African Journal of Pure and Applied Chemistry Vol. 5(5), pp. 111-118, May 2011
Available online at http://www.academicjournals.org/AJPAC
ISSN 1996 - 0840 ©2011 Academic Journals

Full Length Research Paper

Study on the properties of copolymer hydrogel obtained from acrylamide/2-hydroxyethyl methacrylate by the application of gamma radiation

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Accepted 7 April, 2011

Synthesis of copolymer hydrogels from aqueous solution of acrylamide/2-hydroxyethyl methacrylate (HEMA) has been performed with radiation processing technology using Co-60 gamma source. The influence of radiation dose and concentration of HEMA on gel content, swelling properties and thermal stability of copolymer hydrogel has been investigated. Gel content of prepared hydrogel obtained maximum at the radiation dose of 30 kGy. Swelling ratio and equilibrium water content decrease with increased radiation dose and concentration of HEMA in feed solution. The water absorption of hydrogel increases with increased standing time in swelling medium. It is fast up to 24 h and then it becomes slow. The water absorption also decreases with increased concentration of HEMA in the feed solution. The water absorption of copolymer hydrogel obtained at 30 kGy radiation dose decreases from 1800 to 1400% for the increment of HEMA content from 1 to 3%. This type of diffusion of prepared hydrogel is found to be a non Fickian diffusion. The thermal stability of copolymer hydrogel prepared at the radiation dose of 30 kGy increases with increased amount of HEMA in the feed solution.

Key words: Radiation, copolymer, swelling behaviors, acrylamide/2-hydroxyethyl methacrylate.

INTRODUCTION

Hydrogels are cross-linked hydrophilic polymer networks that can swell but does not dissolve in water and retain significant amount of water in their structures. The ability of water absorption is due to hydrophilic nature of functional groups such as alcohols, carboxyls, sulphonic acid, etc on the polymer backbone. Cross linking of hydrophilic polymers/monomers can carry out the synthesis of hydrogel, and cross linking can be done either by chemical method or by radiation method. In radiation processing technology initiator, catalyst and cross linker is not required because ionizing radiation is highly energetic (Jabbari and Nozari, 2000). The radiation processing technique has many advantages like easy process control, simultaneous cross linking of polymer to hydrogel formation and sterility of the product, and the technology is environmentally friendly since it leaves no residue or pollutant in the environment (Rosiak et al., 1999; Fei et al., 2000). Hydroxyethyl methacrylate (HEMA) based hydrogel can be performed and it is biocompatible. Poly(2-hydroxyethyl methacrylate), p(HEMA) is inert to normal biological process, which shows resistance to degradation and is not absorbed by the body (Isik, 2000). Polyacrylamide hydrogel is a highly hydrophilic material. It has many useful chemical and physical properties and as a result, has been investigated for its application as a smart polymer (Li et al., 2002). The applications of polyacrylamide hydrgels include bio-materials (Saraydin et al., 2001), drug delivery systems (Bajpai and Rajpoot, 2001; Becerra-Bracamontes et al., 2007) and adsorbents for heavy metal ion and dyes (Saraydin et al., 2001; Saraydin et al., 1995).

The aim of the present investigation was to synthesize copolymer hydrogel from aqueous solution of acrylamide/ HEMA by the application of gamma radiation and characterized in respect to gel content, swelling behaviors and thermal stability.

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Abbreviation: HEMA, Hydroxyethyl methacrylate.

MATERIALS AND METHODS

Materials

The monomers used in the present investigation are acrylamide and 2-hydroxyethyl methacrylate. They were obtained from Aldrich Chemi UK and Fluka Switzerland, respectively and were used as received. Sodium chloride used in the investigation was obtained from BDH, England. Distilled water was used as solvent.

Preparation of acrylamide and HEMA solution

A 10% acrylamide solution was prepared in distilled water. Then different amount of HEMA was added to the aqueous solution of acrylamide and stirred with a glass rod to make a uniform solution. The prepared solution was taken in several glass test tubes and irradiated from Co-60 gamma radiation source at various radiation doses in air at room temperature. The hydrogels obtained in long cylindrical shapes were cut into pieces of 3-4 mm length. The pieces of hydrogel samples were dried in air and then under vacuum to a constant weight.

Determination of gel content

The dried hydrogel samples were kept in distilled water for 24 h to remove the soluble fraction. Then the gel samples were taken out and dried to a constant weight under vacuum to determine the insoluble content in the samples gravimetrically.

$$\text{Gel content (\%)} = [W_1/W_0] \times 100$$

Where W_1 is the weight of dry gel after extraction in distilled water and W_0 is the initial weight of dry gel.

