

Characterization of Hydrogels Prepared by the γ Irradiation of Aqueous Solutions of Acrylamide and *N*-Vinyl-2-Pyrrolidone Comonomers

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ABSTRACT: Copolymer hydrogels were prepared through the γ irradiation of aqueous solutions composed of different ratios of acrylamide (AAM) and vinyl pyrrolidone (VP) monomers. The chemical structure, thermal stability, and structural morphology of the hydrogels were characterized with Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy, respectively. The IR spectroscopy analysis showed the formation of copolymerization and the presence of hydrogen bonding. The TGA study showed that the AAm/VP-based hydrogels possessed higher thermal stability than polyacrylamide (PAAm). However, the thermal stability of the AAm/VP hydrogels increased with an increasing ratio of the VP component. The study of the swelling kinetics in water showed that all

the hydrogels reached the equilibrium state after 24 h. However, the AAm/VP-based hydrogels showed swelling in water that was lower than that of the hydrogel based on pure AAm. Meanwhile, the degree of swelling of the AAm/VP-based hydrogels decreased with an increasing ratio of VP in the feeding solutions. The results showed that the PAAm and AAm/VP-based hydrogels prepared at 50 kGy were affected by a change in the temperature around 25°C, whereas the hydrogels prepared at 25 kGy did not show this characteristic. However, the hydrogels prepared at different doses displayed reversible pH character. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4202–4208, 2007

Key words: hydrogels; infrared spectroscopy; irradiation; swelling; thermogravimetric analysis (TGA)

INTRODUCTION

There has been increasing interest in the synthesis of new hydrogels for various applications, such as super water absorbents, sensors, separation membranes, and drug delivery systems in medicine and pharmacy.^{1–6} Hydrogels based on polyacrylamide (PAAm) are blood-compatible biomaterials that find applications in the coatings of catheters and controlled release devices. Moreover, they are used widely by biologists and biochemists in the electrophoretic separation of proteins, DNA, and RNA. They are called sieving gels because they delay the movement of protein, DNA, and RNA species. Although they form stable, clear, and homogeneous gels by crosslinking that swell extensively in water, they have poor hydrolytic stability and tensile strength.⁷

Poly(vinyl pyrrolidone) (PVP)-based hydrogels, on the other hand, have promise as ideal wound-dressing materials. In this respect, PVP/chitosan and PVP/hydroxypropyl methacrylate,⁵ PVP/poly(ethylene oxide),⁶ and PVA/PVP hydrogels⁷ show effective absorption of fluids and good transparency and can act as efficient barriers against microbes. It

has been reported that PAAm and PVP in aqueous solutions crosslink under γ irradiation, forming a common network.⁸ Also, thermosensitive and pH-sensitive polymer hydrogels based on semi-interpenetrating polymer networks and comb-type graft hydrogels composed of alginate/poly(*N*-isopropylacrylamide)^{9,10} and graft polymers and blends of chitosan and *N*-isopropylacrylamide¹¹ have been prepared and characterized.

In previous work, the synthesis by ionizing radiation and characterization of hydrogels based on poly(vinyl alcohol) and acrylamide (AAM) mixtures,¹² poly(vinyl alcohol)/sodium alginate,¹³ carboxymethylcellulose/acrylic acid,¹⁴ and hydroxyethyl cellulose/PVP¹⁵ have been studied. In this study, hydrophilic copolymer hydrogels based on AAm and vinyl pyrrolidone (VP) monomers were synthesized by γ irradiation. The hydrogels that formed were characterized with IR spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Moreover, the effects of the temperature and pH on the swelling behavior were studied.

EXPERIMENTAL

Materials

The monomer VP was purchased from Merck Chemicals Co. (Schuchardt, Germany), whereas the mono-

