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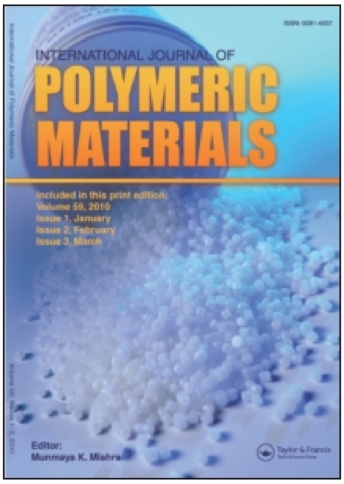

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Fast Swelling and Superabsorbent Properties of Radiation Crosslinked Acrylamide Based Polymers

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Fast Swelling and Superabsorbent Properties of Radiation Crosslinked Acrylamide Based Polymers

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Crosslinked polyacrylamide, PAAm, and acrylamide Na-acrylate copolymer, P(AAm-Na-AAc), were prepared by using electron beam irradiation. It was found that the dose required for achieving the crosslinking of PAAm and P(AAm-Na-AAc), depends on the polymer moisture content. The irradiation dose to obtain PAAm of maximum gel fraction was over 40 and 20 kGy for dry and moist PAAm, respectively. The Structural changes in irradiated PAAM were investigated using TGA, FTIR, and SEM. The swelling properties of such powders in distilled water and real urine solution were determined. The prepared crosslinked polymers reached their equilibrium swelling state in a few minutes. As the gel content and crosslinking density decrease, the swelling of the polymers increases. The ability of the prepared polymers to absorb and retain large amount of solutions suggests their possible uses in horticulture and in hygienic products like disposable diapers.

Keywords: crosslinking, irradiation, polyacrylamide copolymer, superabsorbent, diaper

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INTRODUCTION

Superabsorbent polymer is a network of flexible crosslinked chains exhibiting an intriguing combination of the properties of both liquids and solids. Superabsorbent polymer gels can swell up to hundreds of times their own weight in aqueous media. The term superabsorbers encompasses a number of crosslinked polymers such as poly(vinyl alcohol), poly vinylpyrrolidone, poly(ethylene oxide), carboxymethylcellulose, and polyacrylamide, all having the basic ability to swell in water.

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There has been increasing interest in the synthesis and applications of superabsorbent hydrogels [1]. Polymer hydrogels with crosslinked macromolecules have been studied intensively in recent decades for their promising applications in chemical engineering as sensors [2], in the biomedical field as materials in medicine [3], in pharmacy as drug delivery systems [4], in agriculture and industrial purpose as adsorbents and separation membranes [5–6], in solving some ecological problems [7], and in modern technologies [8].

Acrylamide hydrogels with crosslinked macromolecular networks have found extensive commercial applications as sorbents in personal care and agricultural purposes [9–11]. The interrelation between the structure of acrylamide hydrogels and their properties is of importance and contributes to understanding their potential applications. The swelling behavior of the hydrogel is very sensitive to the network microstructure and its interaction with water. The properties of the crosslinked polyacrylamide depend on the methods through which it is prepared [12–14]. Ionizing radiation has long been recognized as a very suitable tool for the formation of hydrogels with unique properties. Moreover, easy process control, no necessity to add any initiators, crosslinkers, and so on no waste and relatively low running costs make irradiation the method of choice in the synthesis of hydrogels [15–18].

Radiation-induced crosslinking of PAAm was investigated and carried out under various conditions. The molecular weight of the polymer, irradiation dose as well as the external pressure applied, are the most important factors for controlling the PAAm radiation crosslinking process [12–13, 19]. Although the crosslinked PAAm polymer can be directly obtained by irradiating its monomers or polymer in solution [13, 20–21], it is better from the economical point of view if its raw materials are processed by radiation in a solid state to form PAAm microgel. In the present work, crosslinking of PAAm and P(AAm-Na-AAc) powders using electron beam irradiation was investigated. The factors affecting the crosslinking degree and swelling behavior of the prepared polymers were studied. The possible uses of such materials in industries of hygienic products, as fast superabsorbents were discussed.

