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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-Din, Horia M. Nizam , Alla, Safaa G. Abd and El-Naggar, Abdel Wahab M.(2007) 'Radiation Synthesis and Characterization of Hydrogels Composed of Poly(vinyl alcohol) and Acrylamide Mixtures', *Journal of Macromolecular Science, Part A*, 44: 1, 47 – 54

To link to this Article: DOI: 10.1080/10601320601044450

URL: <http://dx.doi.org/10.1080/10601320601044450>

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Radiation Synthesis and Characterization of Hydrogels Composed of Poly(vinyl alcohol) and Acrylamide Mixtures

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Received April, 2006, Accepted July, 2006

Hydrogels based on various compositions of poly(vinyl alcohol) (PVA) and acrylamide (AM) monomer were produced under the effect of γ -irradiation. The hydrogels were characterized by IR spectroscopy and thermogravimetric analysis (TGA). In addition, the effect of temperature and pH on the swelling behavior was studied. It was proved that the composition of the final product corresponds to the initial composition of the preparing solutions. The IR spectroscopic analysis showed the formation of interpenetrating networks and the existence of hydrogen bonding. The thermal study and the calculation of activation energy of the thermal decomposition reaction of PVA/AM hydrogels showed that the PVA/AM hydrogels, over the studied compositions, possessed lower thermal stability than the individual polyacrylamide (PAM) hydrogel. The kinetic studies of swelling in water showed that the neat PAM and PVA/AM hydrogels reached equilibrium after six hours, while neat PVA polymer hydrogel reached equilibrium after three hours. However, PVA/AM hydrogels show swelling in water less than neat PAM and higher than neat PVA. The results showed that PVA/AM hydrogels displayed a temperature responsive character within the temperature range 40–50°C, and showed shrinkage in swelling in the pH range 5–7 depending on composition. This behavior was not clear in the case of hydrogels composed of binary mixtures of PVA and AM components.

Keywords: gamma radiation; crosslinking; thermal stability; responsive hydrogels

1 Introduction

Hydrogels are three-dimensional network and hydrophilic polymeric structures, capable of swelling and absorbing large amounts of water or biological fluids (1–5). Considerable attention, however, has been devoted to responsive hydrogels, which show significant sensitivity to environmental stimuli such as temperature, pH, and electric fields (6–12). The hydrogels swell or shrink in aqueous solutions due to the association, dissociation and binding of various ions to polymer chains. The swelling and shrinkage characters are the basis for many medical applications such as controlled drug delivery, muscle-like actuators, contact lenses, catheters and wound dressing (13–15).

Radiation synthesis of responsive hydrogels has special technique advantages, not only for the strong interaction between chains through covalent bonds, but it also solves

the problem of sterilization, and allows the fabrication of pure product non-contaminated with residuals of toxic initiators (16–19). Our previous studies reported on responsive hydrogels based on various aqueous solutions of carboxymethyl cellulose/acrylic acid (CMC)/AAc formed by electron beam irradiation (20) and hydroxyethylmethacrylate/acrylamide (HEMA/AM) under the effect of gamma radiation (21). The kinetic studies of swelling in water showed that HEMA/AM hydrogels possess a temperature-responsive character within the temperature range 25–30°C, and showed a stepwise behavior in the pH range 2–10, depending on composition.

It has been reported that N-isopropylacrylamide has thermo responsive character alone and pH-temperature behavior when composed with acrylic acid (7) and alginate (8, 9). The present work was undertaken to investigate the responsive character of hydrogels composed of acrylamide monomer and poly(vinyl alcohol) produced under the effect of gamma irradiation. The relation between the composition of the initial preparing solutions and the composition of the final product and the effect on responsive character towards temperature and pH is another aim of this work.

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2 Experimental

2.1 Materials

Acrylamide monomer (AM) used in this study was of laboratory grade chemicals purchased from Aldrich Chemicals Co. (Milwaukee, WI), and used as received. Poly(vinyl alcohol), laboratory grade, was a fully hydrolyzed polymer in the form of powder, average molecular weight (Mw) of 106,000 g mol⁻¹, and was obtained from Laboratory Rasayan, Cairo, Egypt.