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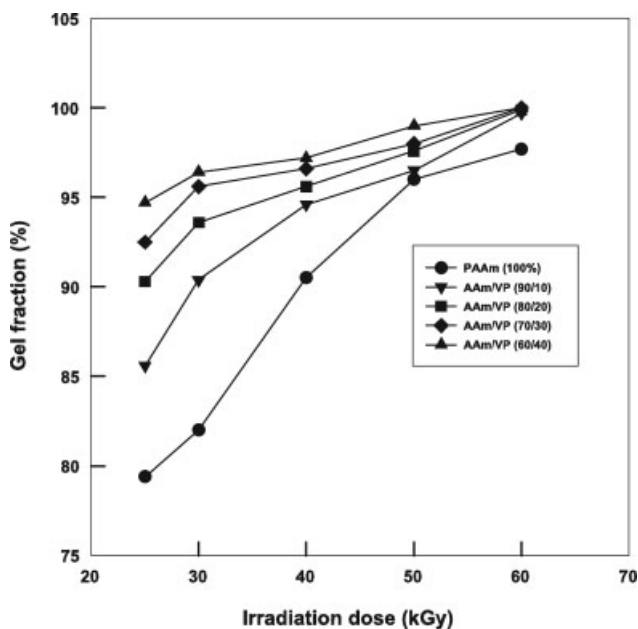


Figure 1 Effect of the irradiation dose on the gel fraction of hydrogels based on pure AAm monomer and AAm/VP comonomers of different ratios.

mer AAm was purchased from El-Nasr Pharmaceutical Chemicals Co. (Cairo, Egypt). All the monomers were chemical-laboratory-grade and were used without purification.

Preparation of the AAM/VP hydrogels

Aqueous solutions containing 90, 80, 70, or 60 wt % AAm were mixed with 10, 20, 30, or 40 wt % VP in test tubes. The tubes were then subjected to different doses of γ radiation (25–60 kGy), which depended

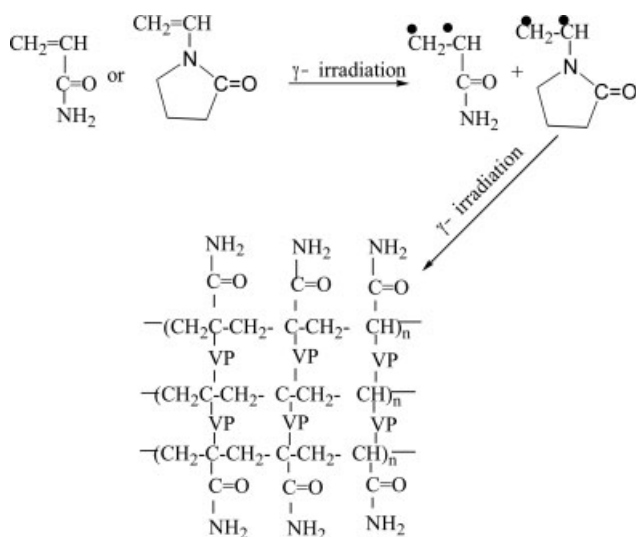


Figure 2 Radiation synthesis of AAm/VP copolymer hydrogels.

on the exposure time, at the dose rate of 6.92 kGy/h. The γ irradiation was carried out in the cobalt 60 cell facility of the National Center for Radiation Research and Technology (Cairo, Egypt). The resultant hydrogels were washed with distilled water to remove unreacted monomers.

Determination of the gel fraction

Samples of the prepared hydrogels were accurately weighted (W_0) and then extracted with distilled water with a Soxhlet system for 6 h. After the extraction, the samples were then removed and dried in a vacuum oven at 80°C to a constant weight (W_1). The gel fraction was calculated according to the following equations:

$$\text{Sol fraction (\%)} = [(W_0 - W_1)/W_0] \times 100$$

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction (\%)}$$

IR spectroscopy analysis

The IR spectra of the different hydrogels were acquired on a Mattson 5000 Fourier (Madison, WI) transform infrared spectrometer over the range of