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EXPERIMENTAL

Materials

Commercial polyacrylamide, PAAm, supplied from El-Nasser Co. Egypt: molecular weight over 5,000,000 and viscosity (0.5% aqueous at 50°C) of 282 cP was used. The powder of 0.3 mm particle size was covered by a stainless steel net and was left to dry in vacuum oven at 45°C for 24 h before its use.

Sample Preparation and Irradiation

Appropriate weights of dry and wetted polymer powders were put in polyethylene bags (the thickness of the bags filled with powder was 3 mm) and irradiated at different doses with an electron beam at a beam current of 4 mA and an acceleration energy of 1.4 generated by a accelerator of 1.5 MeV (maximum beam current: 25 mA, power: 37.5 kW). Then, the irradiated powders were dehydrated for 2 h in absolute ethanol to extract water, left to dry at 37°C (room temperature) for 24 h and stored in vacuum oven at 45°C. The wetted PAAm was obtained by mixing in appropriate amount of water with the dry powder using glass bar before exposure to electron beam irradiation.

Preparation of P(AAm-Na-AAc) Powders

Appropriate weight of dry polymer (14 g) in 200 ml distilled water was stirred at 40°C until it completely dissolved. 1.5 g NaOH in 20 ml-distilled water was added to the PAAm viscose solution. The mixture was stirred for 5 h at 70°C. After cooling, the soluble polymer was precipitated by methanol, washed several time with dry methanol, left to dry at 45°C in vacuum oven, and grained (sieves of 0.3 and 0.2 mesh sizes were used to obtain powder of 0.3 mm particle size). The nitrogen content in the prepared P(AAm-Na-AAC) was determined by the Microanalysis Unit, Cairo University, Cairo Egypt. The % conversion of $CONH_2$ groups to COONa by NaOH treatment was calculated. It was found that the conversion of $CONH_2$ groups to COONa is 19.8%.

Swelling Measurement

Known weights of the dried powder were placed in stainless steel net bags and immersed in distilled water or urine solutions at 30°C for 15 mm in until the equilibrium swelling had been reached (it takes 3–10 min depending on the powder gel content). The bags were removed from the solution, blotted quickly with absorbent paper, and then weighed. For accuracy, the experiment was repeated three times for each sample and the average weight of swelled polymer was taken. The following equation was used to determined hydrogel swelling ratio:

$$\text{Swelling ratio (g/g)} = (\text{Ws} - \text{Wg})/\text{Wg}$$

where Ws and Wg represent the weights of wet and dry gel, respectively.

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Gel Determination

Known weights of dried powder were placed in stainless steel net bags and immersed in distilled water for 48 h at 75°C. The gelled part was taken out and washed several times with hot water to remove the soluble fraction, then dried and weighed. For accuracy, the experiment was repeated three times for each sample and the average weight of insoluble fraction was taken. The gel percent in the powder was determined from the following equation:

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

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

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SEM Examination

The powders were immersed in distilled water for 20 min, freeze dried, and examined with the use of a JEOLJSM-5400 (Japan) scanning electron microscope (SEM) after gold deposition in vacuum for three min.

TGA Measurements

Shimadzu Thermal Gravimetric Analysis (TGA) system of type TGA-50 was used to study the thermal stability of irradiated PAAm under nitrogen atmosphere. The temperature range was from ambient temperature to 600°C at heating rate of 10°C/min.

RESULTS AND DISCUSSION

Crosslinking of PAAm

Dry PAAm was irradiated by means of electron beam irradiation at 30 kGy in air atmosphere and after removal of the air by a vacuum pump. The percent gel content of irradiated PAAm in the presence of air and under vacuum was 52 and 56% respectively. PAAm irradiated under vacuum gave slightly higher gel fraction than that cross linked in air. This result agrees with that obtained by Burilloand and Ogawa who found that the gelation yield of irradiated PAAm did not increase appreciably when the irradiation was carried out in the absence of air [12].

