

# Radiation Synthesis of Hydrogels to Enhance Sandy Soils Water Retention and Increase Plant Performance

H. A. Abd El-Rehim, El-Sayed A. Hegazy, H. L. Abd El-Mohdy

National Center for Radiation Research and Technology, P. O. Box No. 29 Nasr city, Cairo, Egypt

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**ABSTRACT:** Preparation and characterization of superabsorbent hydrogels obtained by radiation induced crosslinking of polyacrylamide (PAAm), poly(acrylic acid) (PAAc), poly(vinyl alcohol) (PVA), and potassium polyacrylate (PAAcK) were investigated individually and in (PAAm)-binary systems for possible uses in agricultural fields. The swelling of the investigated hydrogels was mainly related to the type of their hydrophilic functional groups and/or the presence of polarized charges. The preparation conditions, such as irradiation dose and hydrogel blend compositions, that influence the water absorbency of PAAm/PAAcK copolymers and alter their gel content and crosslinking density were investigated. The higher the irradiation dose, the higher the gel content, and the lower the water absorbency. PAAm/PAAcK copolymer, possessing pore structure and fast swelling, was prepared by mixing the hydrogel components with a gas-forming agent, namely, ammonium carbonate. Studies were also made on the applications of such hydrogels to improve the physical and water retention prop-

erties of sandy soil for agricultural purposes. The effect of different types and amounts of hydrogels added to sandy soil on the emergence, vegetative growth, and wilting time of corn (*Zea mays*) plants was investigated. As the hydrogel level increased, the average of plant height, leaf width, total dry weight, corncob production, and time to wilt increased. The obtained results suggested that the PAAm/PAAcK hydrogels can improve sandy soil properties for cultivation, because they often absorb and keep water one thousand times more than their own weight, reduce watering frequency of the plants, and enhance water retention of soil matrix that results in an increase in plant growth and performance. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1360–1371, 2004

**Key words:** radiation; crosslinking; polyacrylamide; potassium polyacrylate; agriculture; superabsorbent hydrogels; wilting time

## INTRODUCTION

Superabsorbents are highly swollen hydrophilic materials that are insoluble in water. They can absorb large amounts of water many times their own weights, resulting in drastically increased volumes. Some of them are currently commercialized and used in various fields such as industry,<sup>1–2</sup> medicine,<sup>3</sup> and other advanced technologies,<sup>4–7</sup> where water absorbency and water retention are important.

In recent years, there has been renewed interest in applying water superabsorbent materials for alleviation of certain agricultural problems.<sup>8–9</sup> They have been successfully used as soil amendments in the horticulture industry to improve the physical properties of soil in view of increasing their water-holding capacity and/or nutrient retention of sandy soil<sup>10–11</sup> to be comparable to silty clay or loam.<sup>12</sup> Superabsorbent hydrogels potentially influence soil permeability,<sup>13</sup> density, structure, texture,<sup>14</sup> evaporation,<sup>15</sup> and infil-

tration rates of water through the soils.<sup>16</sup> The hydrogels reduce irrigation frequency<sup>17</sup> and compaction tendency,<sup>18</sup> stop erosion and water runoff,<sup>19</sup> and increase the soil aeration<sup>20</sup> and microbial activity.<sup>21</sup> The hydrogels also act as a slow release system by favoring the uptake of some nutrient elements, holding them tightly, and delaying their dissolution.<sup>22</sup> Consequently, the plant can still access some of the fertilizers, resulting in improved growth and performance rates.<sup>23</sup>

On the other hand, superabsorbent polymers in agriculture can be used as retaining materials in the form of seed additives<sup>24</sup> (to aid in germination and seedling establishment), seed coatings,<sup>25</sup> root dips,<sup>26</sup> and for immobilizing plant growth regulator<sup>27</sup> or protecting agents for controlled release.<sup>28</sup> Moreover, some hydrophilic polymers such as polyacrylates could also be used to remediate the sandy soil contaminated with heavy metals and improve the plant growth by reducing the metal solubility and decreasing their concentrations in the shoots.<sup>29</sup>

Many kinds of superabsorbent hydrogels were prepared from synthetic and natural polymers; the following four types of them have so far been developed as agricultural polymers: (1) starch-graft copolymer

Correspondence to: H. A. Abd El-Rehim (ha\_rehim@hotmail.com).

(obtained by graft polymerization of polyacrylonitrile onto starch followed by saponification of the acrylonitrile units); (2) crosslinked polyacrylates; (3) crosslinked polyacrylamides; and (4) crosslinked acrylamide–acrylate copolymers containing a major percentage of acrylamide units.

The superabsorbents were prepared by graft copolymerization, crosslinking polymerization, and other hydrophilization and water insolubilization. Noticeable interest in the application of radiation techniques to obtain hydrogels for different purposes began in the late 1960s.<sup>30</sup> A radiation technique seems to be promising for the preparation of hydrogels, because a polymer swollen state undergoes crosslinking on irradiation to yield a gel-like material containing chemically stable C—C bond. This polymer is not contaminated with foreign additives and loses its ability to dissolve in its customary solvents, and its mechanical properties are improved. Acrylamide and Reclamer-ameliorator (terpolymer grafted on a cellulosic polymeric gels) are prepared by  $\gamma$ -radiation and successfully used as carriers of agrochemicals and soil conditioners for sandy soil plantation.<sup>31–32</sup>

Relatively low cost, high reduction of irrigation-induced erosion and soil loss, ease of use, and integration make polyacrylamide (PAAm) the best management practice worth looking into by any agricultural operation.<sup>33–35</sup> Because PAAm tends to coil in aqueous systems, it needs an ionic charge instead of a neutral one to enhance intramolecular electrostatic repulsion responsible for polymer chains extension.<sup>36</sup> Most of the hydrogels marketed for agriculture come from the ionic hydrogels, which represent a recent advance in polymer technology for crop protection.

In this work, superabsorbent hydrogels, obtained by radiation-induced crosslinking of PAAm, poly(acrylic acid) (PAAc), potassium polyacrylate (PAAcK), or poly(vinyl alcohol) (PVA), were prepared individually and in PAAm–binary systems for possible agricultural uses as soil conditioners and seed additives. The factors affecting the hydrogel swelling properties, including nature of polymer, irradiation doses, polymer crosslinking density, and copolymer compositions, were studied. The ability of such hydrogels to enhance the sandy soil water retention and aid in corn (*Zea mays*) emergence and performance was investigated.

