Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article El-Mohdy, H. L. Abd , Hegazy, El-Sayed A. and El-Rehim, H. A. Abd(2006) 'Characterization of Starch/Acrylic Acid Super-Absorbent Hydrogels Prepared by Ionizing Radiation', Journal of Macromolecular Science, Part A, 43: 7, 1051 — 1063

To link to this Article: DOI: 10.1080/10601320600740249

URL: http://dx.doi.org/10.1080/10601320600740249

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:1051–1063, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600740249

Characterization of Starch/Acrylic Acid Super-Absorbent Hydrogels Prepared by Ionizing Radiation

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Copolymerization of acrylic acid (AAc) and gelatinized maize starch in aqueous medium using γ-irradiation, followed by neutralization with alkali solution was carried out. The preparation conditions, such as irradiation dose and starch/AAc compositions were investigated. The higher the irradiation dose, as well as the AAc content in the feed solution, the higher the gel content. The copolymers were characterized by FTIR spectroscopy, thermo-gravimetric analysis (TGA) and scanning electron microscopy (SEM). SEM revealed that the higher the dose, the lower the copolymer pore size. Starch/AAc copolymers have thermal stability higher than that for starch and poly acrylic acid individually. The swelling of starch/AAc hydrogels reduced as the gel content increases. The maximum water absorption obtained for starch/AAc hydrogels in distilled water was 200 g/g, and for neutralized starch/AAc hydrogels was 350 g/g. The swelling ratio of starch/AAc hydrogels of different compositions in NaCl solution is lower than that obtained in distilled water. The results suggest that the neutralized starch/AAc hydrogels have a high swelling property, and can be used in a variety of commercial applications.

Keywords starch, copolymerization, radiation, superabsorbent, hydrogel

Introduction

Starch is a renewable and biodegradable natural polymer, found to be useful in a variety of commercial applications due to its most practical property of gelatinization. During gelatinization, starch swells irreversibly by absorbing immense quantities of water. This property has been made useful in the textile and paper industries by incorporating starch as a thickener and sizing agent. Polyacrylic acid gives more stability to starch when grafted onto it due to the hydrogen bonding between its carboxylic groups and the starch hydroxyl groups (1, 2). The polyacrylic acid/starch copolymer exhibits different properties depending on the composition and type of interactions within the network, due to chemical crosslinking and hydrogen bonding interactions. Moreover, the combination of the hydrophilic acrylic polymer properties with the biodegradable character of starch based blends, may lead to interesting hydrogels with potential

Received December 2005; Accepted January 2006.

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applications especially as hydrogels for personal care products, food packages, and agricultural purposes (3).

Masuda et al. (4) and Wong (5) have patented the water absorbing resins prepared from starch using AAc as one of the components. Nukushina presented a review on the properties and uses of super-absorbents based on crosslinked copolymers of starch grafted with acrylonitrile and acrylic acid (6). Buchholz described the uses of super-absorbents based on crosslinked, partially neutralized poly(acrylic acid) and graft copolymers of starch and acrylic acid (7). Recently, Athawale et al. listed some of the important commercial applications of super-absorbents based on starch grafted with acrylic acid and its sodium salt (3, 8).

As with other free-radical polymerizations, starch-graft- acrylate copolymers can be prepared through either chemically (9, 10) initiated or radiation-induced process (11, 12). Starch and poly(acrylic acid), contain a large number of hydroxyl and carboxylic groups respectively, in their structure. The hydrophilicity of these groups makes these copolymers better raw materials for hydrogels. The chemical binding by means of grafting of acrylic acid onto gelatinized starch enhances the ability of water absorption of each component.

The present work is aimed at preparation of starch/AAc copolymers using gamma-rays as initiators. Suitable conditions for copolymerization of AAc onto gelatinized maize starch were investigated. Characterization and possible applications of the prepared copolymers were discussed.

Experimental

Materials

The commercial grade maize starch was supplied by El Nasr Pharmaceutical Chemicals Co., Egypt. Acrylic acid (purity 99%; Merck, Germany) was used as received. The other chemicals, such as solvents and inorganic salts, were reagent grade and used without further purification.

Methods and Apparatus

FT-IR Spectroscopy

Analysis by FTIR Spectroscopy, using Mattson 1000, Unicam, Cambridg, England, was carried out in the 400–4000 cm^{-1} range.

pH Measurements

The pH of solutions was determined by using a Jenway 3310 pH Meter.

TGA Measurements

Thermal Gravimetric Analysis (TGA) was determined on a Shimadzu TGA system (Type TGA-50). The temperature range was from ambient temperature to 600°C at a heating rate of 10°C/min, under a nitrogen atmosphere.

Scanning Electron Microscopy (SEM)

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

Preparation of Graft Copolymers of Starch with Acrylic Acid

Starch solutions (1–5 g in 100 ml distilled water) were gelatinized and mixed with various amounts of acrylic acid and then exposed to γ-ray radiation from a ^{60}Co source. The formed gels were cut into small pieces, air dried, and milled to a powder.