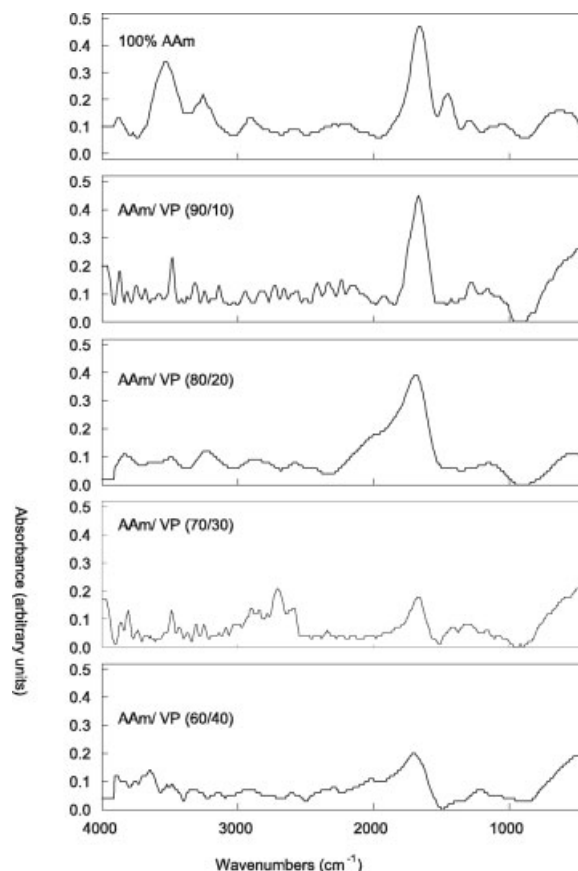


Figure 3 IR spectra of PAAm and AAm/VP hydrogels at different ratios formed with 25 kGy of γ irradiation.