Determination of swelling ratio

The swelling ratio of hydrogel was determined by gravimetric method. The dried gel to a constant weight was immersed in distilled water and other test solution until the maximum swelling was obtained at room temperature. Then hydrogel sample was weighed after removing excess water on the surface of sample with a tissue paper. The swelling ratio was calculated as:

$$\text{Swelling ratio} = [(W_2 - W_1)/W_1]$$

Where W_2 is the weight of swelled gel and W_1 is the weight of dried gel.

Determination of equilibrium water content

The gel sample was dried to a constant weight and was kept in distilled water at a room temperature. Swelling of the gel was continued to reach the constant weight and weighed after removing any surface water with a tissue paper. The equilibrium water content was calculated as:

$$\text{Equilibrium water content (\%)} = [(W_3 - W_1)/W_3] \times 100$$

Where W_3 is the weight of gel after water absorption and W_1 is the weight of dried gel.

Determination of water absorption

The gel sample was dried to a constant weight and was kept in distilled water at a room temperature and then the gel sample was periodically weighed after soaking the surface water by tissue paper. The water absorption was calculated as:

$$\text{Water absorption (\%)} = [(W_t - W_1)/W_1] \times 100$$

Where W_t is the weight of swelled gel at time t and W_1 is the weight of dried gel.

Determination of thermal property

The melting temperature of dried hydrogel sample was measured using the thermo-mechanical analyzer (LINSEIS TMA, L-77, USA). The experiment was carried out in an inert atmosphere at the heating rate of 5°C/min. The dimension of the samples was 5x5x2 mm^3.

RESULTS AND DISCUSSION

Figure 3 shows the gel content of copolymer hydrogel obtained from acrylamide/HEMA with a different radiation dose and varying the amount of HEMA in the feed solution. Gel content of copolymer hydrogel increases with increased radiation dose which was up to 30 kGy, after which the gel content levels off. It was also found that the gel content increases with increased amount of HEMA in the feed solution. The gel content increases from ~97 to ~98% with increased HEMA content from 1 to 3% at the radiation dose of 30 kGy. When aqueous solution of acrylamide/HEMA is subjected to irradiation with gamma rays, free radicals are generated on monomer. Random reactions of these radicals lead to formation of copolymer of acrylamide and HEMA. When the radiation dose has been increased beyond a certain value, the polymer chains cross link and then a gel-like material is obtained (Figure 1). For the formation of cross linked macromolecules, the subsistence of two radicals on neighboring chains and their subsequent combination are required. At the higher concentration of polymer, the macromolecules come close and that ease to form cross linking. In the present study, the concentration of monomers increases with increase of HEMA content in 10% aqueous solution of acrylamide and this may be the cause of increase in the gel content with increased concentration of HEMA in feed solution.

Swelling is a result of balance between two forces. One is osmotic force and the other is dispersing force. Osmotic force pushes water into the polymer network whereas dispersing force exerted by the polymer chains resist it. Increase in cross link density enhances the dispersing force. So with the increased cross linked density, a limited scope is available for free water to enter into the vacant spaces of cross linking network. Figure 4 shows the effect of radiation dose and concentration of HEMA on swelling ratio of copolymer hydrogel. From the