2.2 Preparation of PVA/AM Hydrogels

The hydrogels were prepared by dissolving separately different ratios of PVA (4–10 wt%) and AM monomer (20 wt%) in distilled water. The polymer and monomer solutions were then mixed with continuous stirring until complete miscibility was achieved. The ratio of PVA and AM in the mixture can be 20/80, 30/70 and 50/50. The mixtures were then poured into test tubes and subjected to gamma irradiation for different durations to obtain different doses. Prior to irradiation, the solutions were made free from oxygen by purging nitrogen gas for 5 min and the tubes were sealed. Irradiation to the required doses was carried out in a ⁶⁰Co gamma cell (made in Russia) facility of the National Center for Radiation Research and Technology, Cairo, Egypt.

2.3 Determination of Gel Fraction

Samples of the prepared hydrogels were accurately weighed (W_0) and then extracted with distilled water using a Soxhlet system and then dried in a vacuum oven at 80°C to a constant weight (W_1). The soluble fraction was calculated according to the following equation:

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

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

2.4 IR Spectroscopic Analysis

The infrared spectra of the different hydrogels were performed on a Mattson 5000 FT-IR spectrometer (Mattson Instruments, Madison, WI) over the 500–4000 cm⁻¹ range. The samples for IR analysis were dried in a vacuum oven, ground to a very fine powder, mixed with a highly dried KBr powder (30 mg), and then pressed to obtain transparent disks.

2.5 Thermogravimetric Analysis (TGA)

The TGA thermograms were performed on a Shimadzu-50 instrument (Kyoto, Japan) at a heating rate of 10°C/min under flowing nitrogen (20 ml/min) from room temperature to 500°C. The primary TGA thermograms were used to

determine the kinetic parameters such as activation energy and order of the thermal decomposition reaction.

2.6 Swelling Studies of PVA/AM Hydrogels

Swelling studies were conducted on PVA/AM hydrogels as a function of time, temperature, and pH of the swelling medium. A known dry weight of insoluble hydrogel (W_d) was immersed in water for different durations up to 24 h at 25°C. After each time, the sample was removed and blotted on filter paper to remove excess water and weighed (W_s), in which the percentage swelling was calculated according to the following equation:

$$\text{Swelling (\%)} = [(W_s - W_d)/W_d] \times 100$$

The equilibrium water content (EWC) is defined as the ratio between the absorbed water and the weight of hydrogel at equilibrium swelling, and was calculated according to the following equation:

$$\text{EWC (\%)} = [(W_{es} - W_d)/W_{es}] \times 100$$

The responsive characters of PVA/AM hydrogels were determined by investigating the swelling in different external environments. In this regard, dry weight (W_d) of pure PVA and PVA/AM hydrogels was immersed in water at different temperatures (10–60°C) to equilibrium time and then were weighed (W_{et}). The percentage swelling was calculated in terms of the change between W_{et} and W_d with respect to W_d . The same procedure was followed to investigate the pH- response character of PVA/AM hydrogels.

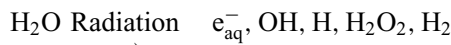
3 Results and Discussion

3.1 Mechanism of γ -Radiation Synthesis of PVA/AM Hydrogels

In a previous work, it was found that the formation of hydrogels based on mixtures of HEMA and acrylamide monomer (AM) at any composition or gamma irradiation dose was not possible unless a small ratio of trithioglycolic acid (TTGA) is added to the mixtures (21). In addition, the formation of hydrogels containing higher ratios of AM above 50% was not possible. In the present work, PVA was used to form a copolymer or interpenetrating network hydrogels with AM monomer under the effect of γ -irradiation. This is because PVA and AM may provide a combination of properties based on the hydroxyl and amide groups.