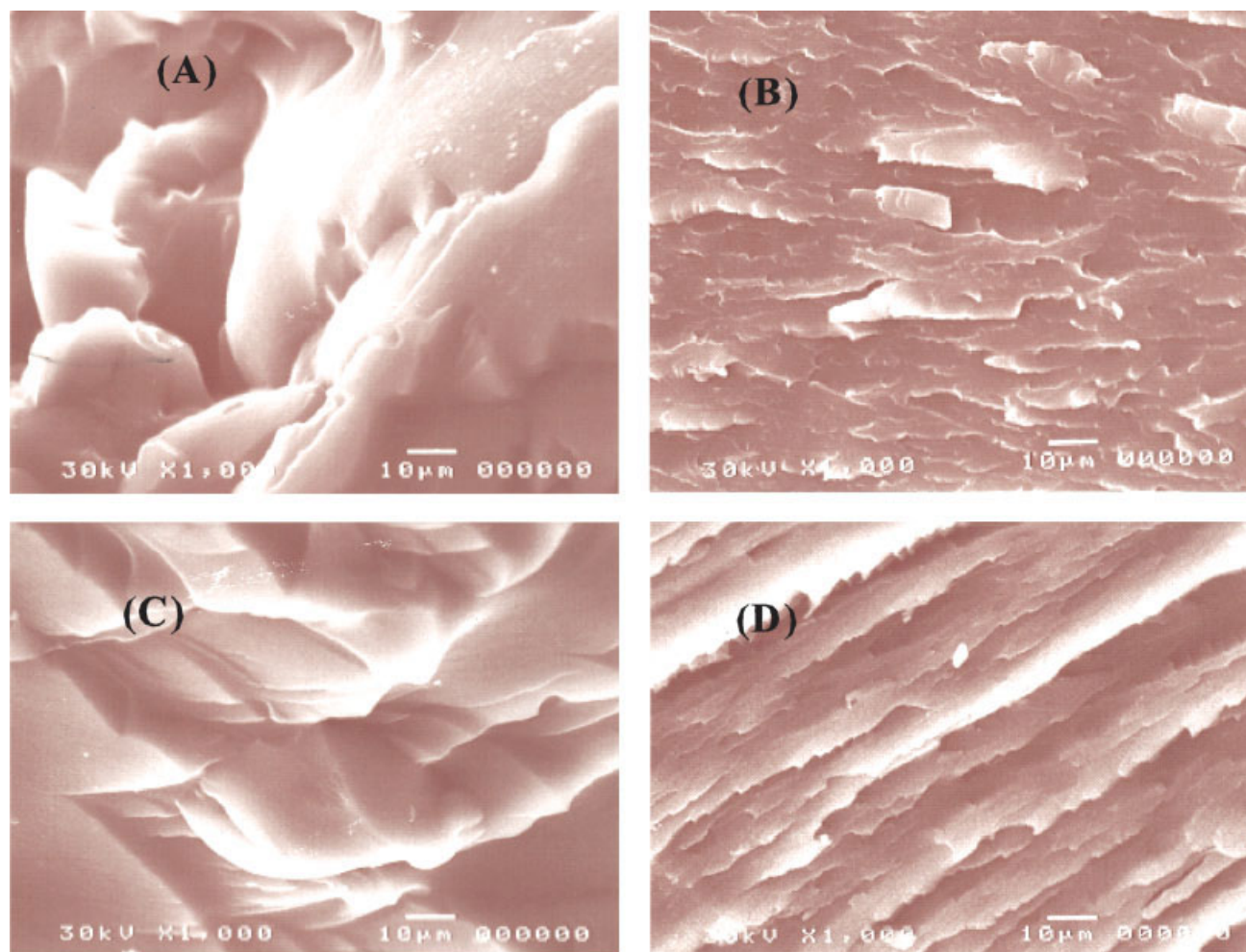


Figure 4 SEM micrographs of AAm/VP hydrogels based on different compositions formed at different irradiation doses: (A) 80/20 AAm/VP with 25 kGy, (B) 80/20 AAm/VP with 50 kGy, (C) 70/30 AAm/VP with 25 kGy, and (D) 70/30 AAm/VP with 50 kGy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

500–4000 cm^{-1} . The samples for IR analysis were dried in a vacuum oven, ground to a very fine powder, mixed with a highly dried KBr powder, and then pressed into transparent discs. The spectra were taken with a resolution of 4 cm^{-1} and were averaged over 16 scans.

TGA

TGA studies were carried out on a Shimadzu (Kyoto, Japan) model 50 instrument at a heating rate of 10°C/min under flowing nitrogen (20 mL/min) from room temperature to 500°C.

SEM

SEM was used to examine the structural morphology of the fracture surfaces of the hydrogels based on AAm and AAm/VP. SEM micrographs were taken with a JSM-5400 instrument (JEOL, Tokyo, Japan). A sputter coater was used to precoat conductive gold

onto the fracture surfaces before the microstructure was observed at 30 kV.

Swelling behavior of the AAm/VP hydrogels

A known weight of the insoluble hydrogel (W_1) was immersed in distilled water for different times up to 24 h at room temperature. At each time, the samples were removed and blotted on filter paper to remove the excess water or solvent on the surface and were weighed (W_2). The swelling percentage was calculated according to the following equation:

$$\text{Degree of swelling (\%)} = [(W_2 - W_1)/W_1] \times 100$$

RESULTS AND DISCUSSION

Radiation synthesis of the AAm/VP copolymer hydrogels

Figure 1 shows the gel fraction dependence on the γ -irradiation dose and comonomer composition of

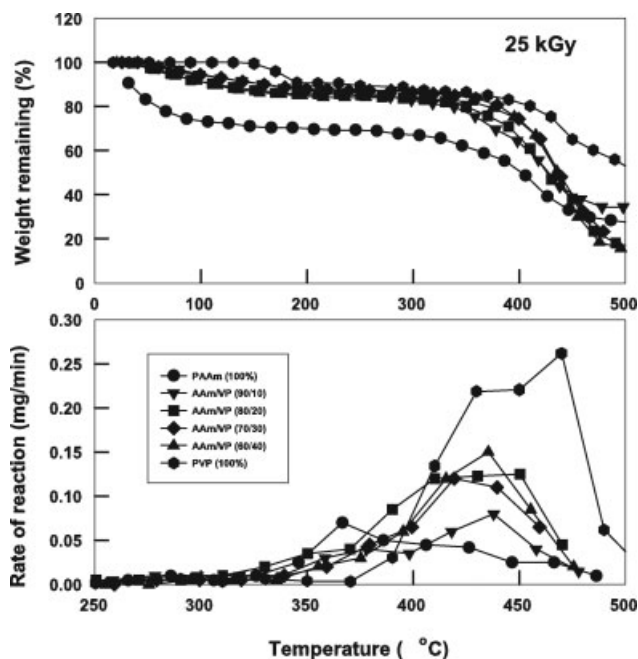
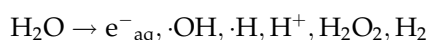


Figure 5 Initial TGA thermograms and rate-of-reaction curves for hydrogels based on pure AAm and different ratios of AAm/VP formed at a dose of 25 kGy of γ irradiation.

the AAm/VP hydrogels. The gel fraction (%) of the AAm/VP hydrogels depended on the comonomer composition as well as the irradiation dose. The gel fraction of PAAm at a dose of 25 kGy was increased from 79 to 86% by the use of 10% VP in the initial comonomer solution. Also, the gel fraction of the hydrogel based on 10% VP was increased from 86 to 95% at the dose of 50 kGy. On the other hand, the gel fraction increased as the irradiation dose and the ratio of VP in the initial feeding comonomer solutions increased. However, the difference in the gel fraction caused by an increase in the ratio of VP in the feeding solutions decreased as the irradiation dose increased from 25 to 50 kGy.