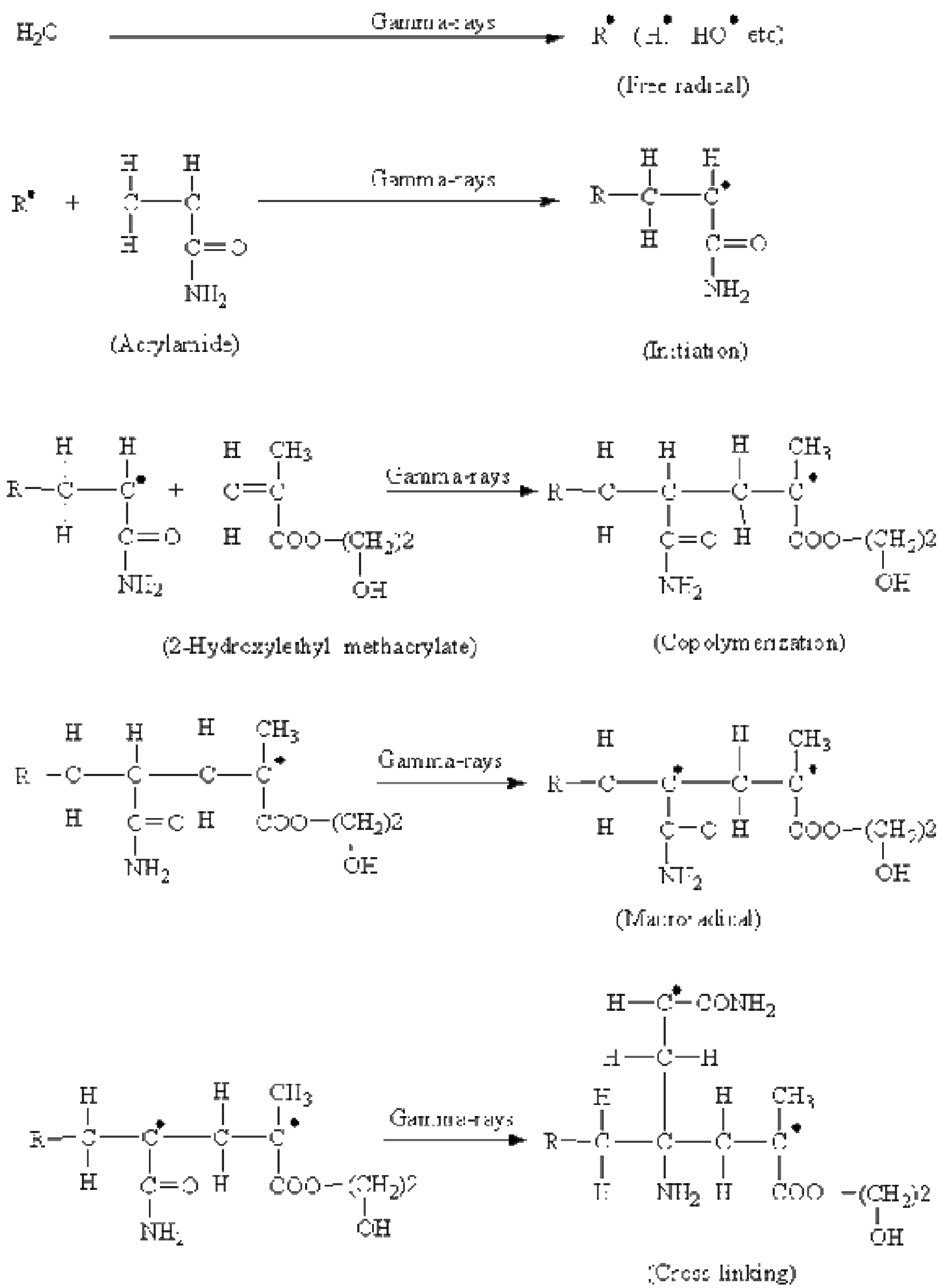

Figure 1. Possible reaction mechanism of copolymerization and cross-linking of copolymer obtained from acrylamide and 2-hydroxyethyl methacrylate.

results it was found that the swelling ratio decreases with increased radiation dose. The values of swelling ratio reduce from ~30 to ~ 16 for the radiation dose of 10 to 40 kGy with 1% HEMA in feed solution. Swelling ratio of copolymer hydrogel also decreases with increased concentration of HEMA. It decreases from ~18 to ~15 for the concentration of HEMA from 1 to 3% in the feed solution at the radiation dose of 30 kGy. These results

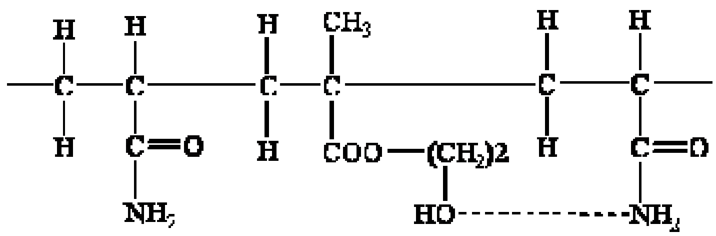

Figure 2. Intermolecular hydrogen bonding between acrylamide and 2-hydroxyethyl methacrylate.