Preliminary experiments showed that approximately complete gelation of PVA and PVA/AM mixtures was obtained at a dose of 20 kGy of gamma radiation. The percentage gel fractions at this dose of PVA and PVA/AM mixtures having 50, 70 and 80% AM were determined to be 89, 94, 97, and 99%, respectively. We did not use higher doses to avoid the oxidative degradation of the AM component. It was reported that the start of gelation of polyacrylamide in

aqueous solutions needs at least 2 kGy of γ -irradiation at ambient temperature, in which the polymerization and cross-linking occurs by the products of the radiolysis of water, which is present in appropriate quantities, as reported in the very early stage of radiation chemistry as follows (22):



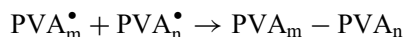
The mechanism of crosslinking of polymers and the polymerization of monomers in solution by γ -radiation was studied by Chaprio (22, 23), Saito (24, 25) et al. (26, 27). The mechanism of crosslinking of PVA and PVA/AM in aqueous solution can be briefly outlined as follows:

(1) the polymer PVAH and the solvent HOH absorb the γ -radiation and go to the transient activated states PVAH* and HOH*, which dissociate causing the formation of the radicals PVA \cdot , HO \cdot and H \cdot .

(2) the transfer of radical from water to polymer increases the concentration of PVA radicals and increases the rate of crosslinking and gelation:



(3) two polymer radicals PVA \cdot with m and n repeat units combine to form a crosslinked point:



The unit fractions of PAM to PVA in the final PVA/AM hydrogel products were determined by the Kjeldahl method based on percentage nitrogen element. It was found that the unit fractions of PAM in the hydrogel products prepared initially from solutions containing 50, 70, and 80% of AM monomer are ~ 60 , 75, and 90%, respectively, leading to the fact that the initial composition of hydrogel mixtures is related to the composition of the final product.

3.2 IR Spectroscopic Analysis

IR spectroscopic analysis was used to illustrate the nature of bonding of the formation of hydrogels by gamma radiation. Figure 1 shows the IR spectra of PVA gel and PVA/AM hydrogels of various compositions formed under the effect of a constant dose of 20 kGy of gamma radiation. It should be noted that the samples for IR analysis were dried in a vacuum oven at 80°C for 2 h to exclude the effect of H-bonding to water in the samples. As is common for almost all organic compounds, an absorption band at 2950 cm^{-1} with a weak shoulder, arising from the C-H stretching, can be seen in the IR spectrum of pure PVA. The IR spectra of the different PVA/AM hydrogels showed a distinctive absorption band around 1700 cm^{-1} , arising from the C=O stretching. These findings indicate that the final composition of the hydrogels corresponds to the initial mixtures, in which the intensity of the C=O stretching was found to increase with increasing AM content. Also, it may be concluded that the formation of PVA/AM hydrogels is conducted through interpenetrating polymer network, since most of the features present in the IR spectrum of PVA are lost.

Hydrogen bonding changes the position and appearance of the IR absorption bands due to OH stretching. The appearance of absorption bands at 3320, 3420, and 3520 cm^{-1} in the IR spectrum of pure PVA hydrogel indicates the formation of hydrogen bonding between the hydroxyl groups. The IR spectra of PVA/AM hydrogels with increased AM contents showed the appearance of a wide broad absorption bands and starting from 3225 cm^{-1} and slopes to 3593 cm^{-1} , which indicates that the existence of hydrogen bonding. The hydrogen bonding in this case, might be formed between the hydroxyl groups of PVA and the NH_2 of the amide groups of PAM.

