Effect of Various Environmental Conditions on the Swelling Property of PAAm/PAAcK Superabsorbent Hydrogel Prepared by Ionizing Radiation

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ABSTRACT: Polyacrylamide/potassium polyacrylate (PAAm/PAAcK) superabsorbent hydrogels were prepared by using ionizing radiation for possible use in agricultural purposes. The influence of environmental conditions such as water quality, fertilizer salts, soil pH, and surrounding temperature on PAAm/PAAcK water absorbency and retention was investigated. The water absorbency apparently decreased with an increase in the valence and ionic strength of the salt solutions. The swelling of PAAm/PAAcK immersed in the solutions containing fertilizer of different nitrogen sources followed the order: Urea $>$ NH_4NO_3 $>$ $(NH_4)_2SO_4$. The PAAm/PAAcK water absorbency in solutions containing different types of phosphate sources was in the order: $H_3PO_4 > KH_2PO_4 > K_2HPO_4$. However, the water absorbency of PAAm/PAAcK in the solution of different types of potassium salts followed the order: $KCl > K_2SO_4 > K_2HPO_4$. PAAm/PAAcK hydrogel is fully swollen at pH 6. The relation between the ability of PAAm/PAAcK to retain water against time at different temperatures was studied. As the environmental temperature increases, the water retention of PAAm/PAAcK decreases. Potential application of PAAm/PAAcK in agriculture was evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3955–3962, 2006

Key words: superabsorbent; radiation; polyacrylamide; fertilizer salts; water retention

INTRODUCTION

Much attention was paid to superabsorbent polyelectrolyte gel applications, which are widely used in many fields such as feminine napkins and disposable diapers, gel actuators for drug delivery systems, and soil conditioner for agriculture and horticulture.[1–9] Water-holding amendments could be used to improve aeration and drainage, and reduce compaction of the soil as well as increase plant survival and growth.[10–20] Hence, some researchers attempted to improve the properties of such absorbent polymers to enhance their absorbency, strength, and initial absorption rate as well as their ability to retain certain chemical compounds.[1,21,22]

In landscape situations, fertilizers are often applied with hydrogels. With the exception of carbon, hydrogen, and oxygen, plants must obtain 13 essential mineral nutrients from the growing medium solution. Many mineral nutrients, including the nitrogen in the ammonium $(NH_4)^+$ or nitrate $(NO_3)^-$ form, potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}), and so forth, exist in the growing medium solution as electrically charged ions until plant roots utilize them for growth. The water-holding capacity of hydrogels drops significantly at sites, where the source of irrigation water contains high levels of dissolved fertilizer salts.[23–26] The magnitude effect of fertilizer salts on hydrogel absorbency differs from one system to another and depends on the type, valence, and charge of fertilizer ions in addition to the gel functional groups.

Hydrogels used in horticulture are usually the formulations commonly made of starch–polyacrylonitrile graft copolymers (starch copolymers), vinyl alcohol–acrylic acid copolymers (polyvinylalcohols), and acrylamide sodium acrylate copolymers (crosslinked polyacrylamides, PAM).[27] All hydrogel classes showed reduction in their water absorption capacity, by the addition of fertilizer. The solutions containing potassium and ammonium (monovalent cations) reduced the water absorption ability of PAM hydrogels by 75%; however, calcium, magnesium, iron, etc. (divalent cations) reduced the hydrogel absorption capacity by 90%.[23,26,27] In fact, there is no sufficient information available to predict which plant species might be aided by the use of hydrogels and which type of hydrogel might be used. Also, the studies on the effect of various environmental conditions on hydrogel properties, especially those correlated with the plant growth, are limited. The quality of irrigation water, the pH and temperature of agricultural soil, herbicides and inorganic fertilizer, or the nutrient ions

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remaining in the soil for plant performance consider the important factors that affect the hydrogel water absorbency when are considered supersorbent hydrogels.

In this respect, polyelectrolyte polyacrylamide/potassium polyacrylate (PAAm/PAAcK) hydrogel that is commercially used in agriculture as soil conditioner was successfully prepared by using electron-beam irradiation. PAAm/PAAcK is ionic in nature and can undergo a volume phase transition in response to change in surrounding conditions. One of the interests of the present studies is to determine not only the effect of the different types of fertilizer salts at various concentrations but also the effect of other environmental factors such as soil pH and the surrounding temperatures on PAAm/PAAcK swelling and water retention properties.

MATERIALS AND METHODS

Polyacrylamide (PAAm) granules of MW 500,000–600,000 were of commercial grade. Potassium polyacrylate was prepared by neutralizing polyacrylic acid with KOH. The other chemicals, such as inorganic salts, and other reagents were reagent grade and used without further purification.