## EXPERIMENTAL

### Materials

Commercial PAAm granules (average  $M_w$  5,000,000–6,000,000) and AAc (purity 99%; Merck, Darmstadt, Germany) were used as received. PAAcK was prepared by neutralizing poly(acrylic acid) with KOH. PVA ( $M_w$  14,000) was supplied by Laboratory Rasayan (India). The other chemicals, such as solvents and

inorganic salts, were reagent grade and used without further purification.

### Methods and apparatus

#### Preparation of hydrogels

An appropriate weight of dry polymer (4 g) in distilled water (96 mL) was stirred at 60°C until it completely dissolved. The solution of polymers or a blend of them was poured into a petri dish, left for 3 h, and exposed to electron beam irradiation of high energy: 1.5 MeV; beam current: 25 mA; power: 37.5 kW; scan width: variable up to 90 cm. The obtained crosslinked hydrogel was cut into small pieces and left to dry at 25°C.

#### Gel determination

To extract the insoluble parts of the hydrogels (i.e., the gelled part), the prepared hydrogels were soaked in water for 48 h at 100°C. Then, they were taken out and washed with hot water to remove the soluble part, dried, and weighed. The gel percent in the hydrogel was determined from the equation

$$\text{Gel (\%)} = (W_e/W_g) \times 100$$

where  $W_e$  and  $W_g$  are dry hydrogel weights after and before extraction, respectively.

#### Swelling measurement

The dried hydrogels of known weights were immersed in distilled water or saline solution at 25°C until the swelling equilibrium was reached (almost 24 h). The gel was removed, blotted quickly with absorbent paper, and then weighed. For accuracy, the experiment was repeated twice for each sample. The following equation was used to determine water uptake

$$\text{Water absorbency} = (W_s - W_g)/W_g$$

where  $W_s$  and  $W_g$  represent the weights of wet and dry gel films, respectively.

#### Soil preparation

Many plots of  $2 \times 2 \text{ m}^2$  were constructed in sandy loam soil. Each plot acted as a replicate and was divided into four ridges 2 m long at equal distances of 25 cm. Eight holes per ridge were pigged to 12 cm depth into which the proper amount of hydrogel was added and each experiment uses four replicates per treatment. Similarly, other plots were prepared for sandy loam soil reference (control) without any treat-

**TABLE I**  
Physical and Chemical Characteristic of the Soil  
Used in the Agricultural Experiments

Characteristics of loam soil	
% Total Sand	74
Texture of sand	
% above 1.00 mm	3
% between 1.00 and 0.5 mm	6
% between 0.5 and 0.25 mm	20
% between 0.25 and 0.05 mm	45
% Silt	19
% Clay	7
% Organic matter	3.5
pH	7.5

ment. The physical and chemical characteristics of the soil used in this study are shown in Table I.

#### Plantation

Corn (*Z. mays*) plant seeds were sown 5 cm apart from the gel-soil holes. Water of irrigation remained constant for all replicates in different experiments. The average number of emergent corn plants at different time intervals was calculated. The average of plant height and leaf width was determined by a ruler and the average of total dry weight of plant was detected.

#### Scanning electron microscopy

The lyophilized dried hydrogels were examined with a JEOL JSM-5400 scanning electron microscope (SEM). The surfaces of the dry hydrogels were sputter-coated with gold for 3 min.

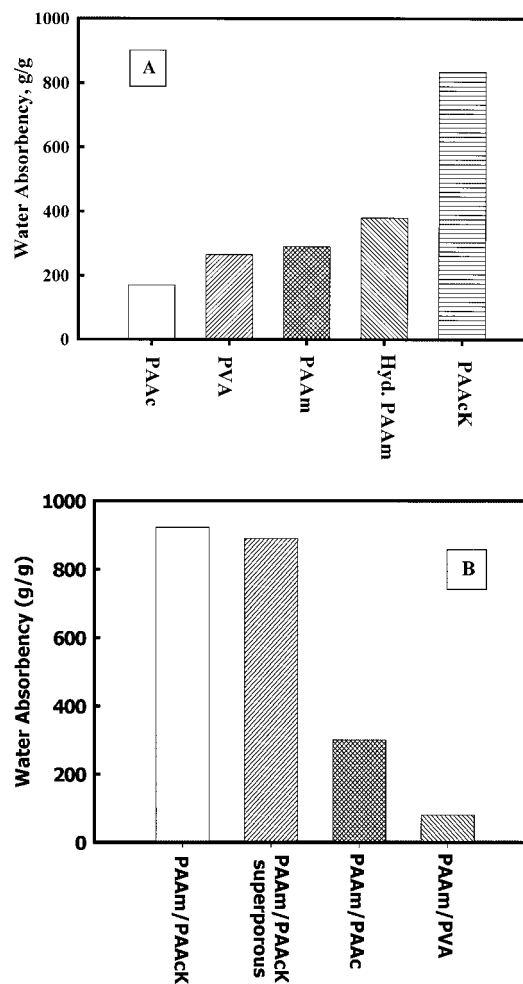
## RESULTS AND DISCUSSION

#### Preparation of superabsorbent materials

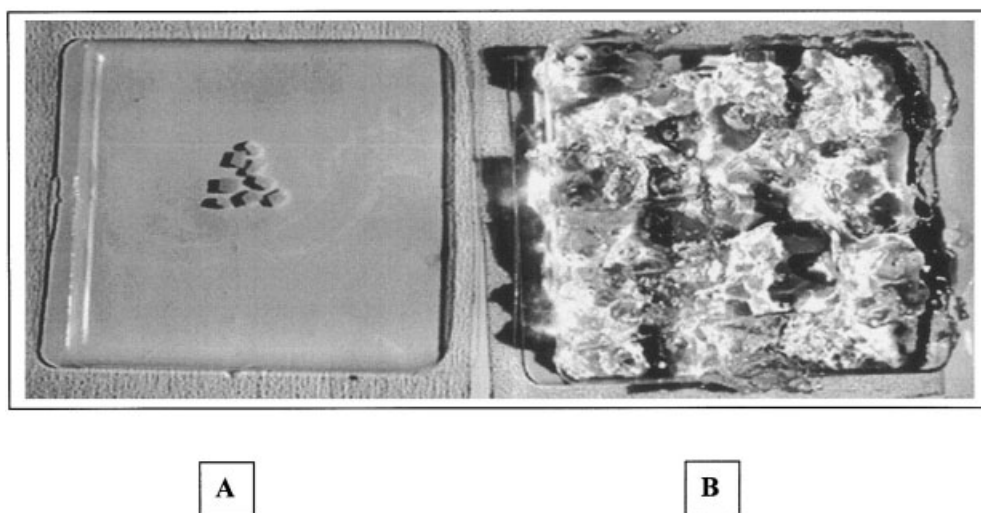
Different types of polymers, including neutral and charged hydrogels such as PAAm, PVA, PAAc, and PAAcK, were crosslinked individually and in PAAm-binary systems by using electron beam irradiation. Accordingly, the swelling behavior of such hydrogels in distilled water was determined and is shown in Figure 1(A, B). For individual systems, it is observed that the swelling degree of ionic crosslinked PAAcK hydrogel is higher than that of crosslinked PAAm, PAAc, and PVA. The water absorbency of prepared crosslinked hydrogels decreases in the order: PAAcK, KOH hydrolyzed PAAm, PAAm, PVA, and PAAc [Fig. 1(A)]. Meanwhile, the swelling degree of PAAm-binary systems follows the order: PAAm/PAAcK  $\cong$  superporous PAAm/PAAcK [in which PAAm/PAAcK was prepared in the presence of 1%  $(\text{NH}_4)_2\text{CO}_3$  (wt/wt) and dried in ethanol] > PAAm/