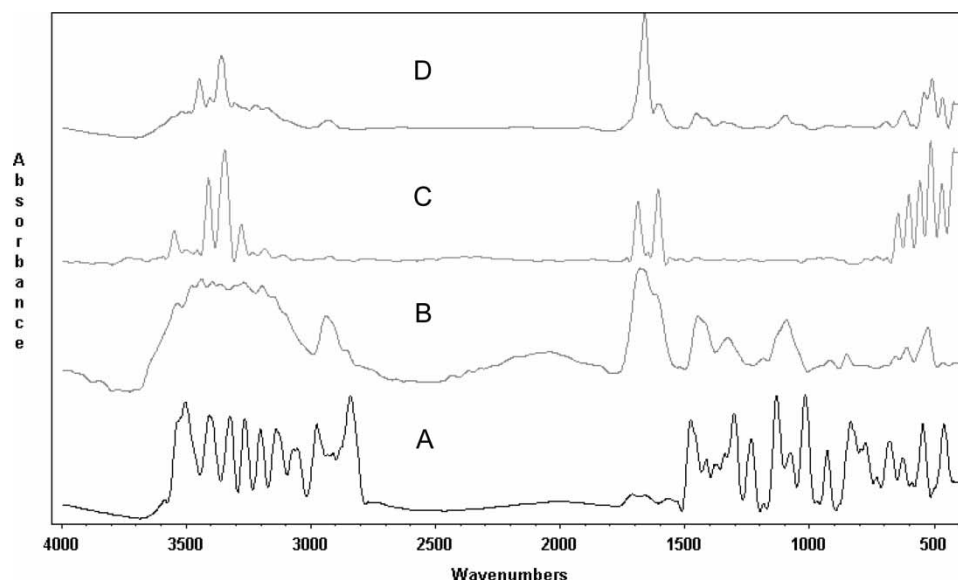


Fig. 1. IR spectra of (A) PVA polymer hydrogel, (B) PVA/AM (20/80%) copolymer hydrogel, (C) PVA/AM (30/70%) and (D) PVA/AM (50/50%). All hydrogels were formed at a 20 kGy dose of gamma radiation.

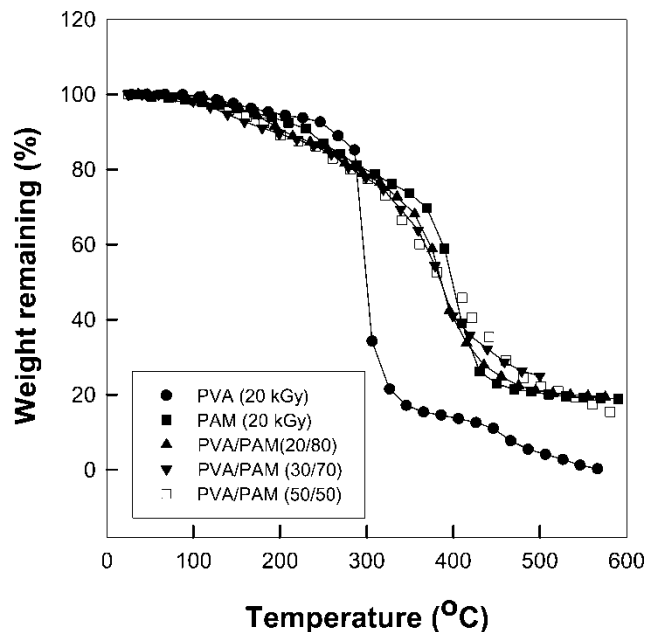


Fig. 2. Primary TGA thermograms of PVA and PAM polymer hydrogels and their copolymer hydrogels at different compositions prepared at a constant dose of 20 kGy of gamma radiation.

3.3 Thermal Decomposition Behavior

The average complete dissociation energy for PVA and PAM, based on the reported theoretical dissociation energies of the different covalent bonds forming the polymer molecules, were 401 and 416 kJ/mole, respectively (28). Thus, it may be expected that the formation of hydrogels with increased AM ratio will eventually result in hydrogels with higher thermal stability than pure PVA.