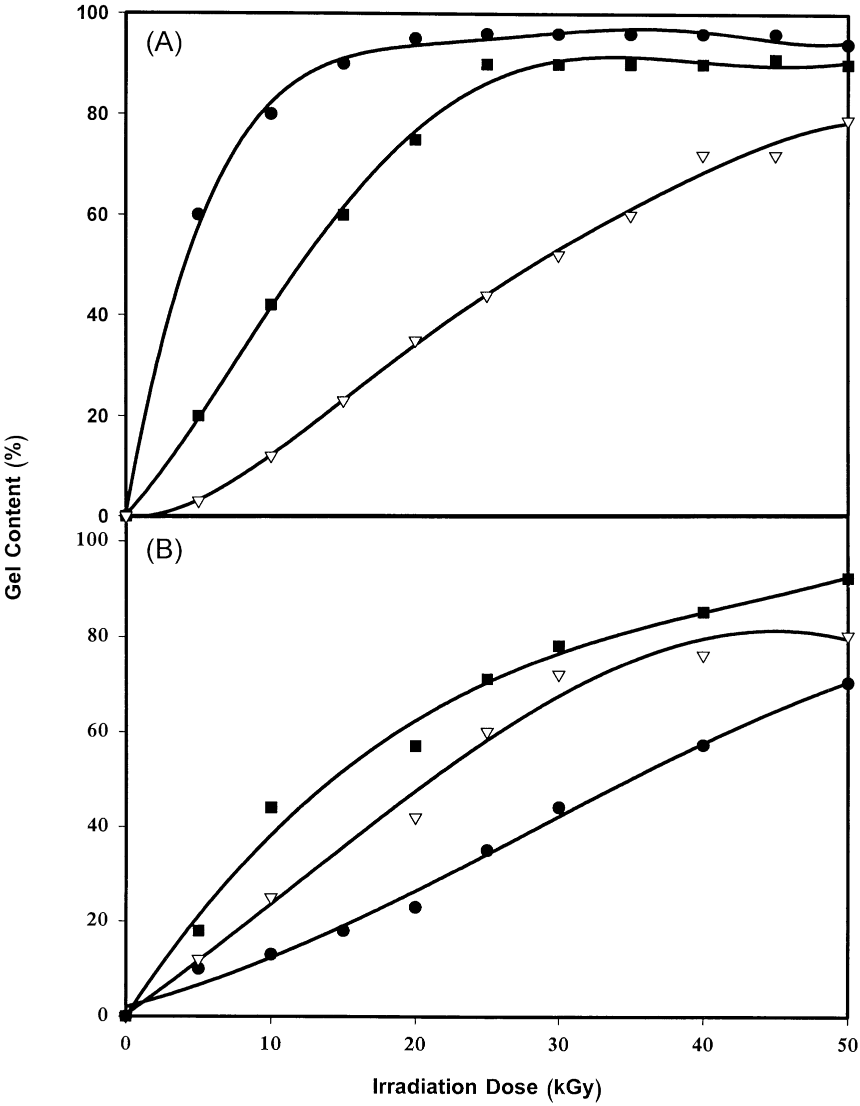

FIGURE 1 (A): The gel fraction of cross linked PAAm as a function of irradiation dose. (▽) Sample irradiated: in dry form, (■) with 10% (Wt/Wt) water, (●) with 20% (Wt/Wt) water. (B): The gel fraction of crosslinked P(AAm-Na-AAc) as a function of irradiation dose. Sample irradiated: (●) in dry form, (▽) irradiated with 5% (Wt/Wt) water, (■) irradiated with 10% (Wt/Wt) water.

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PAAm in a dry or moist form was irradiated at different doses in air atmosphere to produce polymer network. The gel fraction of PAAm as a function of irradiation dose is illustrated in Figure 1A. It is observed that the PAAm gel content increases as the irradiation dose increases to reach its maximum over 40 kGy and 20 kGy for dry and moist PAAm, respectively. Thereafter, any increase in irradiation doses leads to insignificant increase in gel content. Also, it can be seen that at the same corresponding irradiation doses, the gel content of PAAm irradiated in dry form is lower than that of PAAm irradiation in wet form. The minimum irradiation dose to obtain PAAm of maximum gel fraction depends on polymer moisture content. As the moisture content in the PAAm increases the dose required for maximum gel fraction decreases.