Preparation of hydrogels

Appropriate weight of dry polymers (4 wt %), at different compositions in distilled water, was stirred at 60°C until it completely dissolved. The solution of the blend was poured in petri dish (the thickness of solution was about 3 mm), left for 3 h, and irradiated at different doses with an electron beam of 1.5 MeV (maximum beam current, 25 mA; power, 37.5 kW). The parameters of the accelerator are electron energy (1.45 MeV), electron beam current (4 mA), scanner with 90 cm, and conveyor speed at 20kGy and 3.6 m/min. The obtained crosslinked hydrogel was cut into small pieces and left to dry at 25°C. The details were described in the previous work.[28]

Swelling measurement

The dried hydrogels of known weights were immersed in distilled water or salt solutions at 25°C until the equilibrium swelling have been 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 the water uptake.

$$\text{Water absorbency (\%)} = (W_s - W_g)/W_g \times 100$$

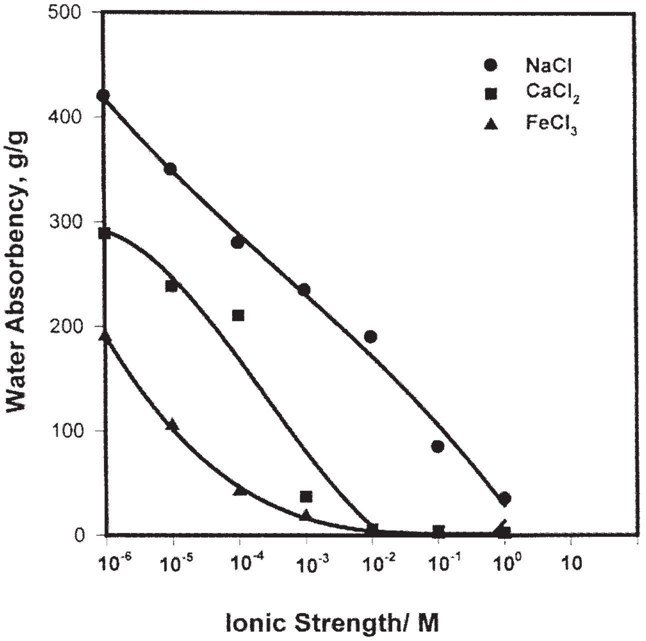

Figure 1 Effect of ionic strength of various types of cation solutions on water absorbency of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

where W_s and W_g represent the weights of wet and dry gels, respectively.

Water retention

The wet gel of known weights was exposed to different temperatures. The weight loss against time was calculated at interval times. The following equation was used to determine percentage of water retention of hydrogel.

$$\text{Hydrogel water retention (at certain time) \%} = [\text{weight of gel at certain time/initial weight}] \times 100$$

For accuracy, the experiment was repeated twice for each sample.

RESULTS AND DISCUSSION

Effect of type and valence of cations on PAAm/PAAcK swelling

The swelling behavior of PAAm/PAAcK hydrogels immersed in various salt solutions of different ionic valences and equal ionic strengths is shown in Figure 1. Under a given ionic strength, water absorbency decreases with the increase in ionic valence of the salt, resulting minimum in trivalent ions (Fe^{3+}) and maximum in monovalent ions (Na^{+}) solutions. The swelling behavior can be principally attributed to the dissociation degree of electrostatic attraction of PAAm and PAAcK when the PAAm/PAAcK was swollen in various ion solutions. Alkali metal ions can freely move all over the entire network. Addition of divalent or trivalent counter ions leads to a volume transition in PAAm/PAAcK gels, governed by the interactions between the polyion and the counter ions. —COOK and $—CONH_2$ groups of PAAm/PAAcK cannot chelate with the alkali and alkaline earth-metal ions such as K^+ and Ca^{2+}. Alkaline earth-metal ions bind strongly with double carboxlyate groups, and its mobility through the polymer network become limited. However, PAAm/PAAcK network exhibits strong chelating ability with heavy metal ions (Fe^{3+}), and as a result, the ion mobility is restricted.

It was reported that the amount of gel water retained is affected by chemicals or divalent cations present in the water. These cations develop strong interactions with the polymer gels and are able to displace water molecules trapped within the gel.[29,30] Even though monovalent cations such as Na^+ can replace water molecules, this effect is not as pronounced as with the divalent counterparts. Furthermore, the process is fully reversible by repeated soaking with deionized water.

Effect of ionic radius on swelling behavior of hydrogels

The swelling behavior of PAAm/PAAcK hydrogel in monovalent or divalent cation solutions of different ionic strengths is represented in Figures 2 and 3, respectively. The results show that the water absorbency of the PAAm/PAAcK hydrogels increases with decreasing atomic radius both in monovalent and in divalent cation solutions.