Neutralization of Starch/AAc Hydrogels

Starch/AAc hydrogels were immersed in sodium hydroxide solution (5%) for 3 h at room temperature. After treatment, the hydrogels were soaked in distilled water, three times, for 6 h, washed and dried in vacuum oven at 50°C for 24 h.

Swelling Determination

Dried irradiated gels of known weights were put in stainless steel net bags and immersed in distilled water or saline solutions at 30°C. After 24 h, equilibrium swelling was reached. The bags were removed from the solution, blotted quickly with absorbent paper and then weighed. The experiment was repeated three times for each sample and the average weight of the swelled copolymer was determined. The following equation was used to determine the swelling ratio of the hydrogels:

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

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

Gel Determination

Dried samples of a known weight were put in stainless steel net bags and immersed in distilled water for 48 h at 80°C. The gelled part was washed several times with hot water to remove the soluble fraction, then dried and weighed. The experiment was repeated three times for each sample and the average weight of insoluble fraction was taken. The gel percent in the hydrogel was determined from the following equation:

$$\text{Gel (\%)} = (\text{Wg}/\text{Wi}) \times 100$$

where Wg and Wi are dry hydrogel after and before extraction, respectively.

Results and Discussions

Gel Content

Gel content and crosslinking network density of prepared copolymer greatly influence the 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, such as polymer compositions and irradiation dose.

The effect of starch/AAc compositions on the starch/AAc copolymer gel content at different irradiation doses was investigated and shown in Figure 1. It is clear that the gel

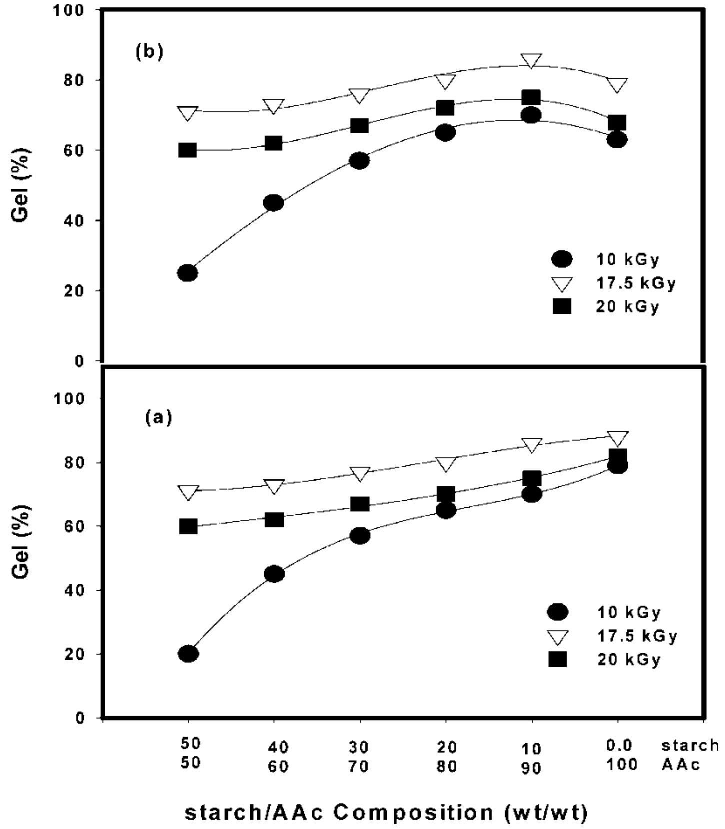

Figure 1. Effect of starch/AAc compositions prepared at different irradiation doses on the gel (%); (a) starch/AAc and, (b)neutralized starch/AAc hydrogels.

content of starch/AAc copolymer increases with increasing the AAc content in the polymeric feed solutions. On the other hand, by increasing the irradiation dose, the gel content increases to reach a maximum value at 17.5 kGy. Thereafter, any increase in irradiation dose, leads to decrease in gel (%). At a high irradiation dose the starch tends to degrade and as a consequence, the gel content decreases.

FT-IR Spectroscopy

The IR spectra of both pure and grafted starch (Figure 2) both show a broad absorption band characteristic of the glucosidic ring of starch, in the range of 3200–3450 cm^{-1}. Other bands, such as those at 2931 and 2927 cm^{-1} (C—H stretching) and peaks around 1157.2 cm^{-1} (C—O stretching) due to hydroxyl groups, can also be seen. The spectrum of starch/AAc showed a new band at 1708.8 cm^{-1} (—C═O stretching) for the PAAc acid grafted chains.