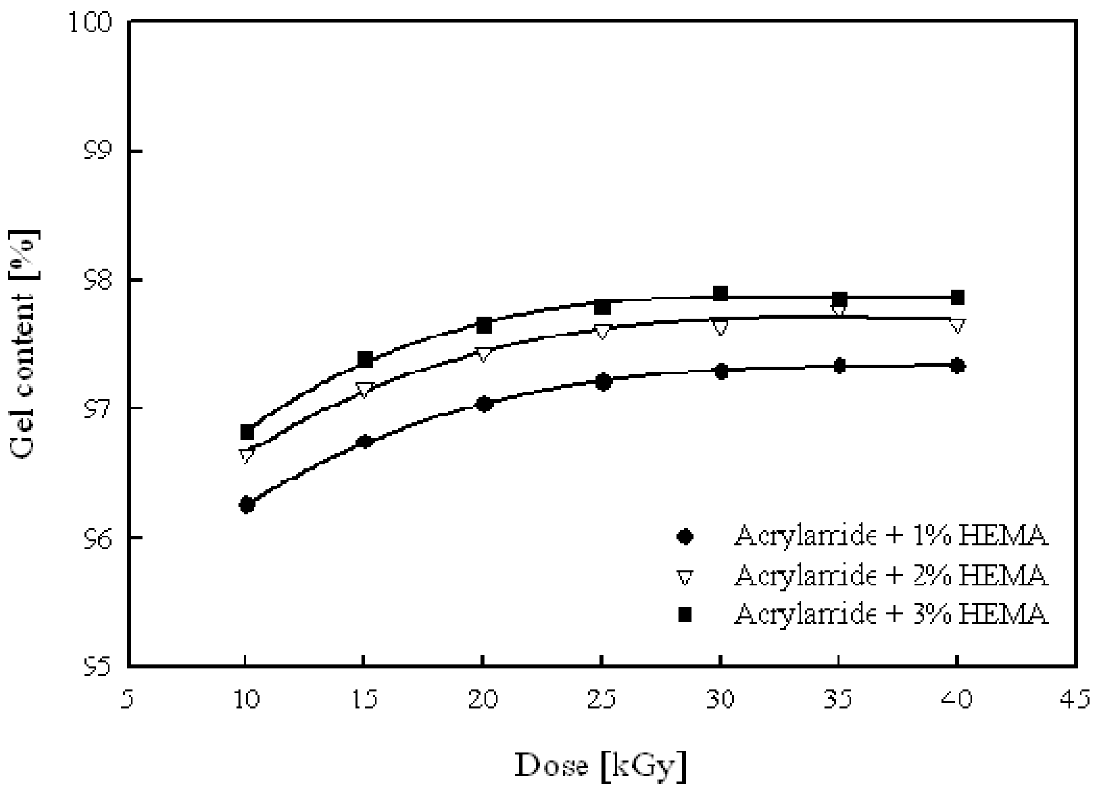

Figure 3. Effect of radiation dose and concentration of HEMA on gel content of copolymer hydrogel obtained from acrylamide/HEMA.

indicate that increased radiation dose and concentration of HEMA in the feed solution increases cross linked density. Besides this, swelling ratio of HEMA rich copolymer hydrogel may be controlled by the HEMA part. The cause of this is probably due to the intermolecular hydrogen bonding between hydroxyl and amide groups of HEMA and acrylamide, respectively (Figure 2). Therefore, the hydrophilic group numbers of copolymer hydrogels decreases with increased HEMA content. Equilibrium water content also decreases with increased radiation dose and concentration of HEMA in copolymer hydrogel (Figure 5). It reduces from ~97 to ~94% for the increment of radiation dose from 10 to 40 kGy with 1% HEMA content. It also reduces from ~95 to ~93% for increased concentration of HEMA from 1 to 3% in the aqueous solution of acrylamide/HEMA at 30 kGy radiation dose. Figure 6 shows the effect of sodium chloride in swelling medium on swelling ratio of copolymer hydrogel obtained from aqueous solution of acrylamide/HEMA at the radiation dose of 30 kGy. Swelling ratio decreases with increased concentration of sodium chloride in swelling medium. When the hydrogel is placed in sodium chloride solution, the osmotic pressure developed may be lower when compared to distilled water because the external solution contains Na^+ and Cl^-. As a result, it is found that the swelling ratio of prepared copolymer hydrogel in water (Figure 4) is higher than that of copolymer hydrogel in sodium chloride solution. Figure 7 shows the effect of standing time and concentration of HEMA on water absorption of copolymer