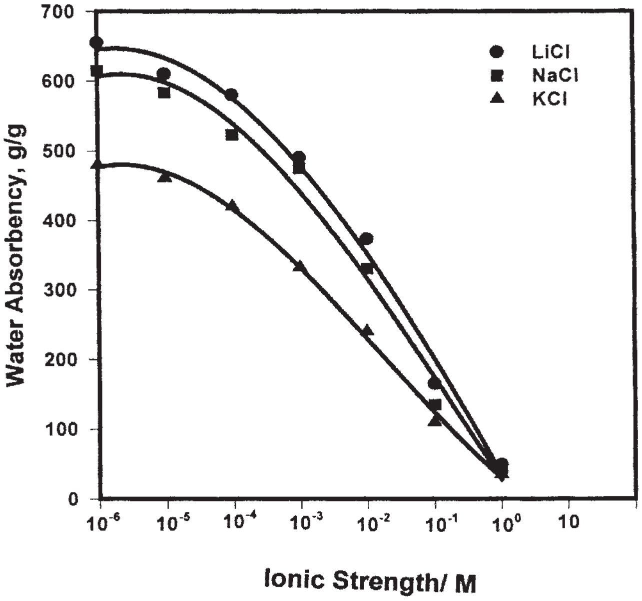

Figure 2 Effect of ionic strength of various types of monovalent cation solutions on water absorbency of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

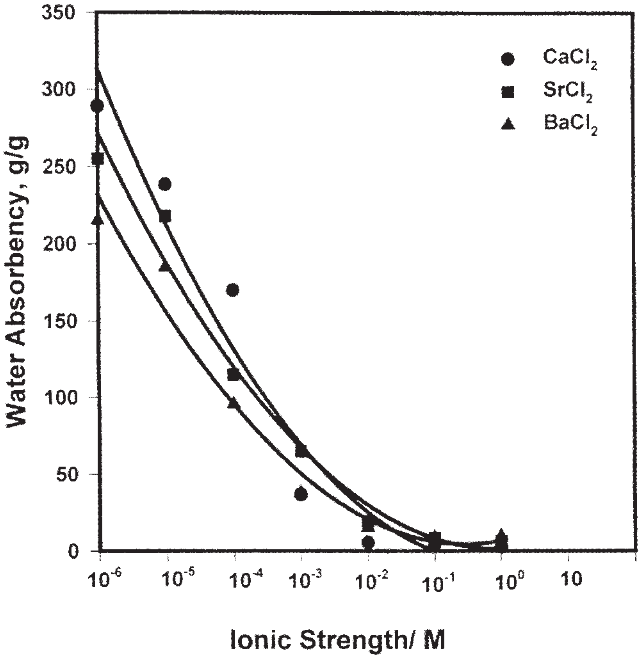

Figure 3 Effect of ionic strength of various types of divalent cation solutions on water absorbency of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

The results obtained can be explained taking into account that the radius of the small cation is surrounded and shielded by a large number of water molecules. Therefore, the cationic charge density becomes low and its bonding ability to the carboxylate group is weak. However, the cation with a large radius tends to enter the network and easily binds to the hydrogel carboxylate groups, resulting in decrease of its water absorbency capacity.

The swelling behavior of PAAm/PAAcK is also significantly affected by the ionic strength of salt solutions. Figures 1–3 and Table I show the swelling of PAAm/PAAcK at different ionic strength solutions. The data demonstrated that the PAAm/PAAcK water absorbency apparently decreases with an increase in the ionic strength of the immersing solution. The decrease in swelling ratio of hydrogels with increasing salt concentration in the external solution is due to a decrease in the expansion of the hydrogel network in salt solutions. This is not only due to the decrease in the osmotic pressure difference between the gel and the external solution but also due to the screening of the ionic charges bound to the hydrogel network.

TABLE I
Water Absorbency of PAAm-*co*-PAAcK in Solution Containing Various Concentrations of Different Salts and Fertilizers[a]

Conc. (M)	Water absorbency (g/g)											
Conc. (*M*)	Urea	NaCl	NH_4NO_3	H_3PO_4	KCl	$(NH_4)_2SO_4$	K_2SO_4	KH_2PO_4	K_2HPO_4	NaH_2PO_4	$CaCl_2$	$FeSO_4$
10^{-6}	1043.0	615.0	520.0	470.0	480.0	460.0	455.0	440.0	415.0	395.5	368.4	332.5
10^{-5}	613.0	583.0	485.0	410.0	461.0	448.6	446.0	395.0	386.0	372.8	351.7	325.0
10^{-4}	601.0	523.0	376.0	370.0	420.0	420.2	418.0	352.0	345.0	342.9	316.5	318.0
10^{-3}	570.0	475.0	345.0	355.0	332.0	270.0	265.0	322.0	310.0	329.5	37.7	52.0
10^{-2}	490.0	330.0	286.0	265.0	240.0	145.2	143.0	230.0	205.0	150.5	4.5	6.9
10^{-1}	458.0	135.0	179.0	187.0	110.0	94.7	94.0	144.0	122.0	67.8	3.3	5.9
10^{0}	430.0	43.0	96.0	75.0	35	50.3	8.5	46.5	42.0	21.2	2.2	5.6

[a] PAAm-*co*-PAAcK composition (25/75 wt/wt).