Swelling of Starch/AAc Copolymer of Different Compositions

The swelling of starch/AAc and neutralized starch/AAc hydrogels of different compositions in distilled water was investigated and shown in Figure 3(a-b). It is clear that the

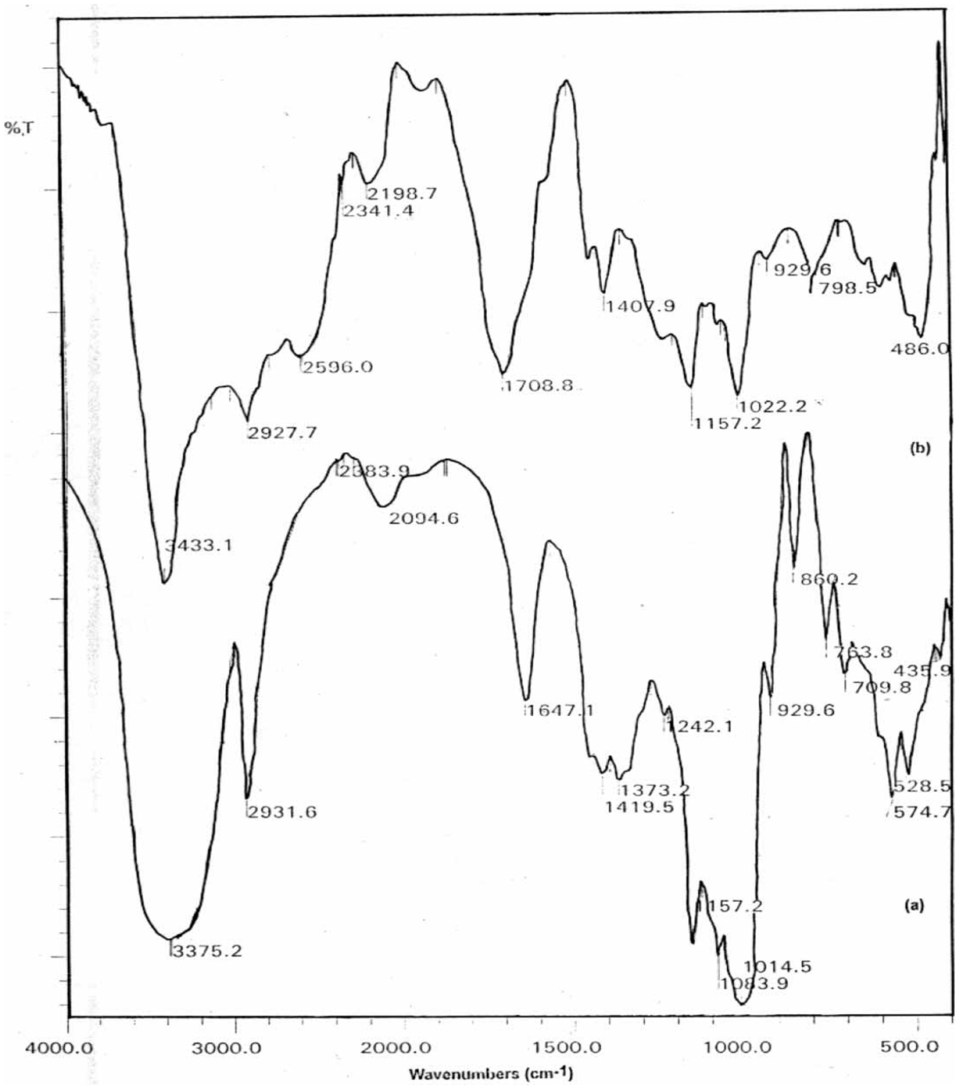

Figure 2. FTIR- spectra for of starch (a) and starch/AAc (b).

swelling increases with increasing AAc content for untreated starch/AAc Figure (3a). Meanwhile, for neutralized starch/AAc hydrogel, the swelling increases with increasing AAc content and the maximum swelling was obtained at (10/90) starch/AAc as shown in Figure 3b. At the same composition and irradiation dose, the swelling of neutralized starch/AAc is higher than that for untreated starch/AAc. The interaction and hydrogen bonding between the free carboxylic groups of PAAc and hydroxyl groups of starch reduces the swelling of starch/AAc copolymers. Probably, hydrogen bonding favors the formation of a continuous and strong network, which can restrict water diffusion and chain expansion. It was reported that strong inter-chain hydrogen bonding takes place between the grafted side chains of poly(acrylic acid) and the hydroxyl groups of the starch backbone (13, 14).