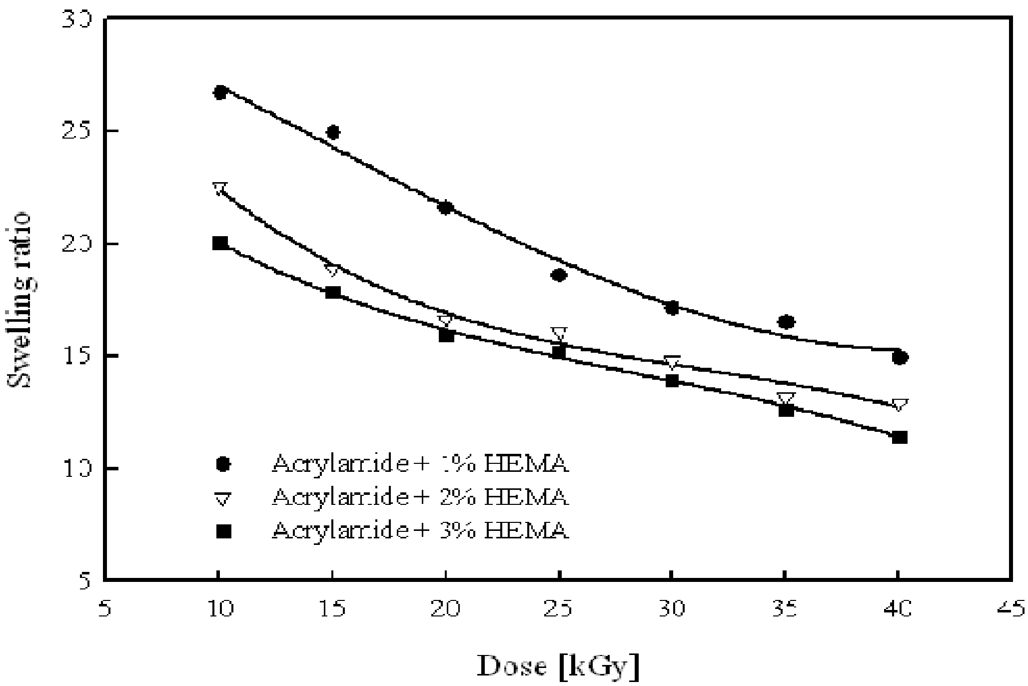

Figure 4. Effect of radiation dose and concentration of HEMA on swelling ratio of copolymer hydrogel obtained from acrylamide/HEMA.

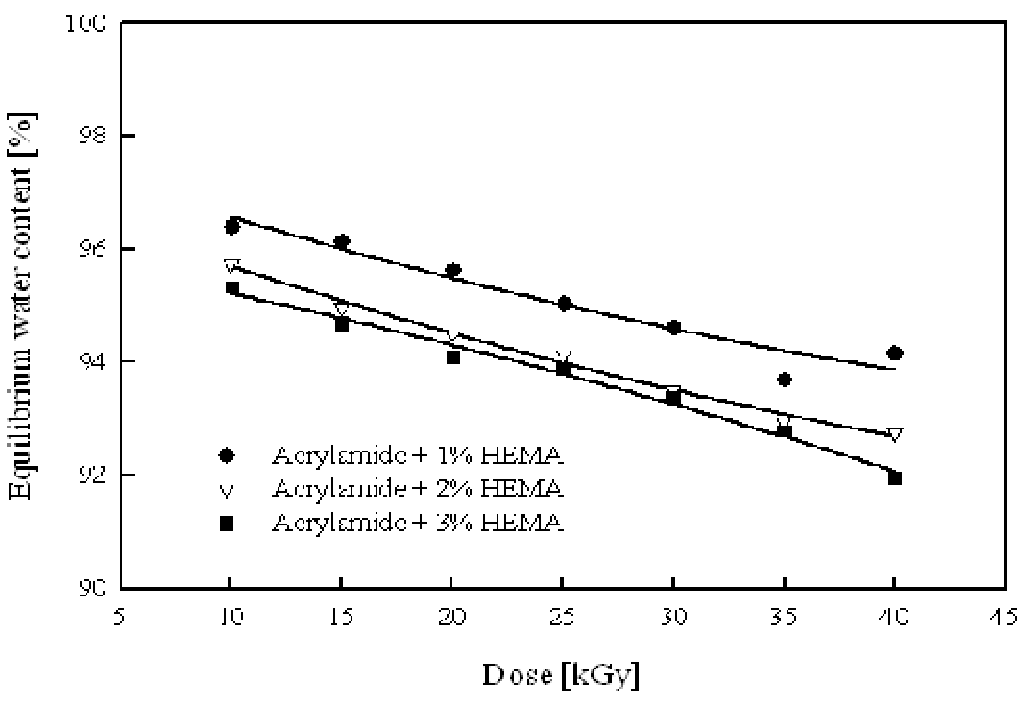

Figure 5. Effect of radiation dose and concentration of HEMA on equilibrium water content of copolymer hydrogel obtained from acrylamide/HEMA.