In the case of radiation crosslinking of PAAm in dry form, it is well known that the radiation creates radicals localized mostly on the main chains. The random recombination of these radicals creates covalent chemical bonds between the polymer chains. It causes an increase in the branching rate and increase of average molecular weight of the polymer, which results in properties such as insolubility and infusibility. Radiation dose higher than the gelation dose changes the linear PAAm chains into a three-dimensional network.

In radiation processing of wetted PAAm, there are two ways for the water to contribute to the corsslinking process of PAAm. First, it enhances mobility and elasticity of the PAAm chains. As a consequence, the molecular movement of all chains or their parts increases, allowing closing of the distances between the macro radicals to recombine and enhance intermolecular and intramolecular recombination reactions to occur. Second, the products of water radiolysis, namely, hydrogen and hydroxyl radicals, create macro-radicals by abstracting H from the polymer chains. Thus, the crosslinking process of PAAm occurs faster and easier in the presence of water [17]. To enhance the crosslinking reactions, the water should be homogenously dispersed in the powder before the irradiation.

Crosslinked P(AAm-Na-AAc) copolymers were also produced by radiation and their gel contents were determined (Figure 1B). It can be seen that the effect of radiation and polymer moisture content on the crosslinking process of P(AAm-Na-AAc) is similar to that observed for PAAm crosslinking; however, the introduction of sodium acrylate to PAAm reduces the extent of crosslinking and raises the dose required for network formation. This is due to the change in PAAm structure and properties when moving from neutral polymer to polyelectrolyte copolymer. The electrostatic repulsion plays a role to hinder the recombination of radicals and, consequently, reduces the extent of the copolymer crosslinking.

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Properties of Obtained Hydrogels and Swelling Behavior of the Prepared Hydrogels

The time required for polymer equilibrium swelling was determined. The equilibrium swelling of irradiated polymer is fast, takes place in a few minutes, and results in a drastic increase in its volume. The unirradiated PAAm as expected, absorbed large amount of water and dissolved in it. The time needed for all crosslinked polymer under investigation to reach their equilibrium swelling ranged from 3 to 10 minutes, depending on the polymer crosslinking density. This observation is interesting for practical application of such crosslinked polymers [1].

The distilled water absorbed by irradiated PAAm was determined and shown in Figure 2. The swelling ratio of PAAm irradiated in dry form is higher than that of PAAm irradiated with this same dose in moist form. The swelling ratio of irradiated PAAm follows the order: dry PAAm > PAAm containing 10% water > PAAm containing 20% water.