Effect of different kinds of fertilizers on the swelling behavior of hydrogels

Phosphorous, potassium, and nitrogen salts (NPK), which are added to plant as fertilizers, are the main elements for plant nutrition and have a significant role in plant growth. Therefore, the water absorbency for PAAm/PAAcK hydrogel in the solutions of different types and amounts of phosphate, potassium, or nitrogen fertilizers was studied and are shown in Figures 4–6 and Table II. In all cases, an increase of fertilizer concentration leads to gel shrinkage, which is affected by the type of added salts. The mass of the swollen gel is slightly influenced at low concentration of salt. The increase of salt concentration results in a significant gel shrinkage. This can be explained by theoretical considerations: at high salt concentrations, an additional electrostatic swelling should be completely screened.[31] This causes the swelling force to decrease.

The results also show that the PAAm/PAAcK water absorbency swelling in different types of phosphate sources is in the order $H_3PO_4 > KH_2PO_4 > K_2HPO_4$. Meanwhile, PAAm/PAAcK water absorbency in different types of potassium salts follows the order: KCl $> K_2SO_4 > K_2HPO_4$ at low salt concentrations and KCl $> K_2HPO_4 > K_2SO_4$ at high salt concentrations. This observation suggested that the "charge screening effect" of the cations that shields the charge of the carboxylate groups and prevents an efficient electrostatic repulsion is higher in case of K_2HPO_4 or

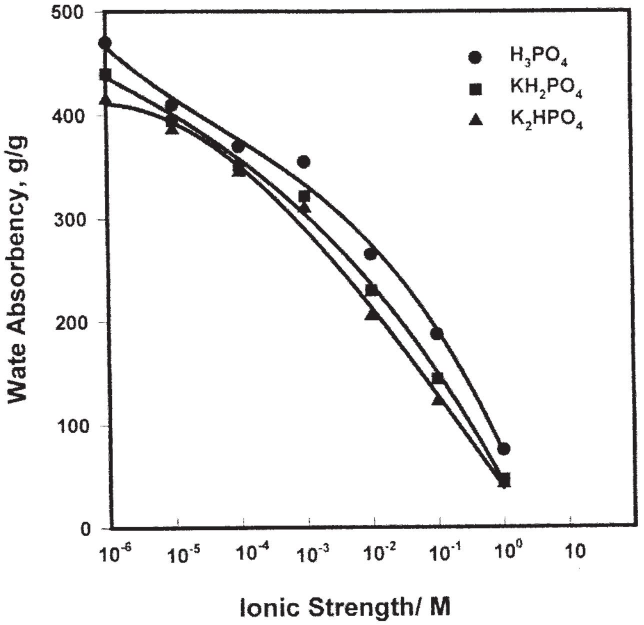

Figure 4 Effect of different ionic strengths of various types of phosphorous salt solutions on water absorbency of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

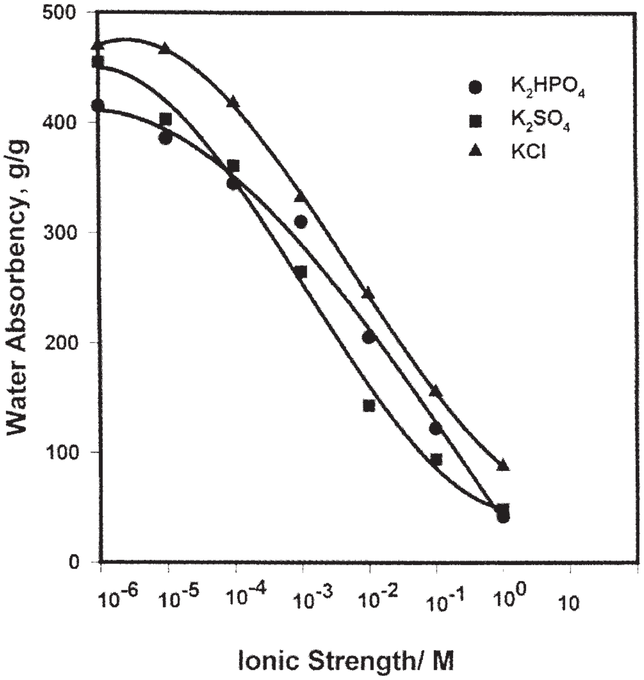

Figure 5 Effect of different ionic strengths of various potassium salt solutions on water absorbency of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

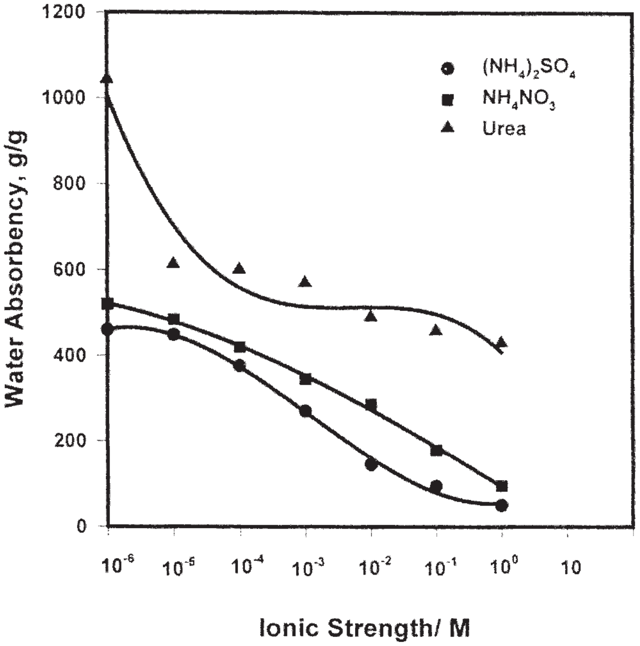

Figure 6 Effect of different ionic strengths of nutrient solutions containing nitrogen on water absorbency of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

