have improved ultraviolet stability. Effect of AAm content in the poly(sodium acrylate-*co*-acrylamide) copolymer superabsorbent hydrogels on the ultraviolet stability is shown in Figure 9 (the content of crosslinker was 0.073 wt %, the neutralization degree of AA was 80%). One can find that the ultraviolet stability of AA-based superabsorbent hydrogels crosslinked by NMBA can be significantly improved by introducing AAm as comonomer; the weight loss decreased from 100% to 0% as the AAm content increased from 0 to 70 wt %. This is because the content of AAm was far more than that of NMBA in the superabsorbent hydrogels, most UV energy was absorbed by the amide group on AAm when the superabsorbent hydrogels was radiated by ultravio-

**Figure 9** Influence of acrylamide on weight loss of the superabsorbent hydrogels (the content of crosslinker was 0.073 wt %, the neutralization degree of acrylic acid was 80%).

let. As for eq. (15), $X_2$ increased when the content of AAm increased leading to $-dW/dt$ decrease.

### CONCLUSION

Ultraviolet-induced decomposition kinetics model of AA-based superabsorbent hydrogels crosslinked by NMBA was developed, and factors which influence ultraviolet-induced decomposition of the superabsorbent hydrogels were investigated by weight loss method under ultraviolet radiation. We conclude that the decomposition rate of the superabsorbent hydrogels was controlled by ultraviolet-induced activation of amide groups on the networks when the intensity of ultraviolet radiation was low, whereas it was controlled by hydrolysis of amide groups on NMBA molecules when the intensity of ultraviolet radiation was high. The ultraviolet stability of AA-based superabsorbent hydrogels crosslinked by NMBA can be improved by increasing the neutralization degree of AA, increasing the dosage of NMBA, or introducing AAm as comonomer. Since change of neutralization degree of AA, change of crosslinker dosage, and introducing AAm as comonomer will influence the amount of water absorption and retention property of the superabsorbent hydrogels, one can design the composition of the superabsorbent hydrogels suitable for special applications based on these findings.
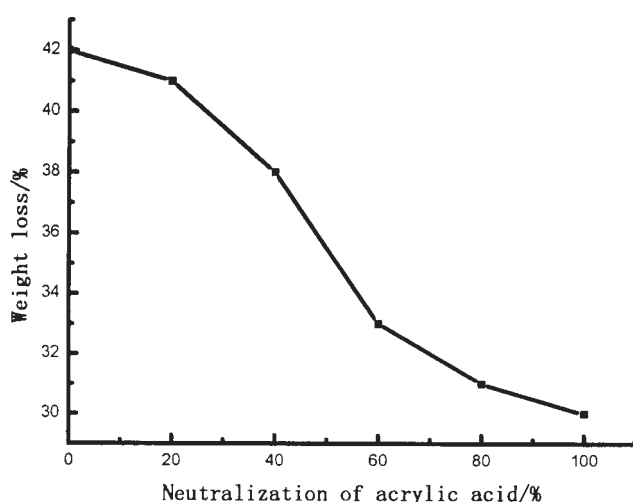
**Figure 8** Influence of neutralization of acrylic acid on weight loss of the superabsorbent hydrogels (the content of AM was 30 wt %, the content of crosslinker was 0.073 wt %).
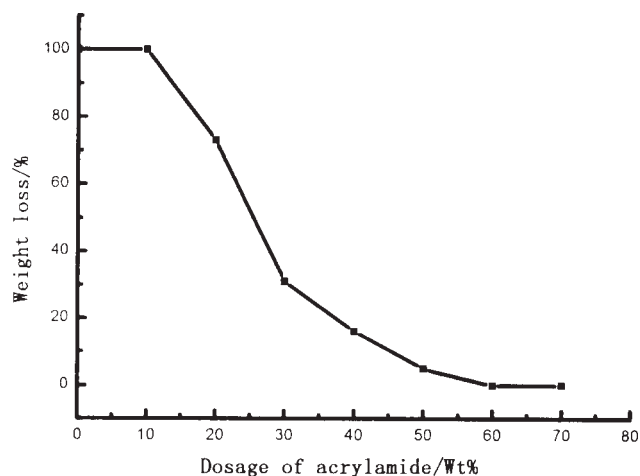
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