The mechanism of the formation of network structures of PAAm and AAm/VP copolymer hydrogels can be proposed to occur in two steps. First, both AAm and VP contain unsaturated C=C double bonds, which absorb γ radiation; this results in the formation of free radicals. In addition, the radiolysis products of water, as reported in the early stage of radiation chemistry (as shown later), increase the concentration of free radicals for both monomers.¹⁶ Second, copolymerization and crosslinking proceed, in which two polymer radicals of AAm and VP with n and m repeat units, respectively, combine to form crosslinked points, after which a network structure is formed, as shown in Figure 2:



IR spectroscopy analysis

An IR spectroscopy analysis was used to illustrate the nature and type of the formation of hydrogels by γ radiation. Figure 3 shows the IR spectra of an AAm gel and AAm/VP hydrogels of various compositions formed under the effect of a constant dose of 25 kGy of γ radiation. The AAm absorption band at 2950 cm^{-1} with a weak shoulder, attributed to C—H stretching, can be seen in the IR spectrum of the pure AAm hydrogel as in almost all organic compounds. The appearance of absorption bands at 3420 , 3520 , and 3600 cm^{-1} in the IR spectrum of the pure AAm hydrogel indicates the formation of hydrogen bonding. The IR spectra of the AAm/VP hydrogels with increased VP contents show the appearance of wide and broad absorption bands starting at 3300 cm^{-1} and sloping to 3600 cm^{-1} ; this indicates the existence of hydrogen bonding.

A distinctive absorption band around 1700 cm^{-1} arose from (C=O) streaking in AAm.¹⁷ This band appears as a broad band in the IR spectrum of pure AAm; the intensity of this band decreases with an increasing ratio of the VP monomer in the initial hydrogel solution. Also, it can be concluded that the formation of AAm/VP hydrogels occurred through interpenetrating polymer networks because most of the features present in the IR spectrum of AAm are lost.

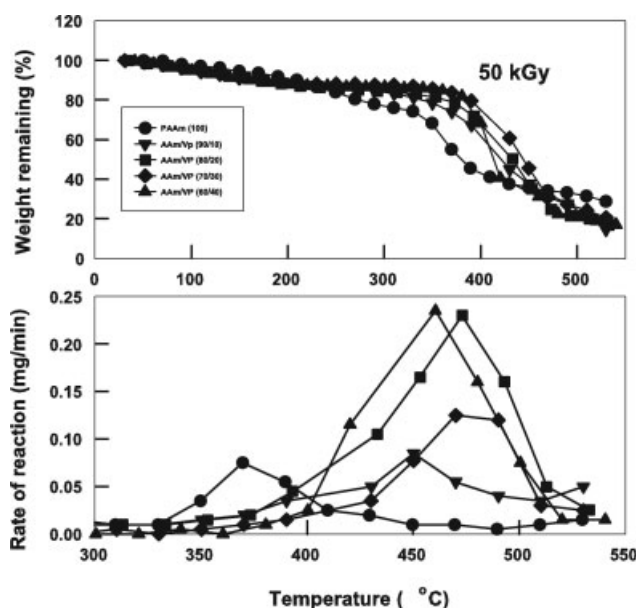


Figure 6 Initial TGA thermograms and rate-of-reaction curves of hydrogels based on pure AAm and different ratios of AAm/VP formed at a dose of 50 kGy of γ irradiation.

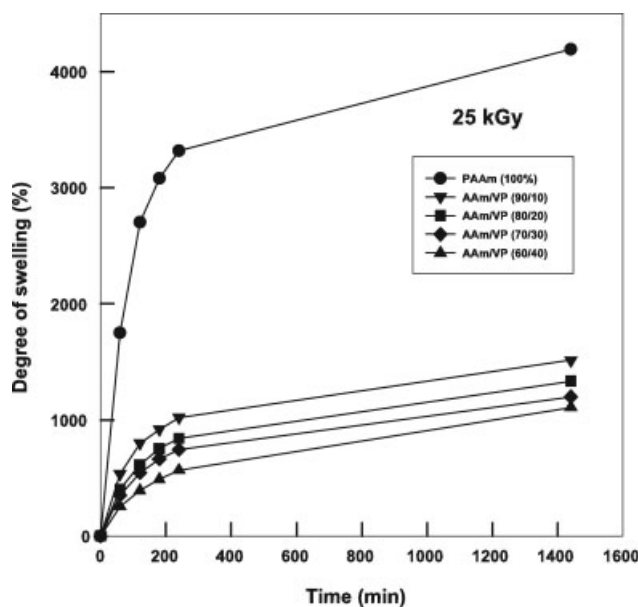


Figure 7 Swelling kinetics of PAAm and AAm/VP hydrogels in water at 25°C (pH = 7) formed at a dose of 25 kGy of γ irradiation.