K_2SO_4.[32] As a result, the difference in osmotic pressure, the driving force for swelling, between the internal and external solutions of the network is decreased.

The hydrogel absorbency in different types of nitrogen sources are in the order; Urea $>$ NH_4NO_3 $>$ $(NH_4)_2$ SO_4. Urea is a nonionic fertilizer, its use results in low reduction in hydrogel water absorbency. However, the ammonium sulfate or nitrate is an ionizable fertilizer salt, and causes high reduction in the swelling of the hydrogel as well as may bind with the hydrogel.

Effect of different fertilizer salts on swelling behavior of PAAm/PAAcK hydrogels at different compositions

The swelling behavior of PAAm-PAAcK hydrogel prepared at different compositions in various mineral salts and fertilizers is shown in Table II. It is clearly observed that the swelling of hydrogels containing PAAm and PAAcK in different compositions is higher than that of hydrogel containing only PAAm. The increase in PAAcK content in the PAAm/PAAcK copolymer results in a slight increase in its swelling behavior.

The results suggested that the absorbency of PAAm in the fertilizer solutions was enhanced by mixing it with PAAcK. These results in general imply that the hydrogel network ability to bind the fertilizer salts is affected by the distribution of amide and carboxylate network groups. The addition of PAAcK increases the charge density on the hydrogel chains and this leads to enhance the electrostatic repulsion on the chain, so the expansion of chain increases.

Owing to the presence of fixed acrylate anions within PAAm/PAAcK hydrogel, the total ion concentration inside the hydrogel is higher than that in the external aqueous solution owing to the local neutrality and equality of chemical potentials of small ions inside and outside the hydrogel, as described by the Donnan equilibrium theory. Accumulation of small ions within hydrogel results in a difference in chemical potentials of water molecules outside and inside the hydrogel. Therefore, the ionic osmotic pressure arises in proportion to the total ion concentration difference. It is expected that the internal total ion concentration increases with the increase in concentration of AAcK units within hydrogel. On the other hand, the total ion concentration difference decreases with the increase in external ionic strength due to the ideal Donnan effect.[33] As the salt concentration increases, the Donnan ratio is expected to decrease and the hydrogel ability to swell also decreases. Therefore, in the presence of a sufficiently high concentration of salt, the total ion concentration difference is approximately equal to the concentration of ionized carboxylate units only.[34]

pH of solution

Since the agricultural hydrogels may be used in different types of soil, it is important to study the effect of different pH media on the hydrogel absorbency. The

TABLE II
Water Absorbency of PAAm/PAAcK of Different Compositions Immersed in Different Salt Solutions of Concentration 0.0001*M*

PAAm/PAAcK composition	Water absorbency (g/g)								
	H_2O	KNO_3	$KHCO_3$	K_2CO_3	KCl	$(NH_4)H_2PO_4$	K_2SO_4	KH_2PO_4	K_2HPO_4
100/0.0	293	275	225	214	268	263	270	240	234
75/25	630	405	330	320	335	380	400	337	333
50/50	915	413	339	329	342	392	410	344	341
25/75	1785	422	344	335	352	407	415	350	345
0.0/100	825	433	350	341	360	417	422	358	352

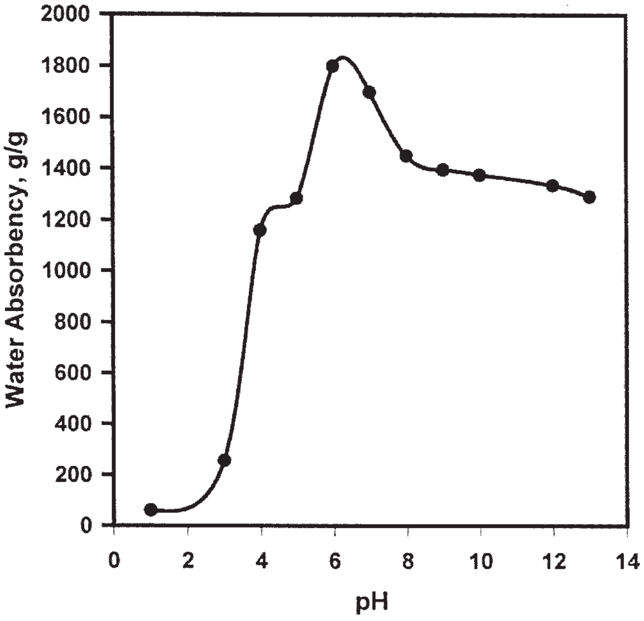

Figure 7 Effect of different pHs on water absorbency of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