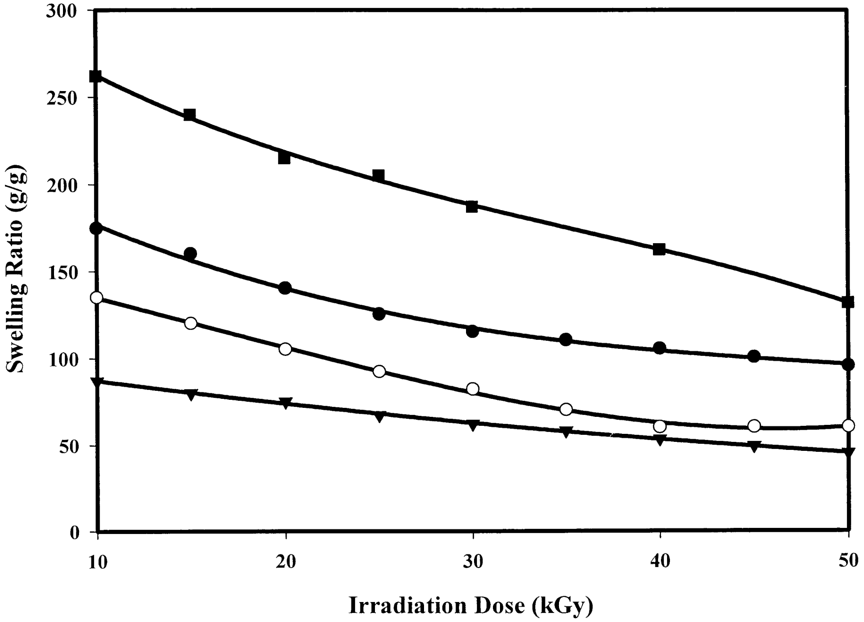

FIGURE 2 The swelling ratio of PAAm and P(AAm-Na-AAc) in distilled water prepared at different conditions. PAAm samples: (●) irradiated in dry form, (○) irradiated in wet form; 10% (Wt/Wt) water, (▼) irradiated in wet form; 20% (Wt/Wt) water. (■) P(AAm-Na-AAc) irradiated in wet form; 10% (Wt/Wt) water.

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The swelling properties of the investigated hydrogel are mainly related to its degree of crosslinking. The reduction in the swelling property of irradiated PAAm containing 20% water is attributed to the high degree of crosslinking, which restricts the mobility of the polymer chains and decreases its swelling ratio.

The lack of ionic character in the PAAm polymers structure greatly reduces their ability to absorb water. Therefore, in order to raise their swelling efficiency in aqueous media, partial hydrolysis of polyacrylamide chains was done to obtain PAAm-based polymers containing both amide and Na-AAc groups.

From Figure 2 it is clear that, at the same absorbed doses, crosslinked P(AAm-Na-AAc) copolymer swelling ability is much higher that that of PAAm.

A major difference between the PAAm and P(AAm-Na-AAc) is in the presence of ionizable hydrophilic Na-AAc groups of polar negative charges in P(AAm-Na-AAc). Thus, the high swelling ability of P(AAm-Na-AAc) can be attributed to the electrostatic repulsion between the polarized charged group on the network chains and the concentration difference of mobile ions inside and outside the hydrogel [5].

FTIR Study

FTIR spectra were obtained from the dry PAAm powders, which were exposed to electron beam irradiation at different doses (Figure 3). The FTIR spectra of irradiated PAAms show a new distinguishing band at $1600\,\mathrm{cm}^{-1}$ for unsaturated double bond. The intensity of this band increases by increasing the irradiation dose. This result suggests that beside the formation of crosslinking bonds between the PAAm chains; Additional reactions take place, resulting in radical disproportionation and unsaturated bond formation. The pale yellow color of irradiated PAAm confirmed the formation of unsaturated bonds.

Pore Structure and Particle Shape of Irradiated PAAm

The pore structure at the surface of hydrogels is thought to be important for their fast swelling property. Thus, freeze dried PAAm hydrogels irradiated in dry form were examined by SEM (Figure 4). The unirradiated PAAm powders exhibited a wide pore size and lost their shapes to form a pastelike structure (Figure 4A), whereas the irradiated powders show distinct aggregated particles of narrow pore size structure (Figure 4B).