hydrogel prepared at the radiation dose of 30 kGy. As seen in this figure, the percentage water absorption increases with increased standing time of copolymer hydrogel in distilled water but after a while, a constant percentage of water absorption is observed. This value of percentage of water absorption is known as equilibrium

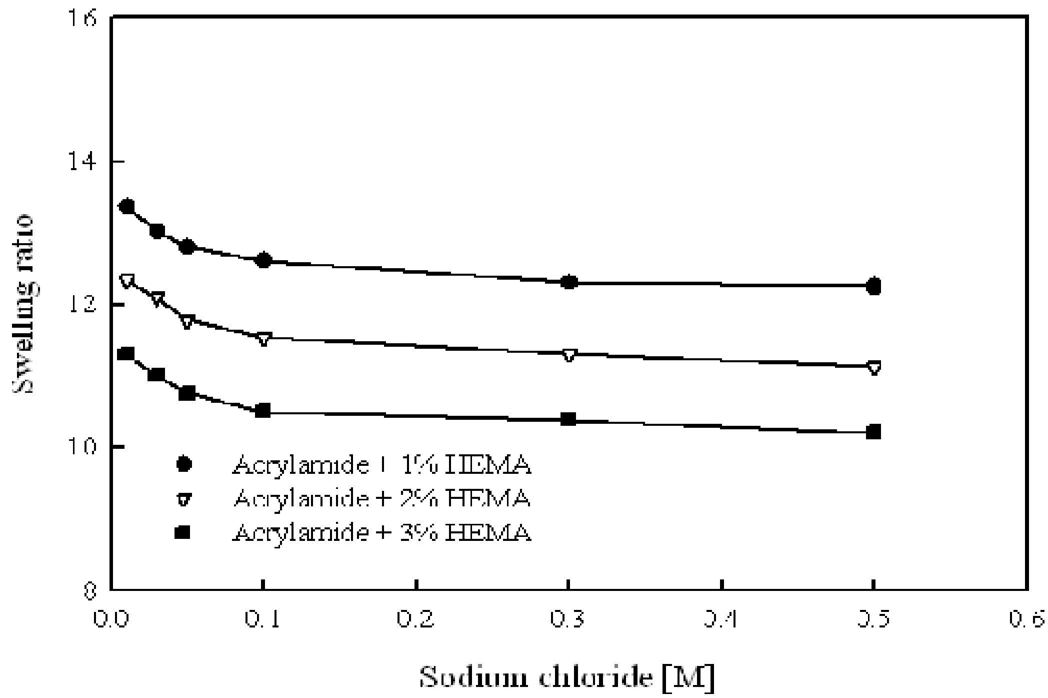

Figure 6. Effect of sodium chloride in swelling medium on swelling ratio of copolymer hydrogel obtained from acrylamide/HEMA at 30KGY.