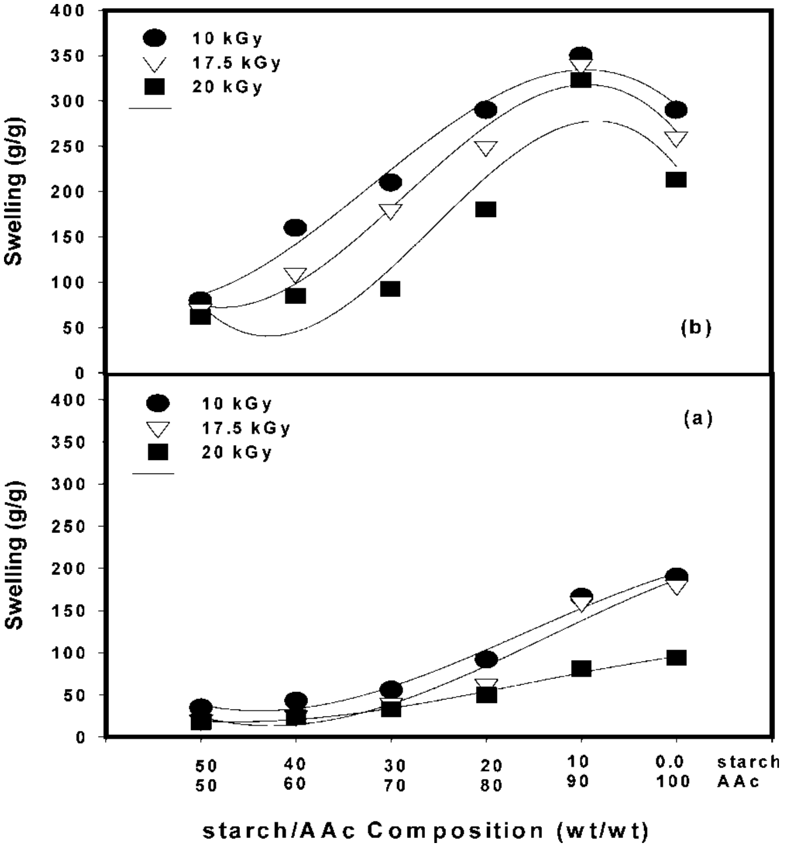

Figure 3. Effect of various starch/AAc compositions on the swelling of (a) starch/AAc and, (b) neutralized starch/AAc hydrogels at different irradiation doses.

On the other hand, the high swelling degree of neutralized starch/AAc in pure water can be attributed to the electrostatic repulsion between charged groups on the network chains and the concentration difference of mobile free counter ions (Na^+) inside and outside the hydrogel. The driving force of the swelling process is the presence of mobile osmotically active counter ions. Therefore, the content of ionizing groups inside the gel has a great effect on the copolymer swelling behavior. As the neutralized AAc increases, the mobile ion (Na^+) concentration inside the gel increases to maintain the electro-neutrality conditions. As the result, the difference between the mobile ion concentration inside and outside the gel increases and creates an additional osmotic pressure that expands the gel (15).

Swelling Rate

The comparative study between the swelling rate of various compositions of neutralized starch/AAc hydrogel in distilled water was investigated and shown in Figure 4. It can be seen that the swelling rate and ratio is significantly influenced by the copolymeric compositions. The equilibrium swelling for neutralized starch/AAc (10/90) and pure polyacrylic acid reached at 220 and 180 min, respectively. Meanwhile, the neutralized

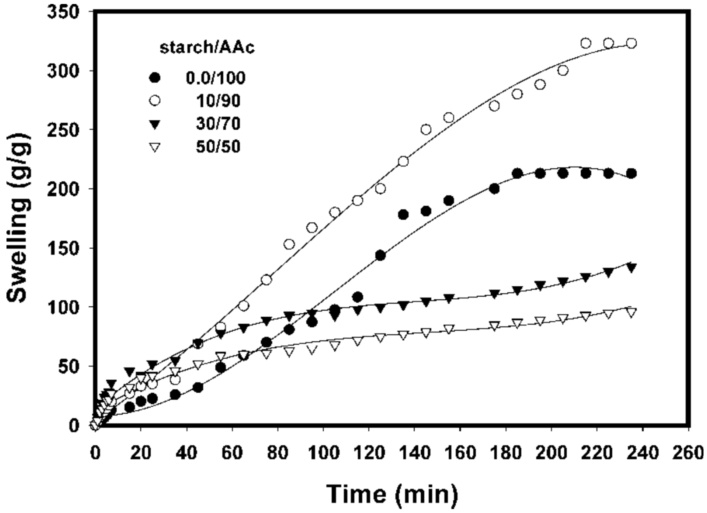

Figure 4. Swelling rate of neutralized starch/AAc hydrogel in distilled water at different compositions. Polymer conc.; 10%, and irradiation dose; 20 kGy.

starch/AAc hydrogels of compositions (50/50) and (30/70) need a long time to reach the equilibrium state. These results could be attributed to the hydrophilic character of the hydrogel. When the hydrophilic character of the hydrogel increases, by increasing the carboxyl groups, its swelling in aqueous medium turns out to be faster. On the other hand, the decreasing in rate of swelling of the starch/AAc hydrogels of compositions (50/50) and (30/70) may be attributed to the increase in crosslinking resulting from the hydrogen bond between hydroxyl groups of starch which reduces the swelling rate.