PAAc > PAAm/PVA [Fig. 1(B)]. The results suggested that the mixing of PAAcK with PAAm enhances the swelling behavior of the latter, which leads to an increase in the PAAcK/PAAm volume without dissolving in water, as shown in Figure 2. However, there is no significant effect on PAAm swelling property when it is copolymerized with PAAc, while a significant decrease in the swelling of PAAm is observed when it is copolymerized with PVA.

The swelling properties of the investigated crosslinked hydrogels are mainly related to the elasticity of the network and the presence of hydrophilic functional groups and/or the polarized charges. Water absorbency of hydrogels which possess weakly hydrophilic  $-\text{COOH}$ ,  $-\text{CONH}_2$ , or  $-\text{OH}$  groups is lower than that of the strong  $-\text{COOK}$  ones. The high swelling of PAAcK can be attributed to the electro-



**Figure 1** (A) Water absorbency of different crosslinked polymeric hydrogels immersed in distilled water. Polymer concentration (4 wt % in water) and irradiation dose (30 kGy). (B) Water absorbency of different crosslinked copolymer hydrogels immersed in distilled water. Copolymer concentration (4 wt % in water); copolymer composition (50 : 50, wt/wt); irradiation dose (30 kGy).

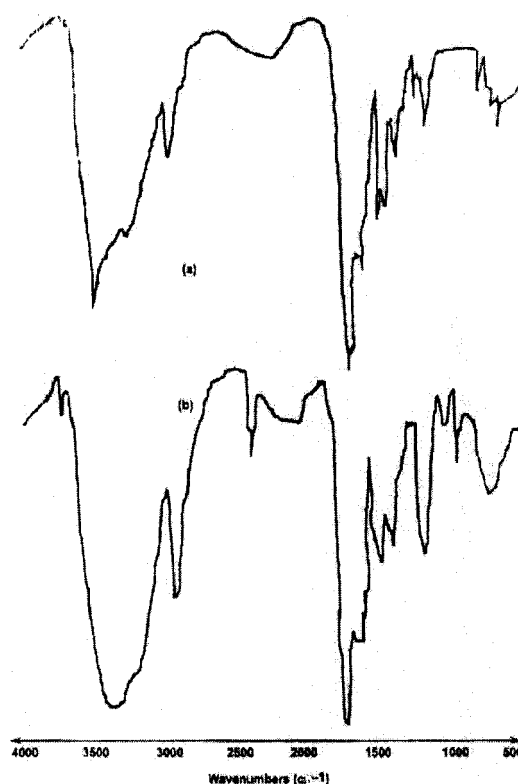


**Figure 2** (a) Dry and (b) swelled crosslinked PAAm/PAAcK hydrogels prepared at copolymer concentration (4 wt % in water); copolymer composition (50 : 50, wt/wt); irradiation dose (30 kGy).

static repulsion between charged groups on the network chains and the concentration difference of mobile ions inside and outside the hydrogel. On the other hand, the swelling of polymer containing weakly hydrophilic  $-\text{CONH}_2$  groups, which is higher than that for  $-\text{COOH}$  and  $-\text{OH}$  groups, can be explained according to the density and strength of hydrogen bonding formed between these functional groups. It is expected that the density and the strength of hydrogen bonding between  $-\text{COOH}$ , or  $-\text{OH}$  groups themselves, are higher and stronger than that for  $-\text{CONH}_2$  groups. Accordingly, the water uptake of PAAm is higher than that of PAAc or PVA. Such hydrogen bonding is responsible for decreasing the swelling behavior of the PAAm/PAAc binary system (i.e., the swelling of PAAm/PAAc copolymer is reduced because of the formation of strong hydrogen bonding between its components). FTIR spectra for individual PAAm and PAAm/PVA binary systems were performed and are shown in Figure 3. It is clear that the  $-\text{C}=\text{O}$  groups for polyacrylamide that appears at  $1690\text{ cm}^{-1}$  is shifted to a lower wave number at  $1675\text{ cm}^{-1}$ , indicating the formation of strong hydrogen bonding between PAAm and PVA.

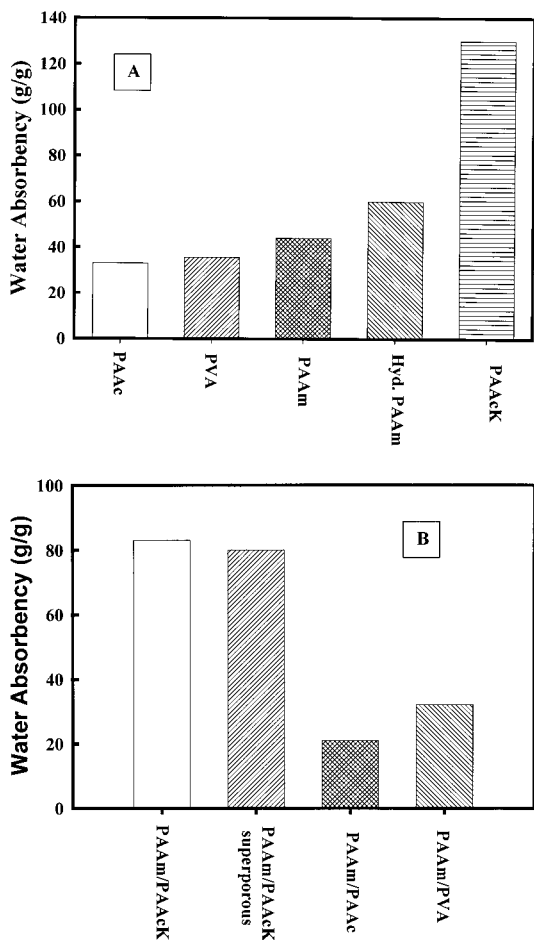
The phenomenon of gel swelling has been the subject of numerous studies in polymer physics. It was demonstrated that minute changes in external conditions such as temperature, solvent composition, and ionic strength can induce drastic changes in the state of the swollen network of the hydrogel.<sup>37</sup> In this connection, it is important to understand the osmotic and structural changes of hydrogel induced by addition of salts in the swelling medium. Therefore, the swelling behavior of different types of prepared hydrogels immersed in 1% NaCl solution (saline solution) was investigated and is shown in Figure 4(A, B). In general,