PAAm/PAAcK water absorbency in solutions of different pHs is shown in Figure 7 PAAm/PAAcK hydrogel is fully swollen at pH 6, while it is relatively collapsed at lower pH's. The hydrogel absorbency decreases rapidly at lower pH (4–2) showing the strong effect of buffer reaction and slowly influences at higher pH (8–13), implying that the buffer action has disappeared. The results can be explained considering the following: at low pH values, the most carboxylate groups on the polymeric chains have been converted to the carboxylic acid groups, and the ratio of the nonionized —COOH groups to the ionized acid ones (—COO—) is increased. This increases the likelihood of the formation of inter- and intramolecular hydrogen bonds and decreases the hydrophilicity of the PAAm/PAAcK hydrogel. At pH 4–7, the hydrogen bonding or attraction force between the —C═O groups of PAAcK and —NH_2 groups of PAAm disappeared and the repulsion between the carboxylate groups, which responded for the higher swelling of the polymer, is predominant. However, at higher pH values (8–12), the PAAm/PAAcK is in a state of higher ionization, and thus, it has a significant ability to be solvated, hence the polymer does not swell. This behavior is mainly due to the screening effect of the counter ions on the polyanion chain.[31] It was reported that the swelling behavior of poly (sodium acrylate-*co*-hydroxy-ethylmethacrylate) in acid medium decreases to zero. However, at a high pH value (>14), the absorbency decreases to 15 times.[35]

Temperature of solution

Figure 8 shows the effect of solution temperature on the swelling of PAAm/PAAcK hydrogel. Water absorbency rate is increased by increasing the solution temperature. The swelling of a hydrogel is greatly concerned with temperature of the swelling medium; a rise in temperature affects the relaxation of hydrogel network chains as well as the diffusion rate of water molecules into the gel.

Water retention

The retention of moisture or water in the soil is a fundamental process upon which all plantations depend. The soil holds water in two ways: as a film coating on soil particles, and in the pore space between particles. Soil porosity depends on soil texture and structure. Water can be held tighter in small pores than in large pores. The small pores allow the soil to hold more water by capillary forces. For this reason, a clayey soil with many small pores can hold more water than sand soils.

The addition of organic materials generally produces a sandy soil with increased water holding capacity, largely as a result of its influence on soil aggregation and associated increased pore space as well as improved the balance between small and large water pores in the soil itself. Superabsorbent polymers markedly increase water-holding ability in the sandy soils by absorbing and retaining large amount of wa-

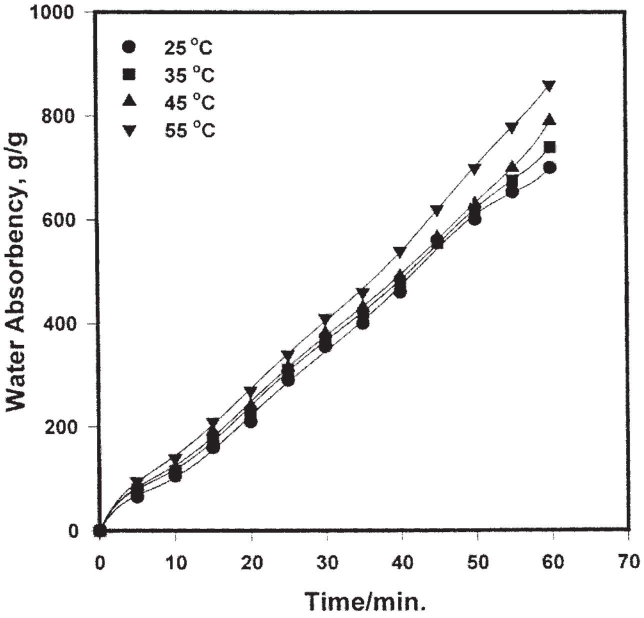

Figure 8 Effect of surrounding temperature on absorbency rate of PAAm/PAAcK hydrogel in distilled water. The hydrogel prepared at copolymer concentration, 4 wt %, (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