Structural morphology of the AAm/VP hydrogels

The effects of the comonomer composition and irradiation dose on the structural morphology of the AAm/VP hydrogels were examined with SEM. Figure 4 shows SEM micrographs of different hydrogels based on initial feeding solutions composed of 20 or 30% VP monomer prepared at different doses. As shown in Figure 1, increases in the VP ratio in the feeding solutions and the irradiation dose were asso-

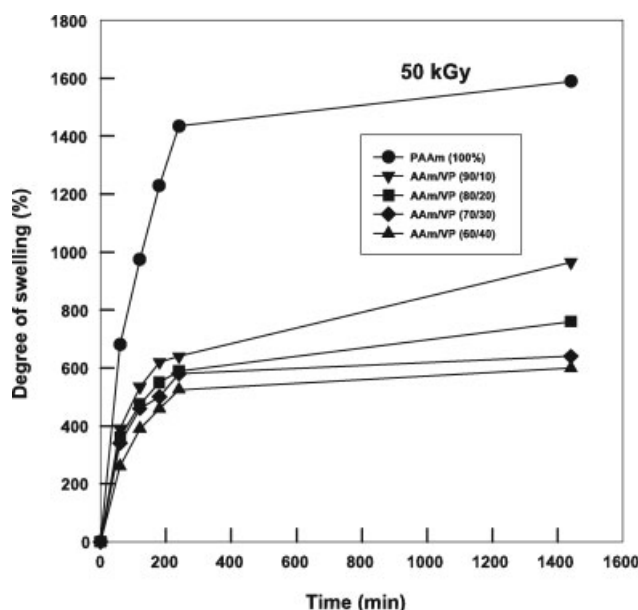


Figure 8 Swelling kinetics of PAAm and AAm/VP hydrogels in water at 25°C (pH = 7) formed at a dose of 50 kGy of γ irradiation.

ciated with an increase in the gel fraction. The formation of the gel appears like snow mountains and valleys with coagulations, as shown in Figure 4(A,C). The presence of combined water inside the hydrogels appears like smooth hills. However, this feature starts to disappear as the ratio of the VP monomer increases in the initial feeding solutions, in agreement with the results for the gel fraction. The effects of the irradiation dose and the subsequent increase in the gel fraction can be seen clearly in Figure 4(B,D), in which the SEM micrographs show different features. The crosslinking through the matrix appears as continuous phases and compact structures corresponding to each hydrogel composition.

Thermal decomposition behavior

TGA was used to investigate the thermal stability of the hydrogel based on the pure AAm monomer and the copolymer hydrogels based on the AAm and VP monomers in different ratios. Figures 5 and 6 show the initial TGA thermograms and the corresponding rate-of-reaction curves for these hydrogels prepared at doses of 25 and 50 kGy of γ irradiation. The theoretical calculation of the average complete dissociation energy, based on the reported energies of the different covalent bonds forming the polymer molecules, suggests that PAAm has higher thermal stability (416.4 kJ/mol) than PVP (396.1 kJ/mol).¹⁸ The experimental TGA study shows that of all the compositions, the copolymer hydrogels formed from initial feeding solutions based on different ratios of AAm and VP displayed higher thermal stability, with lower weight loss, than the PAAm hydrogels, regardless of the irradiation dose. These results indicate clearly that the energy required to thermally dissociate the cyclic pyrrolidone ring is much higher than that of the linear molecules.