the swelling of hydrogels in saline solution is much lower than that obtained in distilled water. Also, it is clear that the swelling of charged hydrogels in saline solution is higher than that of the uncharged ones. The hydrogel water absorbencies follow the order: PAAcK



**Figure 3** FTIR spectra for (a) crosslinked PAAm and (b) PAAm/PVA. Hydrogels prepared at copolymer concentration (4 wt % in water); copolymer composition (50 : 50, wt/wt); irradiation dose (30 kGy).





**Figure 4** (A) Water absorbency of different crosslinked polymeric hydrogels immersed in (1% NaCl solution). Polymer concentration (4 wt % in water); irradiation dose (30 kGy). (B) Water absorbency of different crosslinked copolymer hydrogels immersed in (1% NaCl solution). Copolymer concentration (4 wt % in water); copolymer composition (50 : 50, wt/wt); irradiation dose (30 kGy).

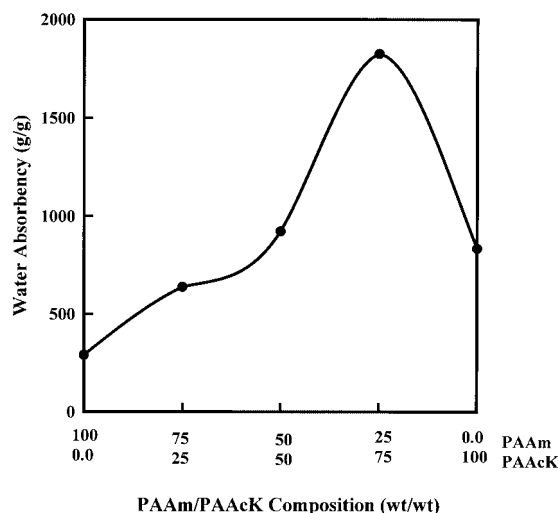
> hydrolyzed PAAm > PAAm > PAAc and PAAm/PAAcK > superporous PAAm/PAAcK > PAAm/PVA > PAAm/PAAc for individual and binary systems, respectively.

The obtained results can be attributed to the drastic effect of salts, which changes the swollen state of the macromolecules network. Salts may cause a swelling volume transition; these effects are usually explained by the changes of the water strength induced by ion dehydration that is responsible for the drastic changes in hydrogel swelling property. In other words, the swelling of PAAm/PAAcK gels is also associated with the difference between the mobile ion concentration inside and outside the gel. The presence of  $K^+$  mobile ions inside the gel increases the electroneutrality conditions and creates an additional osmotic pressure that expands the gel.<sup>38</sup>

The quality of the water absorbed by different types of hydrogels immersed in saline solution was investi-

gated. The salinity degree of the water absorbed by such hydrogels was determined by measuring the salinity of gel-immersing solution before and after the gel soaking process. It was found that the salinity of water absorbed by hydrogels is lower than that of the initial saline solution in which the investigated hydrogels were immersed. Also, the water salinity absorbed by PAAm/PAAcK is lower than that absorbed by PAAm or PAAm/PVA. The water salinity absorbed by PAAm/PAAcK is almost 50% of the initial saline solution; however, the salinity of water absorbed by PAAm and PAAm/PVA is 67 and 80% of initial saline solution, respectively. This means that the prepared hydrogels have the ability to select and absorb fresh water from saline water (i.e., such hydrogels possess the ability to desalinate brackish water).<sup>39</sup> Moreover, hydrogel-containing ionic character has a great ability to absorb fresh water compared with the nonionic ones investigated here. Thus, the salty soil can be reclaimed by using PAAm/PAAcK hydrogels that reduce the salinity around the plant roots by absorbing fresh water, which is suitable for the plant performance.

The previously obtained results showed that the most suitable hydrogel to improve the physicochemical properties of soil particles is PAAm/PAAcK, because it easily absorbs a large amount of water from fresh or saline water, possesses salt rejection properties, and a good ability to salinate brackish water. Therefore, the swelling of crosslinked PAAm, containing different amounts of PAAcK and prepared at different irradiation doses, was investigated.



**Figure 5** Swelling of crosslinked PAAm/PAAcK copolymers of different compositions immersed in distilled water. Polymer concentration (4 wt % in water); irradiation dose (30 kGy).

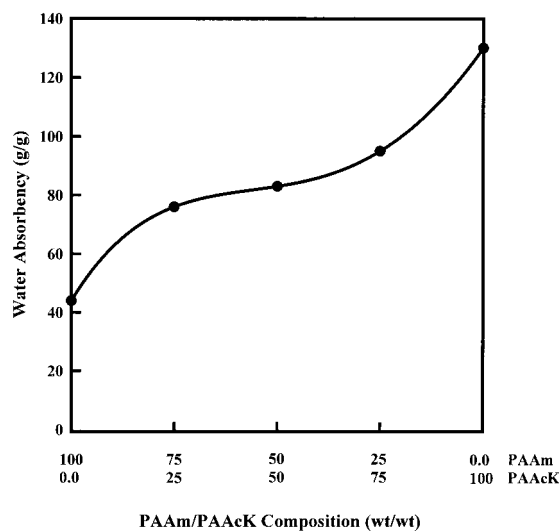
### Swelling properties of PAAm/PAAcK prepared at different copolymer compositions

The ionic charge content of PAAm/PAAcK, which affects its swelling property, is related to the ratio between the PAAm and PAAcK in the feed solution. Therefore, the swelling of PAAm/PAAcK copolymers of different compositions was investigated and the results are shown in Figure 5. It is clear that the water absorbency increases with increasing PAAcK content in the PAAm/PAAcK copolymer, reaching its maximum at a copolymer composition of (75/25) (PAAcK/PAAm). Thereafter, any increase in PAAcK leads to a decrease in PAAm/PAAcK water absorbency.