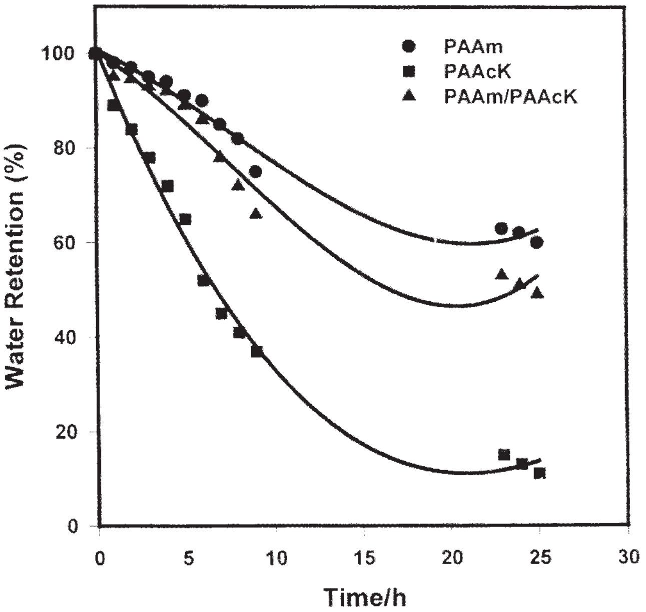

Figure 9 Water retention of different types of hydrogels at room temperature (30°C). The hydrogels prepared at copolymer concentration, 4 wt %; and irradiation dose, 30 kGy.

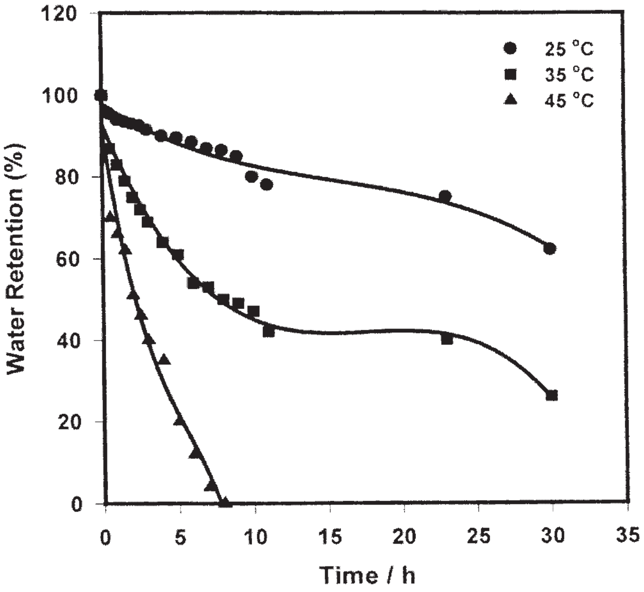

Figure 10 Effect of different temperatures on water retention of PAAm/PAAcK. The hydrogel prepared at copolymer concentration, 4 wt %; (PAAm/PAAcK) composition, (25/75 wt/wt); and irradiation dose, 30 kGy.

ter. Moreover, the hydrogels occupy some space between the sand grains, bind them together, and increase the number of small pore space between sand particles. How soil moisture is affected by the presence of superabsorbent gels? To ensure this caution, the water retention of different types of superabsorbent materials, namely PAAm, PAAcK, and PAAm/PAAcK was investigated at 25°C with time, and are shown in Figure 9. It is clear that the water retention of the PAAcK is lower than that for PAAm and PAAm/PAAcK. External parameters such as temperature may affect the water retention of the polymer. The relation between the ability of PAAm/PAAcK to keep water against time at different temperatures is represented in Figure 10. As the temperature increases, the deswelling rate of gel imbibed water increases, and results in decreasing polymer water retention.

Potential applications of the PAAm/PAAcK in agriculture

Improve soil ventilation in compact soil

The effect of the prepared hydrogel on the properties of compact soil was investigated. As shown in Figure 11, the hydrogel, which mixed with the compact soil, swell during water uptake, and change in the soil volume results in soil cracking (Figures 11(A) and 11(B)). As the amount of hydrogels increases, the cracks increase (Fig. 11(B)). The benefits of this action are reduced soil compaction, enhanced soil porosity, increased permeability, and improved soil ventilation. Improving the physical properties of compact soil through the good aeration ensure good germination, fast root development, and regular growth.

Increase in the sandy soil water retention and enhancement of the plant performance

The application of prepared hydrogel to enhance the sandy properties for agriculture was investigated. In this experiment, the PAAm/PAAcK with water absorbency 1800 g/g were synthesized and applied in agriculture to observe their effect on the growth of corn Zea maize plant (Fig. 12). Details are described in previous work.[18] The Zea maize growth in sandy soil treated with hydrogels seems to be better than that of

Figure 11 The properties of compact clay soil containing (A) 1 g PAAm/PAAcK and (B) 2 g PAAm/PAAcK.

Figure 12 Effect of PAAm/PAAcK with water absorbency 1800 g/g on the growth of corn Zea maize plant. (A) Control plant and (B) plant cultivated in sandy soil treated with PAAm/PAAcK.

control. The presence of hydrogel, not only absorb large amounts of water but also have good water retention capability, which supplies plentiful water to promote the plant performance and enhance root growth. From the preliminary study, it can be concluded that the PAAm/PAAcK hydrogels have potential for applications in agriculture, especially in arid and desert regions.