Swelling of Starch/AAc Copolymer of Different Compositions in Saline Solutions

The phenomenon of gel swelling has been the subject of numerous studies in polymer physics. It has been 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 (16, 17). In this connection, it is important to understand the osmotic and structural changes of polymer gels induced by the addition of salts. Therefore, the effect of NaCl and synthetic urine solution on the swelling behavior of starch/AAc hydrogels prepared by γ-irradiation was investigated and shown in Figures 5 and 6, respectively. In general, the swelling of hydrogels in 0.9 wt% NaCl or synthetic urine solution is much lower than that obtained in distilled water. Also, it is clear that the swelling of neutralized starch/AAc hydrogels in 0.9 wt% NaCl or synthetic urine solution is higher than that for untreated ones. The neutralized starch/AAc of (10/90) copolymer composition had the maximum swelling value, in both distilled water and in 0.9 wt% NaCl or synthetic urine.

Effect of pH on the Swelling

The swelling behavior of starch/AAc and hydrolyzed starch/AAc hydrogels in solutions of various was investigated as shown in Figure 7(a-b). The Figure shows that the swelling increases with the increase of pH value and reaches a maximum at pH 7, then it decreases

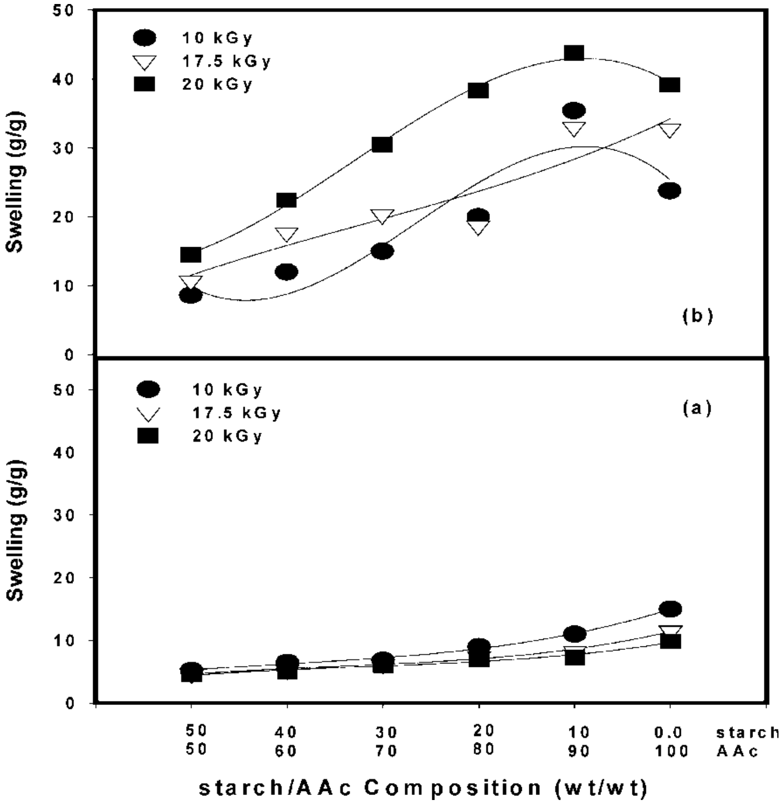

Figure 5. Effect of starch/AAc compositions on the swelling of, (a) starch/AAc and, (b) neutralized starch/AAc hydrogels in 0.9%NaCl at different irradiation doses.

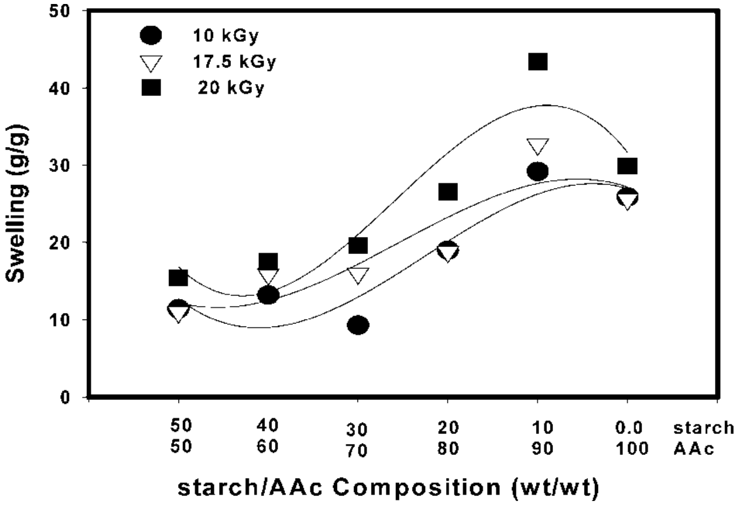

Figure 6. Effect of various starch/AAc compositions on the swelling of neutralized starch/AAc hydrogel in synthetic urine at different irradiation doses.