Improvement of hydrogel water absorbency can be induced by increasing the electrostatic repulsion of its network ionic charges. The increase of charged carboxylate groups in PAAm/PAAcK, which leads to an increase in ionic charge electrostatic repulsion, enhances its affinity toward water. The higher the ionic charge in the copolymer, the higher the water absorbency obtained. However, pure PAAcK hydrogel, that contains the highest ionic charges, shows low water absorbency compared with PAAcK-rich copolymers. This can be attributed to the high PAAcK content in copolymer feed solution, leading to a decrease in copolymer gel fraction. This means that the PAAcK soluble gel part was lost during the equilibrium swelling: as a result, its water absorbency decreased. The above-mentioned results were supported by measuring the gel content of irradiated PAAcK. The soluble part of irradiated PAAcK is higher than that of PAAm/PAAcK at different compositions (Fig. 9).

The swelling ratio of PAAm/PAAcK copolymers of different compositions in saline solution was investigated and the results are shown in Figure 6. As the PAAcK content increased, the swelling of copolymer increased, the maximum swelling value being obtained when pure PAAcK was used. The water absorbency of PAAm/PAAcK in saline solution was lower than that obtained in distilled water (Figs. 5 and 6). While the water absorbency of pure PAAcK in distilled water is lower than that in PAAcK-rich copolymers, it is the highest one in saline solution if compared with the other copolymer compositions swelled in the same solution. This is due to the solubility of the PAAcK in saline solution, which is lower than in distilled water.

The high swelling degree of PAAm/PAAcK in pure water can be attributed to free counterions that remain inside the gel to neutralize the fixed charges on the network chains. The driving force of the swelling process is the presence of mobile osmotically active counterions. The content of ionizing groups inside the gel has a great effect on the swelling behavior. It is clear that as the PAAcK increases; the mobile ion ( $K^+$ ) concentration inside the gel increases to maintain the



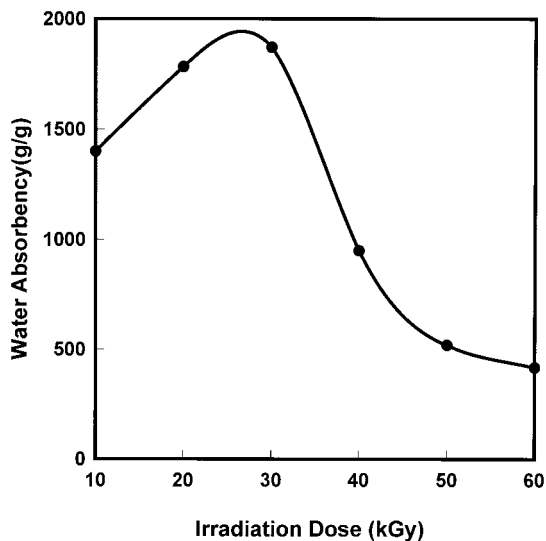
**Figure 6** Swelling of crosslinked PAAm/PAAcK copolymers of different compositions in (1% NaCl solution). Polymer concentration (4 wt % in water); irradiation dose (30 kGy).

electroneutrality conditions. As a result, the difference between the mobile ion concentration inside and outside the gel increases with increasing  $-COOK$  group content, which creates an additional osmotic pressure that expands the gel.<sup>38</sup> When salt is added to the system, some ions diffuse from the solution into the network. The overall concentration of mobile ions in the gel is still higher than before, but the difference between ion concentrations inside and outside the gel matrix is reduced. Consequently, the driving force of swelling decreases gradually with increasing salt concentration.

### Swelling of PAAm/PAAcK prepared at different irradiation doses

Figures 7 and 8 show the absorbency of a PAAm/PAAcK hydrogel in distilled water and saline solutions, respectively, prepared at different irradiation doses. The results indicated that the hydrogel swellability in distilled water increases with irradiation dose to reach its maximum value around 30 kGy. Thereafter, any increase in irradiation dose leads to a decrease in PAAm/PAAcK water absorbency (Fig. 7). At low irradiation doses, the decrease in PAAm/PAAcK water absorbency may be due to the high-soluble fraction content in copolymer. However, at high doses, the reduction in the PAAm/PAAcK water absorbency is attributed to the formation of hydrogel containing a high degree of crosslinking.

It was reported that, as the irradiation dose increases, the number of the small chains increased and the crosslinking density of copolymer system increased. At the same time, the number-average molar-



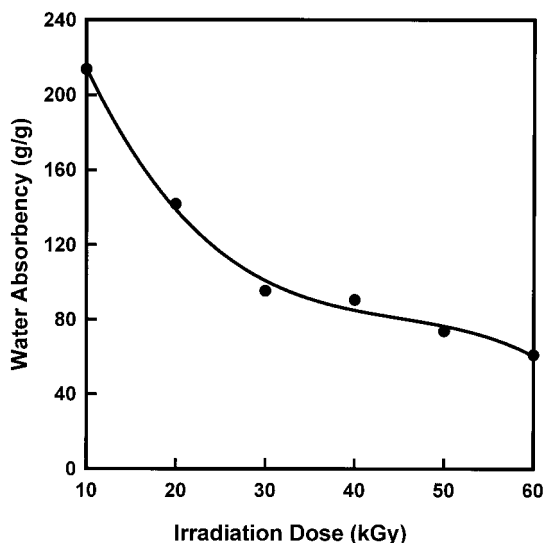
**Figure 7** Water absorbency of PAAm/PAAcK hydrogel in distilled water prepared at different irradiation doses. Copolymer concentration (4 wt % in water); PAAm/PAAcK composition (25 : 75, wt/wt).

mass between crosslinks is smaller than at the lower  $\gamma$ -ray doses.<sup>40</sup>

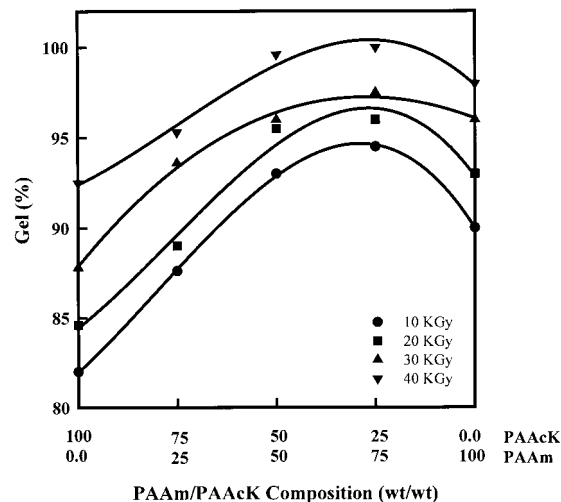
In the presence of the saline solution, the solubility of the hydrogels decreases. The lower the irradiation dose required for copolymer crosslinking, the higher the copolymer water absorbency obtained (Fig. 8).