On the basis of the data from Figures 5 and 6, few conclusions can be made:

1. Over all the heating temperatures, the PVP polymer hydrogel displayed higher thermal stability than the PAAm polymer, as shown in Figure 5. However, the PAAm polymer hydrogel

TABLE I
Degree of Swelling in Water After Different Time Intervals for Hydrogels Based on the AAm Monomer and AAm and VP Comonomers Prepared with Different Doses of γ Irradiation

Hydrogel	Irradiation dose (kGy)	Degree of swelling (%)	
		4 h	24 h
PAAm	25	2400	4200
	50	1240	1240
AAm/VP	25	500–1000	1000–1500
	50	500–640	600–960

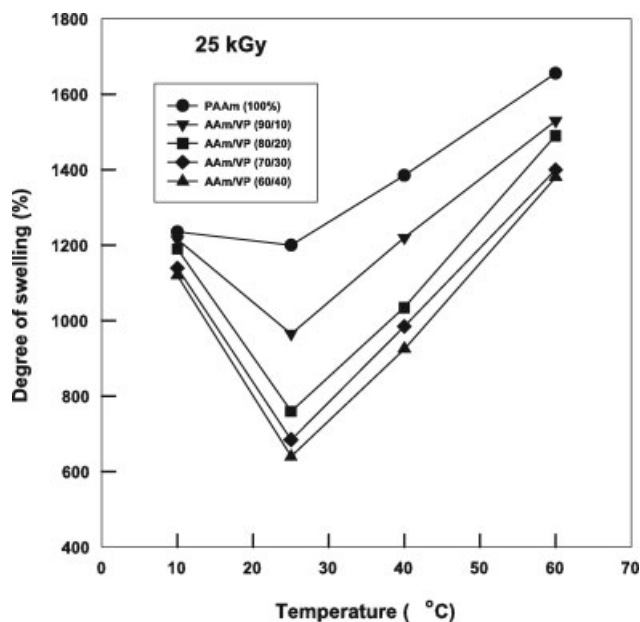


Figure 9 Effect of the temperature on the degree of swelling in water (pH = 7) for hydrogels based on pure AAm monomer and different compositions of AAm and VP formed at a dose of 25 kGy of γ irradiation.

displayed lower thermal stability than all the AAm/VP copolymer hydrogels, regardless of the irradiation dose. The weight loss of PAAm was ~ 2.5 times that of AAm/VP-based hydrogels, regardless of the composition.

- The thermal stability of the AAm/VP-based hydrogels increased with an increasing ratio of VP within the heating temperature range of 300–450°C, in which the major decomposition occurred. Within this range of temperatures, the weight loss of the AAm/VP hydrogels was constantly lower than that of the PAAm polymer hydrogel. Also, the thermal stability of the AAm/VP hydrogels increased with an increasing irradiation dose.
- The rate of reaction showed similar trends; however, the temperature at which the maximum value of the rate of reaction occurred (T_{\max}) differed from one polymer to another. The T_{\max} values of the hydrogels based on the pure AAm monomer and PVP and the hydrogels based on 10, 20, 30, and 40% VP prepared at a dose of 25 kGy were 370, 460, 430, 433, 446, and 440°C, respectively. The T_{\max} values for the same polymer hydrogels prepared at a dose of 50 kGy were 370, 470, 450, 475, 470, and 450°C, respectively.

These findings indicate clearly that the AAm/VP-based hydrogels possessed higher thermal stability than the hydrogel based on the pure AAm monomer.

Equilibrium swelling of the AAm/VP hydrogels

The swelling kinetics in water at 25°C (pH = 7) for the hydrogel based on the pure AAm monomer and the copolymer hydrogels based on different ratios of AAm and VP monomers formed at doses of 25 and 50 kGy of γ irradiation are shown in Figures 7 and 8. The degree of swelling of all the hydrogels increased linearly within the initial time of swelling and then reached the equilibrium state after 24 h. Also, the degree of swelling of the AAm/VP-based hydrogels decreased with an increasing ratio of VP in the initial feeding solutions. However, the PAAm hydrogels displayed higher swelling in water than the AAm/VP-based hydrogels. Table I shows the dependence of the degree of swelling on the irradiation dose. The degree of swelling of all the hydrogels greatly decreased as the irradiation dose increased from 25 to 50 kGy. Also, after 4 or 24 h, the degree of swelling of the PAAm hydrogels was almost two times that of AAm/VP-based hydrogels. These trends can be explained as follows: γ irradiation at higher doses leads to a higher degree of crosslinking, which reduces the mobility of the network structure and thus hinders hydration.