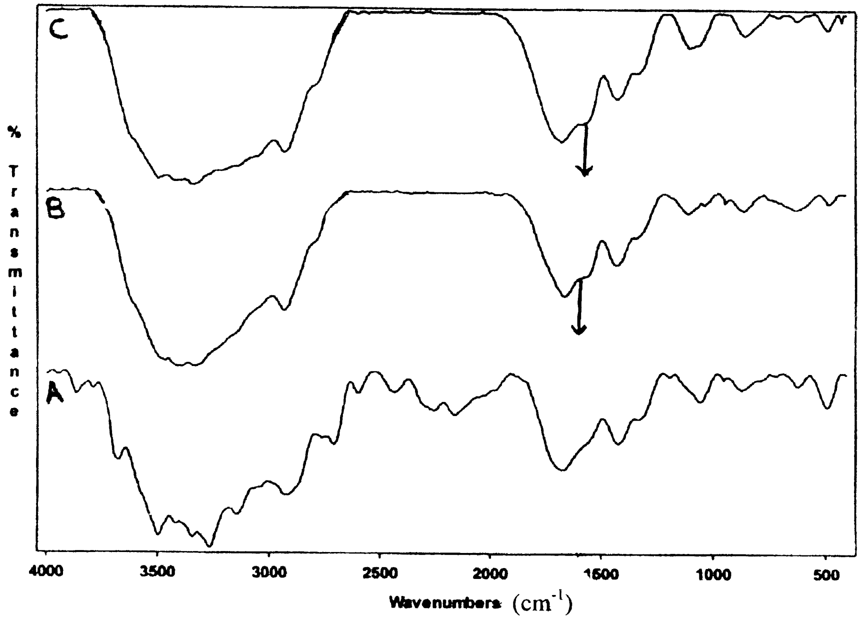

FIGURE 3 FTIR spectra irradiated PAAm prepared in dry form at different irradiation doses: (A) unirradiated PAAm, (B) irradiated at 20 kGy, and (C) irradiated at 40 kGy.

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It is clear that the morphology of PAAm was affected by irradiation. The network structure prevented the PAAm particles from dissolving in water and kept their shape, but in a distorted form.

TGA Study

The thermal stability of irradiated polyacrylamide was investigated by using TGA technique (Figure 5). When PAAm particles were exposed to electron beam irradiation, insignificant effect on their thermal stability was observed. The thermal stability of irradiated PAAm prepared at 50 kGy is slightly higher than that of the unirradiated one. This effect is clearly noticeable when the temperature reached 400°C at which the weight loss is lower than that of unirradiated PAAm.

Practical Evaluation of Irradiated Powders for Possible Uses in the Diaper Industry

Certainly the most important property in a commercial superabsorbent used in the personal care market is the extent of swelling. This

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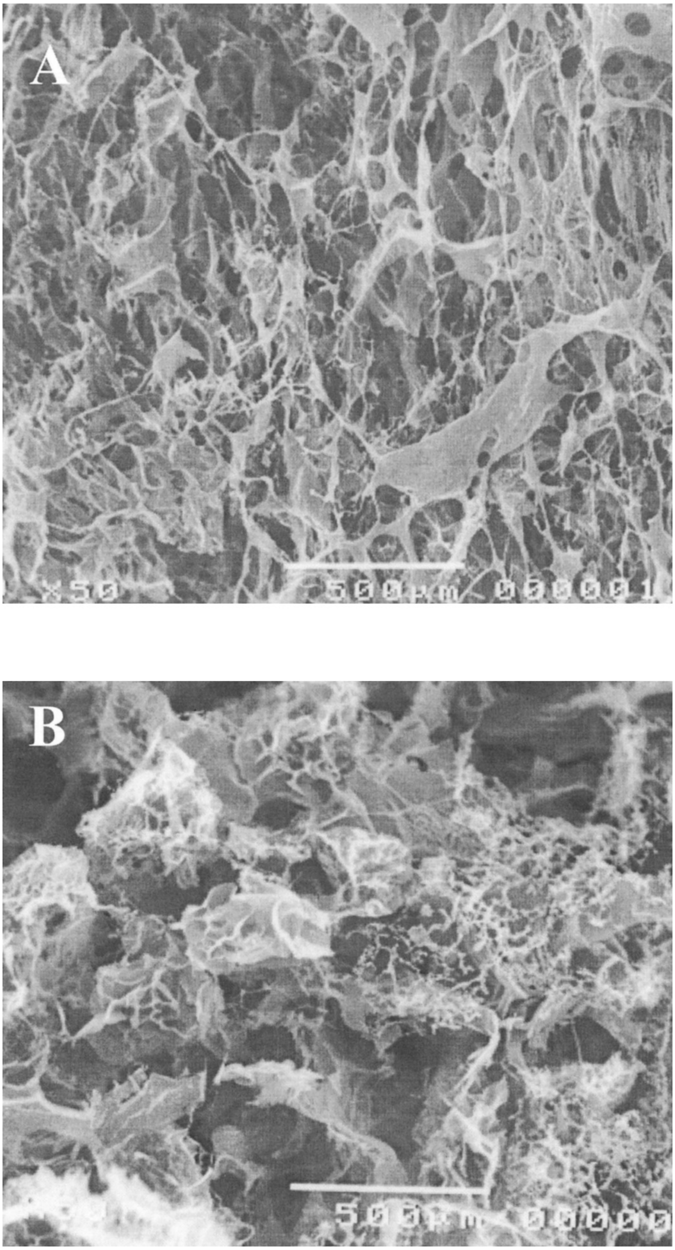