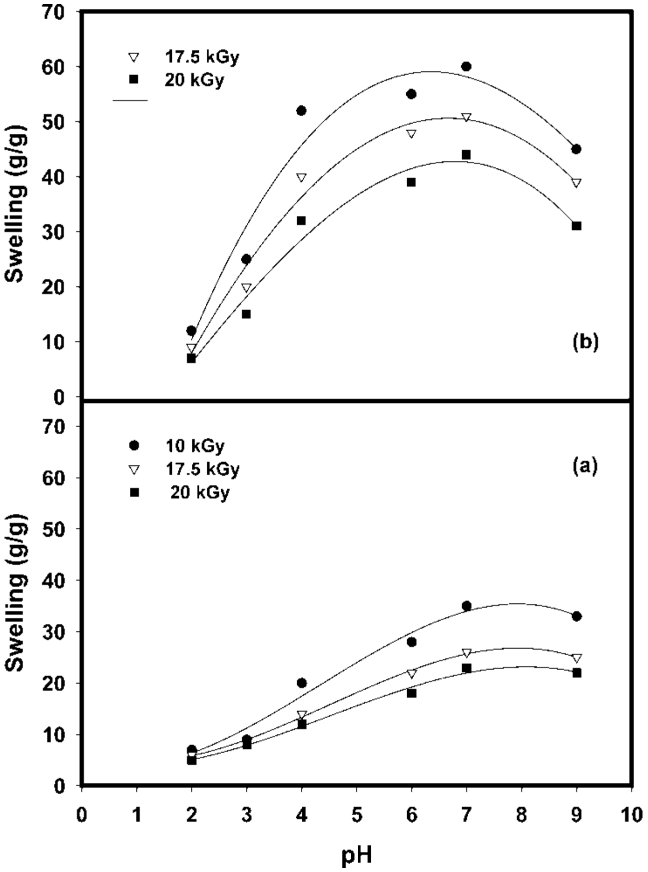

Figure 7. Effect of pH on the swelling of (a) starch/AAc and, (b) neutralized starch/AAc hydrogels.

with a further increase in pH. The results can be explained according to the following: at low pH values, the ratio of the non-ionized —COOH groups to the ionized ones (—COO$^-$) increases [the most carboxylate groups on the polymeric chain of neutralized starch/AAc hydrogel have been reduced to the carboxylic acid groups by the strong HCl acid. This increases the likelihood of the formation of inter- and intra-molecular hydrogen bonds and reduces the hydrophilic nature of the copolymer. At pH 4–7, the hydrogen bond attraction between the —C=O groups in PAA and the —OH groups in starch disappears and electrostatic repulsion which existed in the network chains of the hydrogel is predominant as a result, the copolymer swelling increases. While at higher pH values, the polymer swelling decreases. This behavior is mainly due to the screening effect of the counter ions on the polyanion chain.

Effect of Temperature of Solution

Figure 8 shows the effect of solution temperature on the absorbency rate of neutralized starch/AAc hydrogel. The results demonstrated that the swelling rate at high temperature

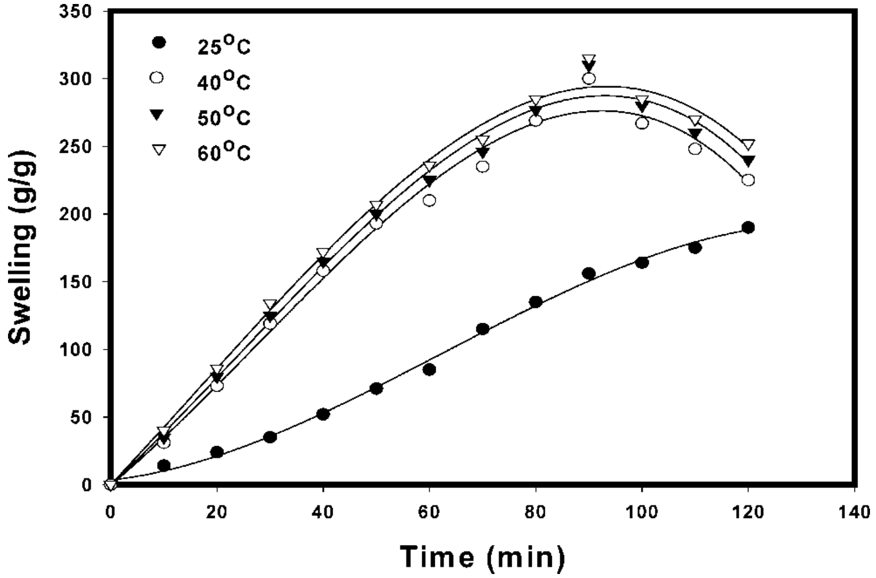

Figure 8. Effect of surrounding temperature on the swelling rate of neutralized starch/AAc hydrogel in distilled water at different irradiation doses. Polymer conc.; 10 %, starch/AAc composition; 10/90 (wt/wt)and irradiation dose; 20 kGy.

is higher and reaches a maximum swelling value faster than that at low temperature. This behavior can be explained as follows: the swelling of a hydrogel is greatly influenced by the temperature of the swelling medium; a rise in temperature affects the relaxation of hydrogel network chains as well as the rate of water molecules diffusion into the gel.