Gel content and crosslinking network density of prepared PAAm/PAAcK copolymers

Gel content and crosslinking density of the prepared PAAm/PAAcK copolymers have a great influence on



**Figure 8** Water absorbency of PAAm/PAAcK hydrogel immersed in (1% NaCl solution) prepared at different irradiation doses. Copolymer concentration (4 wt % in water); PAAm/PAAcK composition (25 : 75, wt/wt).



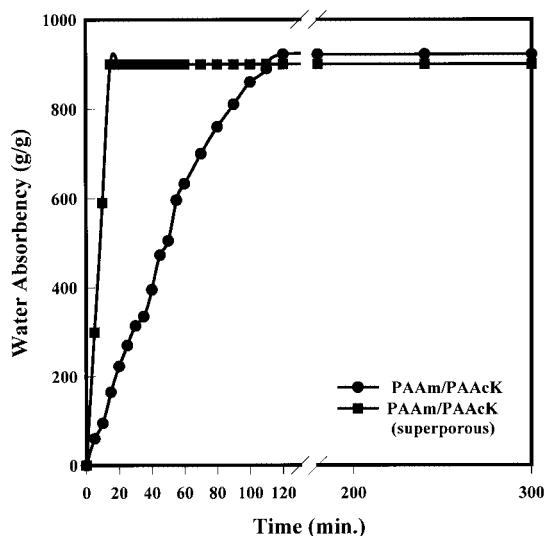
**Figure 9** Gel % of PAAm/PAAcK hydrogel at different compositions and irradiation doses. Copolymer concentration (4 wt % in water).

its swelling character: the higher the gel content, as well as the density of crosslinking, the lower the water absorbency. There are many factors affecting the polymer gel content, among them, polymer compositions and irradiation doses.

The effect of PAAm and PAAcK copolymer compositions on the PAAm/PAAcK copolymer gel content prepared at different irradiation doses was investigated and the results are shown in Figure 9. It is clear that the gel content and crosslinking density of PAAm/PAAcK hydrogel increase with the increase in PAAm content in the copolymer feed solutions and/or irradiation dose. By increasing the PAAcK polymer content in the PAAm/PAAcK binary system, its gel content decreases. The presence of  $K^+$  ions of PAAcK may retard the crosslinking and network structure formed by radiation that controls the polymer swelling degree. As the irradiation dose increases, the gel content increases to reach maximum values ranging from 95 to 98%. Thereafter, any increase in irradiation dose leads to an increase in crosslinking density and a considerable decrease in water absorbency of the copolymer.

#### Pore structure of prepared PAAm/PAAcK copolymers

Because the pore structure at the surface of hydrogels is thought to be important for rapid swelling, a trial was made to synthesize porous supersorbent PAAm/PAAcK hydrogels that reach equilibrium swelling in a few minutes. Thus, hydrogel preparation conditions such as the use of blowing agent, irradiation dose, and polymer compositions as well as the hydrogel dehydration method, which affects the gel pore structure and its diameter, were studied.



**Figure 10** Swelling rate of PAAm/PAAcK hydrogel prepared in the presence (■) and absence (●) of  $(\text{NH}_4)_2\text{CO}_3$ . Copolymer concentration (4 wt % in water); PAAm/PAAcK composition (25 : 75 wt/wt %); irradiation dose (30 kGy).

#### Effect of blowing agent on swelling rate and porosity of hydrogel

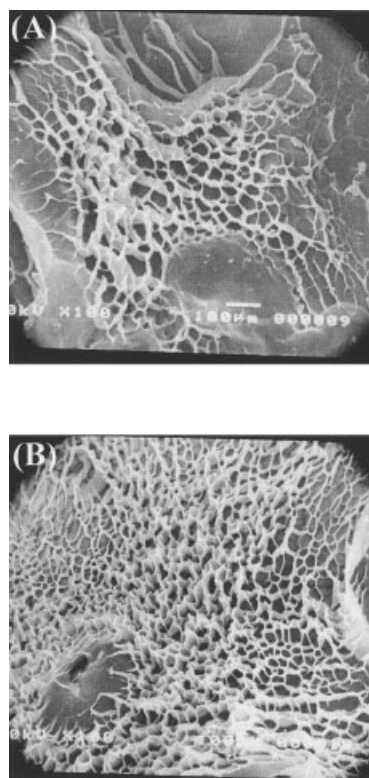
Fast swelling PAAm/PAAcK, called superporous hydrogels, could be synthesized by using a gas blowing technique. A PAAm and PAAcK blend solution was mixed with a gas-forming agent, namely, ammonium carbonate,  $(\text{NH}_4)_2\text{CO}_3$ , and then exposed to electron beam irradiation. The prepared crosslinked hydrogel was dried in ethanol to maintain the capillary channels formed between the pores and reduce their collapsing during the drying process. Thereafter, the comparative study between the swelling rate of hydrogel prepared in the presence and absence of  $(\text{NH}_4)_2\text{CO}_3$  was performed and the results are shown in Figure 10. It is clear that the swelling rate of PAAm/PAAcK prepared in the presence of  $(\text{NH}_4)_2\text{CO}_3$  reagent is higher than that prepared in the absence of such a reagent. The minimum time needed to achieve the maximum swelling capacity for untreated and  $(\text{NH}_4)_2\text{CO}_3$  treated PAAm/PAAcK is 15 and 120 min, respectively.