Effect of the temperature on the swelling of the AAm/VP hydrogels

Figure 9 shows the degree of swelling in water as a function of temperature for the hydrogels based on pure AAm and comonomers AAm and VP in differ-

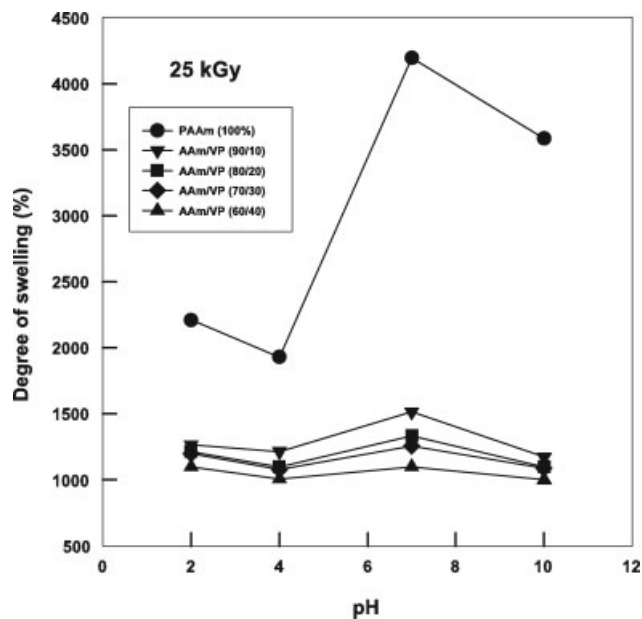


Figure 10 Effect of the pH on the degree of swelling in water for hydrogels based on pure AAm monomer and different compositions of AAm and VP formed at a dose of 25 kGy of γ irradiation.

ent ratios at a dose of 25 kGy of γ irradiation. All the hydrogels exhibited significant changes in the degree of swelling over the temperature range of 10–60°C, in which 25°C was the turning point associated with the lowest degree of swelling. Above this temperature and up to 60°C, the degree of swelling greatly increased. However, at any temperature, the degree of swelling decreased with an increasing ratio of the VP monomer in the feeding solutions. The effect of the temperature on the degree of swelling decreased with an increasing VP ratio in the hydrogels. In this respect, the decrease in the degree of swelling caused by the temperature rising from 10 to 25°C for PAAm, AAm/VP (90/10), AAm/VP (80/20), AAm/VP (70/30), and AAm/VP (60/40) was calculated to be 34, 246, 431, 449, and 480%, respectively. The increase in the degree of swelling at higher temperatures was due to the dissociation of ordered water molecules surrounding the hydrophilic amide groups.¹¹ As a result, the AAm/VP hydrogels underwent a volume phase transition in water in the temperature range of 25–60°C.

Effect of the pH on the swelling of AAm/VP hydrogels

Figure 10 shows the effect of the pH medium on the degree of swelling at 25°C at equilibrium. The degree of swelling underwent an oscillatory change when the pH medium changed from acidic to alkaline. The highest change in the swelling was observed for the hydrogel based on the AAm monomer. Also, the sensitivity toward the pH decreased with an increasing ratio of VP in the feeding solution of the prepared hydrogels. The degree of swelling decreased as the pH value increased from 2 to 4 and then suddenly increased at pH 7. Furthermore, a decrease in the degree of swelling was observed as the pH value increased from 7 to 10. Amides can be hydrolyzed in either acidic or alkaline solutions, and neither type of hydrolysis is reversible. The hydrolysis of amides, in an acidic solution, proceeds through the protonation of carbonyl groups and releases free acids. In a basic medium, they become ionized. At lower pH values, the hydrogels collapsed and the swelling degree was low, whereas at higher pH values, the electrostatic repulsion resulted in the expansion of the network structure.

CONCLUSIONS

The results presented in this study concern the formation of a hydrogel network structure by the radiation polymerization and crosslinking of various compositions of AAm and VP monomers in aqueous solutions. The IR spectroscopy analysis, which was initially used to illustrate the nature of the bonding, showed the formation of hydrogen bonding and a copolymer network. The TGA study showed that the AAm/VP hydrogels based on different compositions possessed higher thermal stability than the hydrogel based on the pure AAm monomer, regardless of the irradiation dose. Also, the degree of swelling decreased with an increasing ratio of VP in the initial feeding solutions of the preparation. These hydrogels may find applications in biomedicine because of superswelling in water and the influence of the pH and temperature conditions.

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