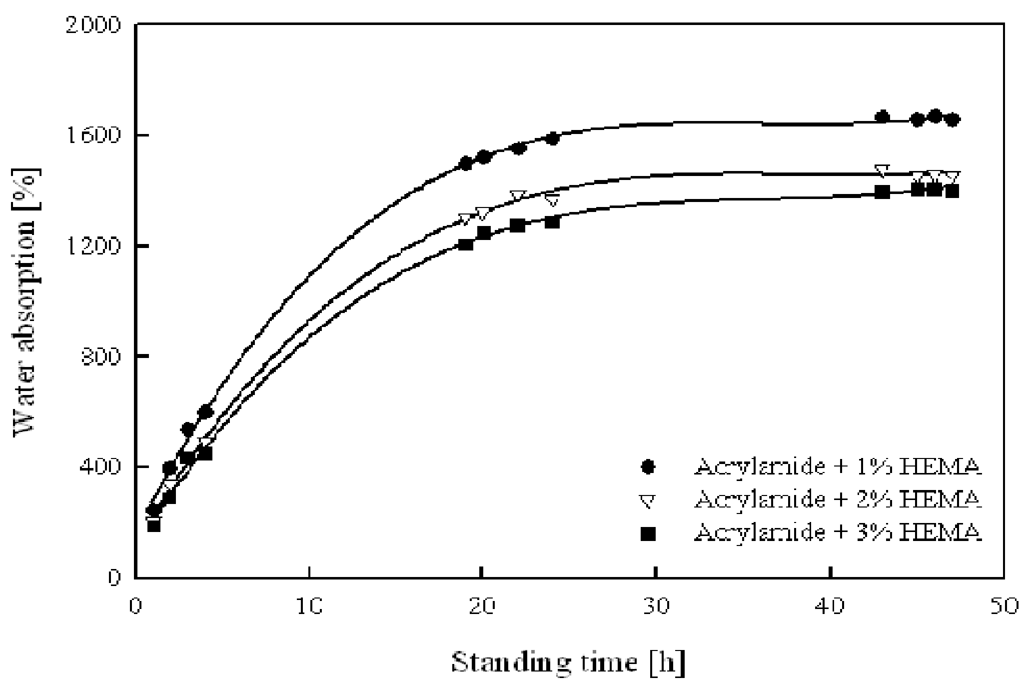

Figure 7. Effect of HEMA on water absorption of copolymer hydrogel obtained from acrylamide/HEMA at 30KGY.

swelling mass. The equilibrium swelling mass in copolymer hydrogel decreases from ~1800 to ~1400% with increased HEMA content (1 to 3%) in the feed solution at 30 kGy radiation dose. Analysis of mechanism of water diffusion in swellable polymeric system has a lot of significance due to the unique applications of hydrogels.

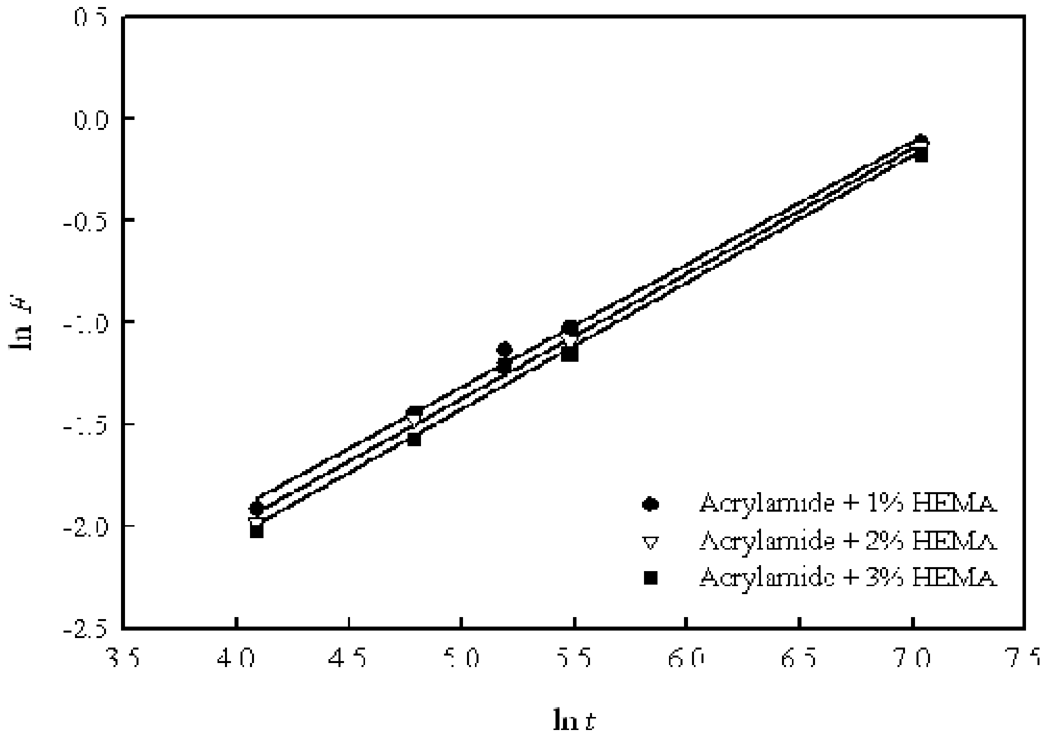

Figure 8. Plot of lnF versus lnt for copolymer hydrogel prepared from acrylamide/HEMA at 30KGY.

Table 1. Values of *n* of copolymer hydrogel prepared from acrylamide/HEMA at 30 kGy radiation dose.