FIGURE 4 SEM photos of (A) Unirradiated PAAm and (B) PAAm particles irradiated in a dry form at dose of 30 kGy.

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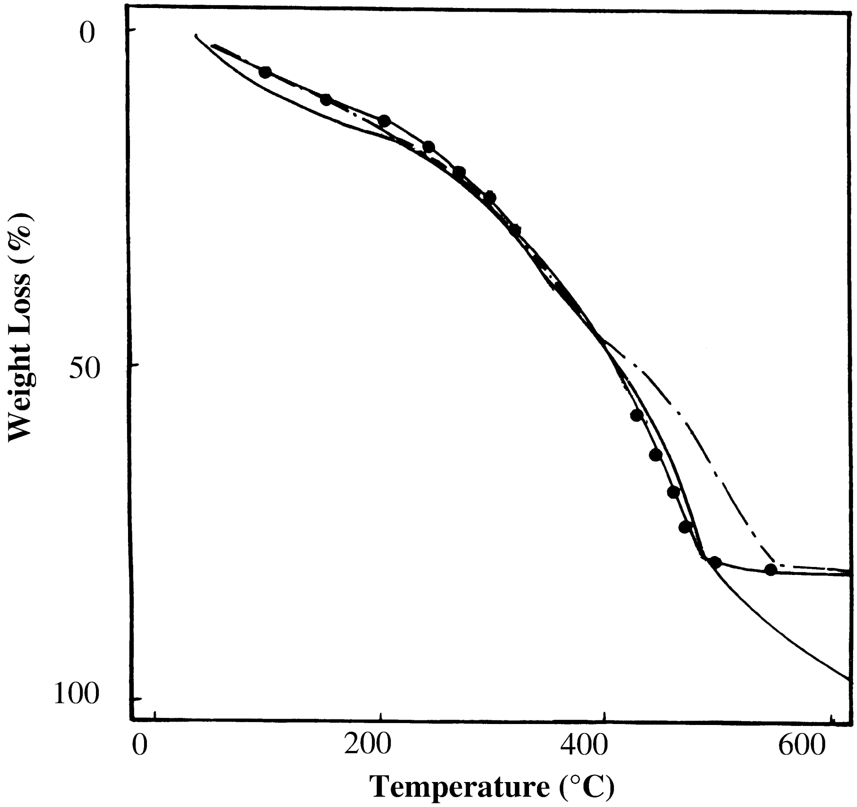

FIGURE 5 TGA thermograms of irradiated PAAm prepared in dry form at different irradiation doses; (–) unirradiated PAAm, (.-.-.) irradiated at 10 kGy, and (-●-) irradiated at 30 kGy.

is true not only because swelling is related to the properties of the network, but also because the principal performance criterion for diapers is the amount of liquid contained per unit cost of diaper. The acceptable swelling capacity is approximately 20–40 g of urine per gram of polymer [1].