The results suggest that the porous structures are formed longitudinally by gas forming agents; the gas rises from the bottom to the top of the copolymer surface and results in superporous hydrogels of oriented pore structures and fast swelling properties. The fast swelling of superporous hydrogels in aqueous solution is due to the absorption of water by capillary pressure through interconnected pores (i.e., open channels), which may have diameters on the order of a few hundred micrometers.<sup>41</sup>

To elucidate the pore structure of the copolymer, the surface morphology of the PAAm/PAAcK superporous hydrogels was examined by SEM, which was

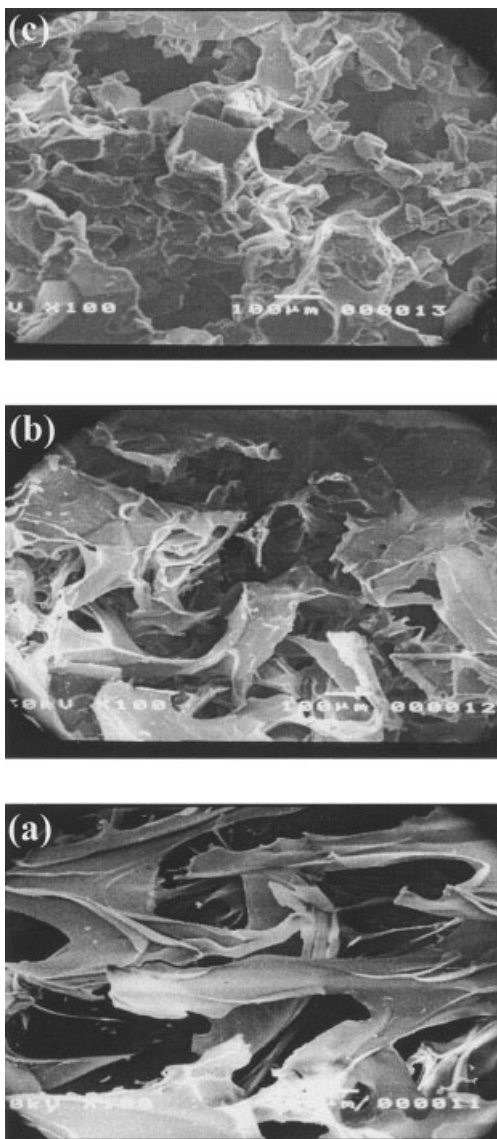
used to observe the micromorphology on fresh cross sections of hydrogel samples dehydrated by freeze-dryer technique. As shown in Figure 11, for the gel prepared in the absence of  $(\text{NH}_4)_2\text{CO}_3$ , fewer pores close to polygons with partially angular edges were observed. However, homogeneous polygonal pores were observed for the hydrogel prepared in the presence of  $(\text{NH}_4)_2\text{CO}_3$ . The high uniform porosity of the superporous hydrogel is achieved by  $\text{CO}_2$  and  $\text{NH}_3$  gases formed during radiation crosslinking process of PAAm/PAAcK. The high polar internal surface and homogeneous capillary structure of PAAm/PAAcK interconnecting pores are responsible for its very fast swelling rate. The fast swelling property is due to absorption of water by capillary force rather than by simple diffusion.

The micromorphology of the prepared hydrogel as well as its pore diameter mainly depends on those factors affecting the swelling properties of hydrogels such as the sample dehydration methods, the type of copolymer, and its crosslinking density. In other words, the copolymer compositions and the irradiation doses seriously affect the copolymer crosslinking degree and micromorphology of the polymer. Therefore, the effect of crosslinking density formed during irradiation process on the pore size and morphological



**Figure 11** SEM for PAAm/PAAcK hydrogel prepared in the (A) absence and (B) presence of  $(\text{NH}_4)_2\text{CO}_3$ . Polymer concentration (4 wt % I water), PAAm/PAAcK composition (25 : 75 wt/wt %); irradiation dose (30 kGy).





**Figure 12** SEM for PAAm/PAAcK hydrogel prepared at different irradiation doses: (a) 30 kGy, (b) 40 kGy, and (c) 50 kGy. Copolymer concentration (4 wt % in water); PAAm/PAAcK composition (25 : 75, wt/wt).

structure of the PAAm/PAAcK hydrogel was investigated and the results are shown in Figure 12. It is clear that the structure of the hydrogel is affected by the irradiation dose; as the irradiation dose increases, the crosslinking degree increases and the pore size decreases.

The copolymer hydrogel of low crosslinking degree forms a relatively regular pore structure. However, the others, which were irradiated at high irradiation doses and possessed high crosslinking degrees, randomly aggregated and exhibited granular structure. These results are due to the differences in the expansion of the polymer network and in the magnitude of the polymer network affinity toward water. Also, the decrease in pore size could be attributed to an increase

in the elasticity of the hydrogel<sup>42,43</sup>; the formation of three-dimensional crosslinking structure improves the elasticity of the hydrogel.

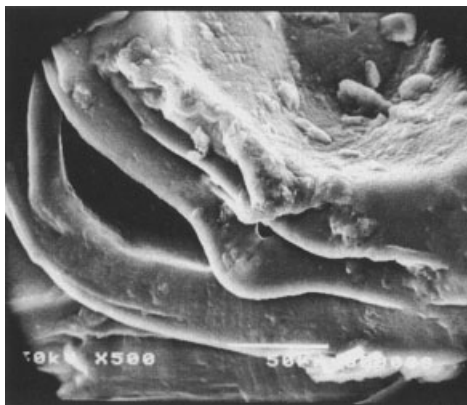
The micromorphology of hydrogels slowly dried in air shows much denser phase structures. It is clear that the denser phase structure differs from the porous structure (Fig. 13). The formation of denser phase structure can be attributed to the slow drying method of hydrogel samples that is helpful to squeeze out water and cause much increased pore collapsing during the drying process.

### Using the prepared hydrogels in agriculture

The influence of polymeric soil conditioner on plant growth and crop yield has been extensively studied.<sup>44</sup> From an economic point of view, agricultural hydrogels should be evaluated through the growth and other responses of plants. Therefore, the effect of the sandy soil treated with different types and various amounts of the prepared hydrogels on the emergence and vegetative growth of corn plants was investigated.

#### Effect of different types of hydrogels on the plant emergence

The emergence rate of corn seeds planted in the soil treated with different types of hydrogels, namely, PAAm, PAAcK, or PAAm/PAAcK, was determined. It was observed that the emergence rate of the corn seeds planted in the soil treated with the different types of hydrogels investigated here is higher than that of the seeds planted in untreated soil (control) (Table II). The time needed for 100% emergence for corn seeds planted in the soil treated with PAAm/PAAcK hydrogel is lower than that required for 100% emergence for corn seeds planted in soil treated with the other hydrogels.



**Figure 13** SEM for PAAm/PAAcK hydrogel dried in air. Copolymer concentration (4 wt % in water); PAAm/PAAcK composition (25 : 75, wt/wt).

**TABLE II**  
**The Emergence Rate of Corn (*Zea mays*) Seed Planted in the Soil Treated with Different Types and Amounts of Hydrogels**

Hydrogel types	Rate of hydrogel (g/m <sup>3</sup> )	Emergence (%) at time/day								
		7	8	9	10	11	12	13	14	15
Control	0	0.0	0.0	9	34	42	58	67	83	100
PAAm	6	0.0	9	50	58	75	83	92	100	—
PAAcK	6	9	17	55	67	78	92	100	—	—
PAAm/P AAcK	6	25	50	67	75	100	—	—	—	—
PAAm/P AAcK	9	33	55	67	100	—	—	—	—	—
PAAm/P AAcK	15	42	58	100	—	—	—	—	—	—

The hydrogel particles around the seeds can absorb large quantities of water. The seeds can extract the water from the hydrogel when required. As a result, survival of seedlings is improved and their probability for early germination becomes high.