Copolymer hydrogel	n
10% acrylamide + 1% HEMA	0.60
10% acrylamide + 2% HEMA	0.62
10% acrylamide + 3% HEMA	0.63

The following equation can be used to determine the type of water diffusion into hydrogels (Buckley et al., 1962; Peppas and Franson, 1983).

$$F = (M_t/M_i) = kt^n$$

Where M_t and M_i represent the amount of solvent diffused into the gel at time t and infinite time, respectively. k is a constant related to the structure of the network and *n* is the diffusion exponent, which is indicative of the type of diffusion. For cylindrical shapes, n = 0.45 – 0.50 corresponds to Fickian diffusion whereas 0.50 < n > 1.0 indicates that diffusion is a non Fickian type. Plot of ln*F* versus ln*t* for copolymer hydrogels obtained from blend of acrylamide/HEMA at the radiation dose of 30 kGy is shown in Figure 8. *n* values was calculated from the slopes of lines and listed in Table 1. From the Table 1, it is clearly seen that the values of diffusion exponent (*n*) are in between 0.60 and 0.63 and found to be over 0.50. Thus the diffusion of water into prepared copolymer hydrogels is taken as a non Fickian type. The thermal property of acrylamide/HEMA copolymer hydrogels are shown in Figure 9. It was found that the thermal stability of prepared copolymer hydrogel improved with increased amount of HEMA in the feed solution. The thermal property, which is, melting temperature of copolymer hydrogels of acrylamide/HEMA increases from 56.2 to 59.0°C for the increment of HEMA from 1 to 3% in the feed solution at the radiation dose of 30 kGy.

Conclusion

In this study, copolymer hydrogels were prepared from aqueous solution of acrylamide/HEMA by radiation processing technique with changing total radiation dose and concentration of HEMA in the feed solution. The properties, like gel content, swelling behaviors and melting temperature were examined. The gel content of copolymer hydrogel increases with increased radiation dose which was up to 30 kGy; after this dose the variation of gel content is not so significant. The gel content also increases with increase in the concentration of HEMA. It is also seen that swelling properties decreases with increase in radiation dose and concentration of HEMA. This type of diffusion of prepared hydrogel is a non Fickian diffusion character. The melting temperature of prepared copolymer hydrogel increases with increased

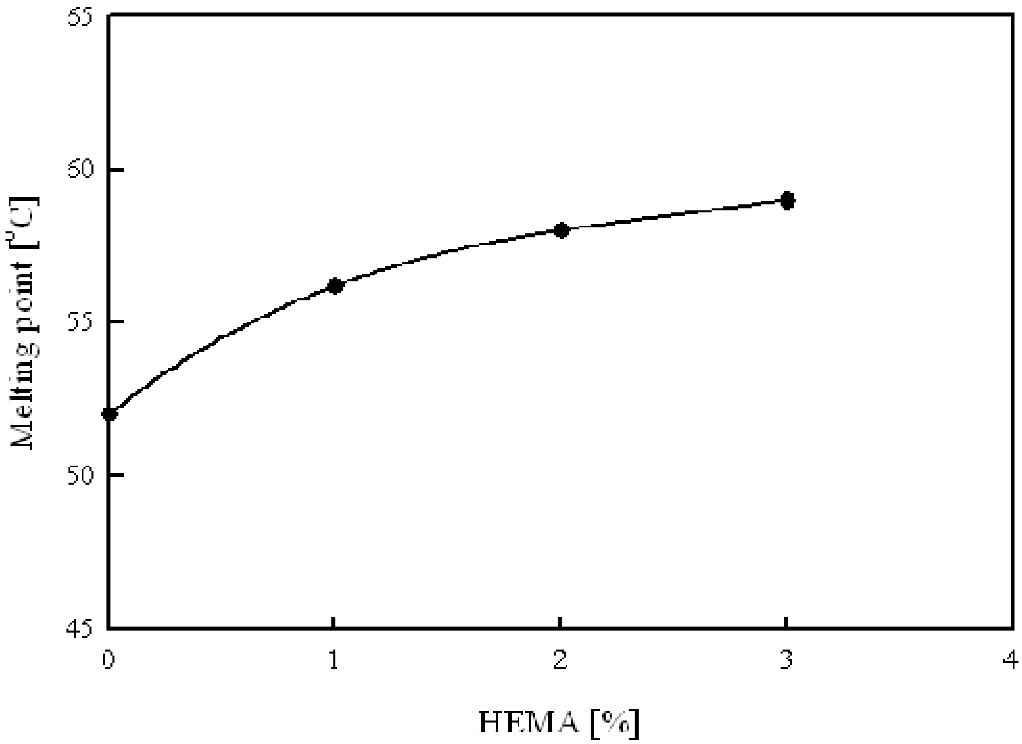

Figure 9. Effect of HEMA concentration on melting point of copolymer hydrogel prepared from acrylamide/HEMA at 30KGY.

amount of HEMA.

Therefore, the copolymer hydrogel obtained from acrylamide/HEMA with different properties can be used as a water retainer for carrying some substances in aquatic fields in agricultural, environment and biomedical applications.

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