CONCLUSIONS

PAAm/PAAcK hydrogels were prepared by using electron beam irradiation. PAAm/PAAcK is ionic in nature and undergoes a volume phase transition in response to change in environmental conditions such as solution ionic strength and soil pH. The presence of the electrolyte in aqueous medium significantly affected the hydrogel absorption capacity. Type and valence of fertilizer ions have a great influence on PAAm/PAAcK Swelling. PAAm/PAAcK could, in fact, be further crosslinked with multivalent ions such as Fe^{3+}. PAAm/PAAcK water absorbency decreases with an increase in ionic valence of salt. The lower the atomic radius, the higher is the hydrogel water absorbency. PAAm/PAAcK hydrogel is fully swollen at pH 6 while it is relatively collapsed at lower pH values. As the environmental temperature increases the water retention of PAAm/PAAcK decreases. The water retention of different types of superabsorbent materials namely PAAm, PAAcK and PAAm/PAAcK followed the order PAAm, >PAAm/PAAcK.> PAAcK. It is recommended that the suitable sources to be used as NPK fertilizers, in the presence of PAAm/PAAcK hydrogels, is urea, H_3PO_4 and KNO_3 at which the PAAm/PAAcK absorption capacity is higher in comparing with the other inorganic fertilizers.

References

1. Buchholz, F. L. In Superabsorbent Polymer Science and Technology; Buchholz, F. L.; Peppas, N. A., Eds.; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1994.
2. Sakiyama, T.; Chu, C. H.; Fujii, T.; Yano, T. J Appl Polym Sci 1993, 50, 2021.
3. Yoshida, M.; Asano, M.; Kumakura, M. Eur Polym J 1989, 25, 1197.
4. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1992, 44, 249.
5. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1993, 47, 249.
6. Hogari, K. A.; Ashiya, F. Advances in Superabsorbent polymers; American Chemical Society: Washington, DC, 1994.
7. Ericksen, P. H.; Nguyen, H. V.; Oczkowski, B.; Olejnik, T. A. Eur. Pat. 40087 (1981).
8. Kobayashi, T. Kobunshi 1987, 36, 612.
9. Osada, Y. Adv Polym Sci 1987, 82, 1.
10. Nimah, M. N.; Ryan, J.; Chaudhry, M. A. Soil Sci Soc Am J 1983, 43, 742.
11. Ben Hur, M.; Keren, R. Soil Sci Soc Am J 1997, 61, 565.
12. Fonteno, W. C.; Bilderback, T. E. J Am Soc Hort Sci 1993, 118, 217.
13. Rubio, H. O.; Wood, M. K.; Cardenas, M.; Buchanan, B. A. J Arid Environ 1990, 18, 33.
14. Ben-Hur, M. Soil Sci 1994, 158, 283.
15. Hedrick, R. M.; Mowry, D. T. Soil Sci 1952, 73, 427.
16. Szmidt, R. A. R.; Graham, N. B. Acta Horticulturae 1990, 287, 211.
17. Baxter, L.; Waters, L., Jr. J Am Soc Horti Sci 1986, 111, 517.
18. Sojka, R. E.; Westermann, D. T.; Lentz, R. D. Soil Sci Soc Am J 1998, 62, 1672.
19. El Sayed, H.; Kirkwood, R. C.; Graham, N. B. J Exp Bot 1991, 42, 891.
20. Henderson, J. C.; Hensley, D. L. HortScience 1987, 22, 450.
21. Chen, J.; Park, H.; Park, K. J Biomed Mater Res 1999, 44, 53.
22. Chen, J.; Park, K. Carbohydr Polym 2000, 41, 259.
23. Bowman, D. C.; Evans, R. Y. HortScience 1991, 26, 1063.
24. Foster, W. J.; Keever, G. J. J Environ Horticulture 1990, 8, 113.
25. Woodhouse, J. M.; Johnson, M. S. Acta Horticulturae 1991, 294, 261.
26. Bowman, D. C.; Evans, R. Y.; Paul, J. L. Am Soc Horti Sci J 1990, 115, 382.
25. Bres, W.; Weston, L. A. HortScience 1993, 28, 1005.
26. Henderson, J. C.; Hensley, D. L. HortScience 1985, 20, 667.
27. Woodhouse, J. M.; Johnson, M. S. Acta Horticulturae 1991, 294, 261.
28. Abd El-Rehim, H. A.; Hegazy, E. A.; Abd El-Mohdy, H. L. J Appl Polym Sci 2004, 93, 1360.
29. Johnson, M. S. J Sci Food Agr 1984, 35, 1063.
30. James, E. A.; Richards, D. Scientia Horticulturae 1986, 28, 201.
31. Khokhlov, A. R.; Starodubtzev, S. G.; Vasilevskaya, V. V. Adv Polym Sci 1993, 109, 123.
32. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, New York, 1953.
33. Chiu, H. C.; Lin, Y. F.; Hung, S. H. Macromolecules 2002, 35, 5235.
34. Atkins, P. W. Physical Chemistry, 5th ed.; Oxford University Press: Oxford, 1994.
35. Lee, W.-F.; Wu, R.-J. J Appl Polym Sci 1996, 62, 1099.