Thermo-gravimetric Analysis (TGA)

The thermal behavior of starch, AAc and their copolymers was investigated by using TGA as shown in Figure 9. Pure starch shows a characteristic two–steps thermogram. The first step shows weight loss about 9.5%, within the temperature range of 25–100°C. The major weight loss (75%) occurs in the second step at a temperature around 300°C. In the case of AAc and starch/AAc of different compositions, the thermograms show multi-degradation steps. No weight loss occurred up to 100°C. A weight loss of 60% occurs at a temperature range from 400 to 450°C. Thus, it is clear that the thermal stability of starch/AAc copolymer of different compositions is higher than that of starch. This means that the addition of AAc to starch improves the thermal stability of the latter.

Scanning Electron Microscopy (SEM)

The pore size of the polymeric material mainly depends on those factors affecting the swelling and micro-morphology properties of hydrogels and seriously affect micro-morphology; the irradiation dose and copolymer composition. The pore size and

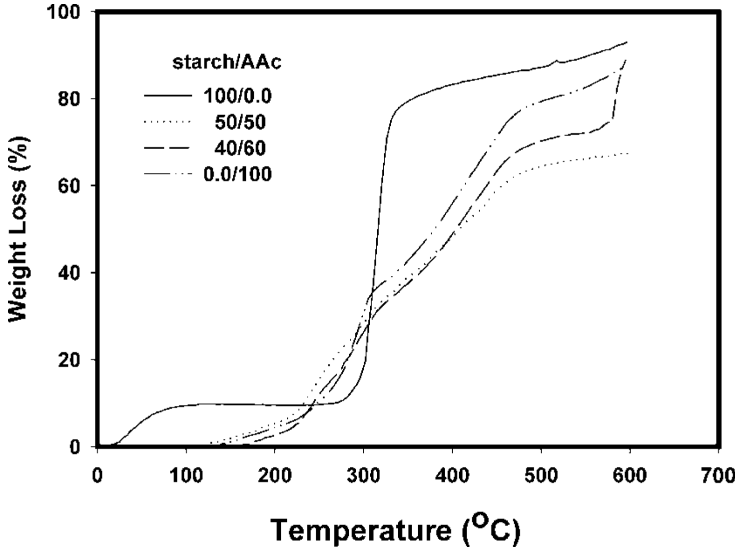

Figure 9. Thermal diagram curve for the different starch/Aac compositions.

morphological structure of the starch/AAc hydrogel irradiated at different doses were investigated and are shown in Figure 10. It is clear that the structure of the hydrogel is affected by the irradiation doses; as the irradiation dose increases the crosslinking density increases and the pore size decreases. The copolymer composition also affects the hydrogel pore structure. As shown in Figure 10, the hydrogel of composition (10/90) (starch/AAc) shows a larger pore structure compared with the other compositions.

The hydrogel containing a low crosslinking density generally forms a wider pore structure. However, the others, containing a high crosslinking density and irradiated at high doses, are randomly aggregated and exhibit a granular structure. This is due to the differences in the expansion of polymer network and in the magnitude of the affinity of the polymer network for water. Also, the decrease in pore size would be attributed to the increase in the elasticity of the hydrogels increases with increasing the gel crosslinking structure.

Conclusions

The starch/AAc hydrogels were prepared by copolymerization of acrylic acid (AA) and gelatinized maize starch in aqueous medium using γ-irradiation. The results showed that irradiation dose and starch/AAc blend composition influence the swelling of the obtained hydrogels and alter their gel content. By increasing the AAc polymer in the starch/AAc blend the gel content increases. The starch/AAc of composition (10/90) had the maximum swelling value. The swelling of starch/AAc at different compositions in NaCl solution is lower than that in distilled water. The maximum water absorption obtained for starch/AAc hydrogels in distilled water was 200 g/g but for neutralized starch/AAc hydrogels was 350 g/g and 15, 43 g/g in distilled water and NaCl solutions, respectively. The swelling of neutralized starch/AAc hydrogel increases with