Therefore, the amount of urine absorbed by different types of dry PAAm-based hydrogels prepared by ionizing radiation was investigated and the results are shown in Figure 6. In general the swelling of hydrogels in urine solution is much lower than that obtained in distilled water (Figures 2 and 6). The absorption of urine decreases as the crosslinking degree of the PAAm based polymer increases. The amount of urine absorbed by P(AAm-Na-AAc) is much higher than that absorbed by PAAm. P(AAAm-Na-AAc) copolymers can swell

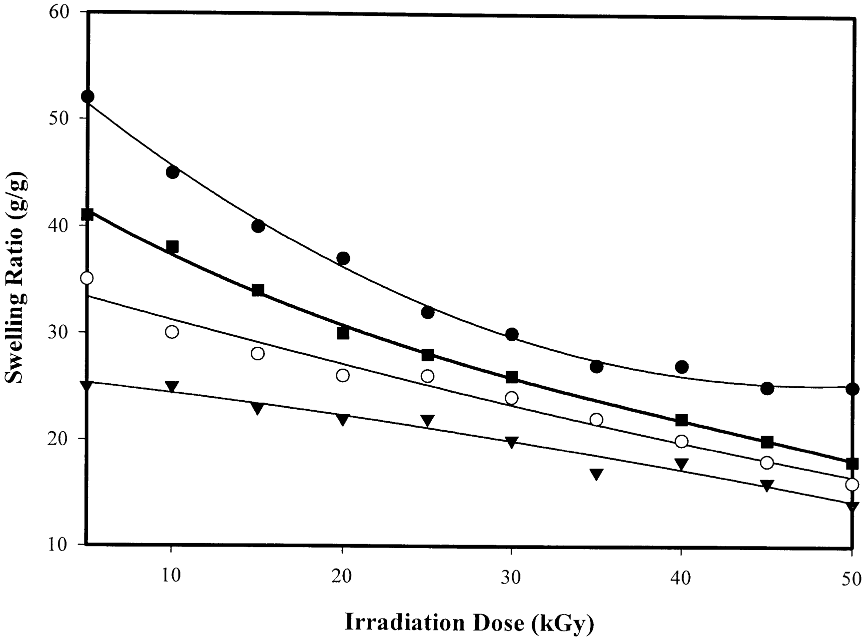

FIGURE 6 The swelling ratio of PAAm and P(AAm-Na-AAc) in urine; (■) PAAm sample irradiated in dry form; (○) PAAm sample irradiated in wet form containing 10% (Wt/Wt) water; (▼) PAAm sample irradiated in wet form containing 20% (Wt/Wt) water; (●) P(AAm-Na-AAc) sample irradiated in wet form containing 10% (w/wt) water.

30–50 times their own weight in urine. However, the PAAm polymers absorb only 15–35 times their weight urine, depending on the polymer crosslinking degree.

It is well known that minute changes in the external conditions such as pH, temperature, solvent composition, and ionic strength can induce drastic changes in the state of the swollen network. Thus, the reduction in polymer swelling in urine can be attributed to the effect of the salts in urine on macromolecules network, which may cause a swelling volume transition. These effects are usually explained by changes of the solution structure induced by ion dehydration that is responsible for the drastic changes in hydrogel swelling property [22–23].

The introduction of the polar negative charges to PAAm leads to a better salt-resistance and solution-absorption rate. The high swelling of P(AAm-Na-AAc) gels in urine is associated with the difference between the mobile ion concentration inside and outside the gel. The

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presence of Na^+ mobile ions inside the gel increases the electroneutrality conditions and creates an additional osmotic pressure that expands the gel [5]. (Please note: the swelling of the prepared hydrogels was also performed in artificial urine prepared according to the method of Kark et al. [24]. The results obtained by the use of the artificial urine were approximately the same as that obtained by using real urine.)

CONCLUSION

An effort was made to make use of the radiation facilities to help to develop the superabsorbents process technology and suggest an easy method for their production. Crosslinked AAm-based polymers, which are already used for the production of commercial superabsorbent, can be produced in a powder form by using electron beam irradiation. The corsslinking extent in the irradiated AAm-based polymers was controlled by the polymer moisture contents and irradiation doses. The prepared crosslinked polymers and copolymers possess high and fast swelling properties in aqueous media. In reference to swelling ratio of the commercialized superabsorbent products in urine or saline solution, the absorbency values (g/g) of the prepared AAm-based polymers in different solutions are in the permitted ranges and acceptable as superabsorbent materials. The promising results obtained reveal that such prepared materials may be of great interest in horticulture and industrial applications.

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