Also, the emergence rate of corn seeds planted in the soil treated with different amounts of PAAm/PAAcK was investigated (Table II). It is clear that, as the amount of PAAm/PAAcK hydrogel increases in the soil, the corn seed emergence rate increases. When the hydrogel rate was 15 g/m<sup>3</sup>, the time needed for 100% corn seed emergence was 9 days. With a hydrogel level of 6 g/m<sup>3</sup>, 100% corn seed emergence needed 11 days; meanwhile, 14 days is the time required for 100% seed emergence at zero rate gel (control). This means that as the hydrogel rate increases, the amount of absorbed water increases and the available water for seed germination increases. As a result, survival of seedlings is improved, especially in arid and semi-arid environments, and emergence rates are enhanced. On the other hand, incorporating hydrogels into the soil reduces the sealing effect of dry soils and creates a permeable layer in which germination was greater for plants.<sup>45</sup>

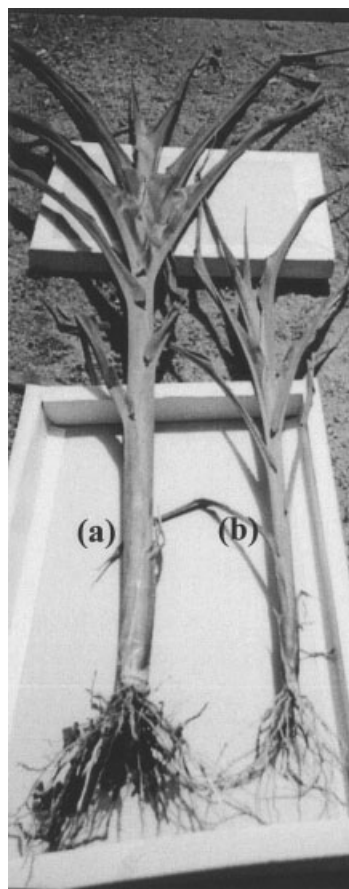
#### Effect of hydrogels on plant growth and corncob production

The growth of a plant can be determined through the change in its height, leaf width, and total dry weight. So, the average of height, leaf width, total dry weight, and cob production of corn plants planted in soil containing different types and amounts of hydrogels was investigated and the results are shown in Figure 14 and Table III. It is clear that the presence of hydrogels in the soil increases the height, leaf width, total dry weight, and corncob production of corn plants compared with the control ones. The average of corn height planted in soil treated with different types of hydrogels decreases in the order: PAAm/PAAcK, PAAcK, and PAAm. The average of plant height and leaf width (cm/week) of corn plants planted in soil treated with PAAm/PAAcK is almost one and

one-half times the control one 12 weeks after planting. Meanwhile, total dry weight of corn plants treated with PAAm/PAAcK is almost twice the control one. The average of double corncob production relative to single corncob production is higher for plants treated with different types of hydrogels than for the control ones.

#### Effect of hydrogels on the time to wilting for plant

The shelf-life (time to wilting) of corn plants grown in sandy soil treated with different types of hydrogels



**Figure 14** corn (*Zea mays*) plant planted in soil (A) treated with PAAm/PAAcK, (B) untreated (control).

**TABLE III**  
**The Average of Plant Height, Leaf Width, a Total Dry Weight, and Cob Production of Corn (*Zea mays*)**  
**Plant Planted in Soil Containing Different Types and Amounts of Hydrogels**

Hydrogel types	Hydrogel rate (g/m <sup>3</sup> )	Average total dry weight (g)	Average plant height (cm) at 12 weeks	Average of leaf width (cm) at 12 weeks	Double corn cob (%)
Control	0	18.6	95	5.3	8.3
PAAm	6	24	115	7	41.6
PAAcK	6	26.6	120	7.7	41.6
PAAm/PAAcK	6	34	143	8.7	50.0
PAAm/PAAcK	9	41	170	10.6	58.0
PAAm/PAAcK	15	47	176	11.4	58.0

such as PAAm, PAAcK, and PAAm/PAAcK was investigated and are shown in Table IV. It is observed that the time to wilting of corn plants planted in the presence of hydrogels is longer than that for the control and follows the order: PAAm/PAAcK > PAAcK > PAAm. Increasing the gel rate in the soil leads to a significant increase in the time to wilting of the corn plants. The use of PAAm/PAAcK hydrogel at a rate of 6 g/m<sup>3</sup> increases the time to wilting of corn by 50% in reference to the wilting time of control. Meanwhile, the time to wilting for corn plants planted in sandy soil treated with PAAm/PAAcK hydrogel at a rate of 15 g/m<sup>3</sup> increases by almost 65% referred to the wilting time of control. The magnitude of the plant wilting response may be due to the fact that, as the gel rate increases, the amount of absorbed water increases, soil water retention improves, and the available water for plant increases, resulting in delaying the wilting of the corn plant.

### CONCLUSION

A series of crosslinked superabsorbents based on acrylamide were prepared by using electron beam irradiation. Highly water-absorbing PAAm/PAAcK was selected and synthesized in an effort to investigate the influence of reaction parameters on its water absorbency. PAAm/PAAcK water swellabil-

ity increases as the PAAm in the copolymer and/or irradiation dose required for crosslinking process decreases. Fast swelling interconnected superporous hydrogels were obtained by mixing the blowing agent, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, with the copolymer feed solution before the irradiation crosslinking process. (PAAm/PAAcK) superporous hydrogel is considered to be one of the potassium-based copolymer types that does not cause salt buildup in the soil, possesses a high ability to absorb water, and significantly prevents plant losses due to drought and water stress in nonirrigated areas. Thus, such a hydrogel could be used as a horticultural soil amendment for plantings and seedlings, to improve the growth of plants and increase production.

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**TABLE IV**  
**Time to Wilting of Corn (*Zea mays*) Plant Planted**  
**in Sandy Soil Treated with Different**  
**Types and Rates of Hydrogels**

Hydrogel types	Hydrogel rate (g/m <sup>3</sup> )	Time to wilting (h)
Control	0	288
PAAm	6	360
PAAcK	6	384
PAAm/PAAcK	6	432
PAAm/PAAcK	9	456
PAAm/PAAcK	15	474

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