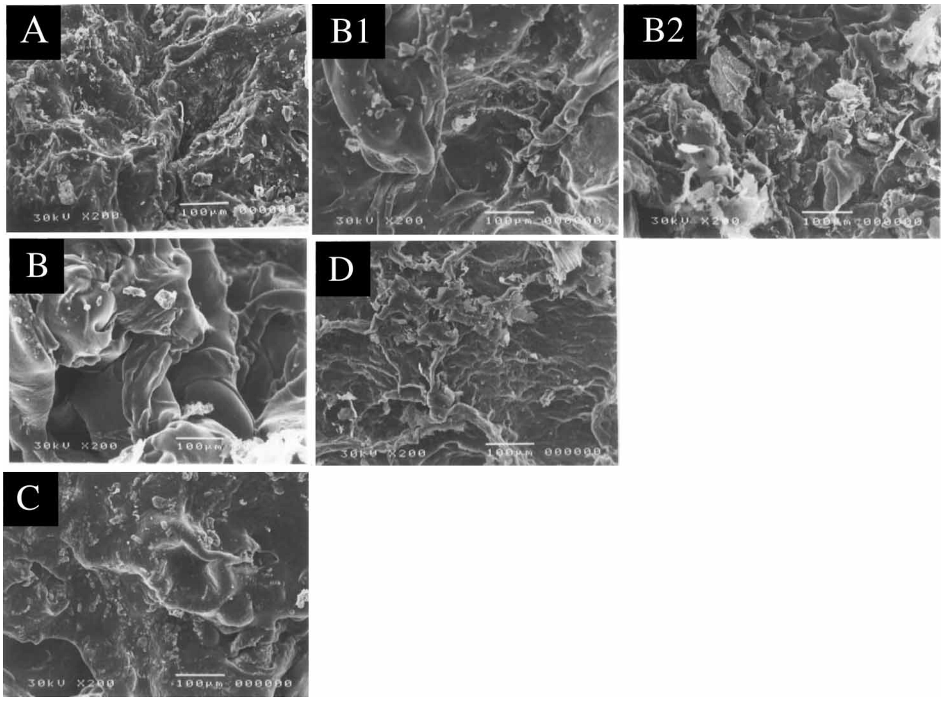

Figure 10. SEM for starch/AAc hydrogel prepared at different compositions; starch/AAc ratio; (A) 0.0/100, (B) 10/90 (C) 30/70 and (D) 50/50, SEM for starch/AAc hydrogel prepared at different irradiation doses; (B) 10 KGy, (B1) 17.5 KGy and (B2) 20 KGy.

increase pH value and reach a maximum at pH 7. The hydrogel swelling rate at high temperature is higher than that at low temperature. The starch/AAc hydrogel is thermally stable than starch. The use of such prepared hydrogel as super-absorbent materials in industrial and agricultural purposes could be possible.

Acknowledgment

This work is supported by The Internathional Atomic Energy Agency (IAEA) under Research Contract No. 13169/R Regular Budget Fund.

References

1. Lee, J.S., Kumar, N.R., Rozman, H.D., and Azemi, B.M.N. (2005) *Food Chemistry*, 91: 203–211.
2. Kiatkamjornwong, S., Chomsaksakul, W., and Sonsuk, M. (2000) *Radiation Physics and Chemistry*, 59: 413–427.
3. Athawale, V.D. and Lele, V. (2001) A Review. *Starch Stuarke*, 53: 7–13.
4. Masuda, F.; Nishida, K.; Nakamura, A. Ger. Pat. 2, 162 846.
5. Wong, A. (Procter and Gomble Co.) (1987) Eur. Pat. EP 210 756.
6. Nukushina, K. (1980) *Yuki Gosei Kagaku Kyokaishi*. 38, 546–554 (Jpn) (Chem. Abstr. 94, 1981, R66783e).

7. Buchholz, F.L. (1994) *Polym. Sci.* (Cambridge, U.K.) 277–281; (Chem. Abstr. 122, 1995, R135045b).
8. Athawale, V.D. and Rathi, S.C (1999) *J. Macromol. Sci. Rev. Macromol. Sci. Rev. Macromol. Chem. Phys.*, C39 (3): 445–475.
9. Pourjavadi, A. and Zohuriaan-Mehr, M.J. (2002) *Starch Sturke*, 54: 140–147.
10. Beliakova, M.K., Aly, A.A., and Abdel-Mohdy, F.A. (2004) *Starch Sturke*, 56: 407–412.
11. Kiatkamjornwong, S. and Meechai, N. (1997) *Radiation Physics and Chemistry*, 49 (6): 689–696.
12. Luo, W., Zhang, W., Chen, P., and Fang, Y. (2005) *Journal of Applied Polymer Science*, 96: 1341–1346.
13. Gruber, E., Alloush, S., John, K., and Schurz, J. (1973) *Stärke*, 25: 325–331(Ger).
14. Gruber, E., Mohammed, J., Alloush, S., and Schurz, J. (1976) *Technol.*, 10 (5): 577–585 (Ger.) (Chem. Abstr.86: 73296m).
15. Yao, K.-J. and Zhou, W.-J. (1994) *J. Appl. Polym. Sci.*, 53: 1533.
16. Chen, P., Zhang, W., Luo, W., and Fang, Y. (2004) *Journal of Applied Polymer Science*, 93: 1748–175.
17. El-Rehim, H.A., Hegazy, E.A., and Abd El-Mohdy, H.L. (2004) *Journal of Applied Polymer Science*, 93: 1360–1371.
18. Gemeinhart, R.A., Park, H., and Park Kinam (2000) *Polym. Adv. Technol*, 11: 617–625.
19. Chen, J., Park, H., and Park, K. (1999) *J. Biomed. Mater. Res*, 44: 53–62.