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of pure PVA, PAM hydrogels and their hydrogels formed at a dose of 20 kGy of gamma radiation, as shown in Figure 2. In addition, the percentage weight losses at different decomposition temperatures for all the hydrogels are summarized in Table 1. Up to a heating temperature of 200°C, the individual PVA and PAM polymer hydrogels displayed higher thermal stability (with less weight loss) than PVA/AM copolymer hydrogels. The thermal stability of PVA/AM hydrogels increases with

increasing the content of AM. Also, within the heating temperature range of 300–500°C, in which the major decomposition occurs, the weight loss of PVA/AM hydrogels was constantly lower than the individual PVA polymer hydrogel and still higher than pure PAM. In this regard, by increasing the ratio of AM from 50 to 80%, the thermal stability was found to increase, in terms of the percentage weight loss.

The derivative of the TGA curves (rate of reaction) for pure PVA and PAM hydrogels showed single stage decomposition, while those for PVA/AM hydrogels showed multiple stage behavior, as shown in Figure 3. The temperatures at which the maximum values of the rate of reaction (T_{max}) and the percentage weight loss at these maxima (between brackets) are shown in Table 2. The first maximum is probably due to the evaporation of water molecules from hydrogels depending on compositions. It seems that the water molecules are more strongly bonded in the PAM polymer component than in PVA, in which the T_{max} increases with increasing the content of AM in the initial composition hydrogels. The second T_{max} may be attributed to the breaking of the hydrogen bonding existing in the hydrogels, in which it increases with increasing the content of AM in the initial mixture of PVA/AM hydrogels.

The thermal stability was further confirmed by determining the kinetic parameters of the thermal decomposition reactions. A method based on the rate of reaction proposed by Anderson and Freeman (29) was utilized, in which the quantities $\Delta \log(dw/dt)$ and $\Delta \log w$ corresponding to a constant small difference of $\Delta(1/T)$ over the entire course of the initial TGA curve were first determined. The Anderson–Freeman equation, which relates these quantities, is given below:

$$\Delta \log(dw/dt) = n \Delta \log w - (E^*/2.303R) \Delta(1/T)$$

Where dw/dt is the rate of thermal decomposition reaction (mg min^{-1}), w is the reactant mass (mg), R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), E^* is the activation energy (J mol^{-1}), and n is the order of reaction. When $\Delta \log(dw/dt)$ is plotted against $\Delta \log w$, it gives a straight line of slope 'n' and the intercept gives the activation energy ' E^* '. When $\Delta \log(dw/dt)$ was plotted against $\Delta \log w$ for the pure PVA and PAM hydrogels over the entire range of temperatures, the data points did not fall on a straight line. Therefore, based on the Anderson-Freeman equation, the thermal

Table 1. Weight Loss (%) at different decomposition temperatures of pure PVA, PAM and PVA/AM Hydrogel at various compositions formed at a constant 20 kGy Dose of gamma radiation

PVA/AM composition (%)	Weight loss (%)					
	200°C	300°C	350°C	400°C	450°C	500°C
PAM (100)	5.6	21.2	26.3	60.9	77.1	81.1
PVA/AM (20/80)	9.7	20.9	29.6	61.9	73.6	79.2
PVA/AM (30/70)	10.4	22.2	33.3	63.4	74.2	75.0
PVA/AM (50/50)	10.9	22.5	36.7	65.3	77.2	77.7
PVA (100)	7.5	65.7	78.7	86.3	88.9	95.8

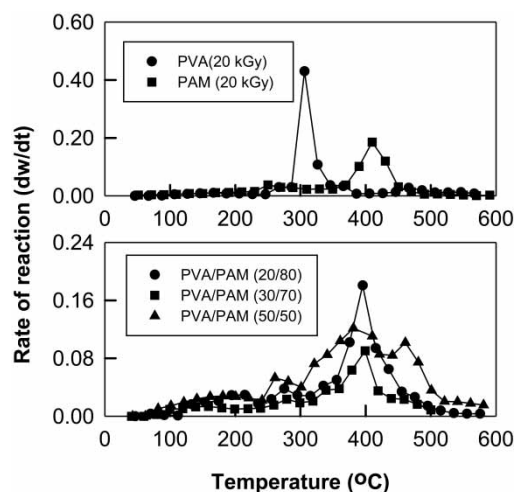


Fig. 3. Reaction rate (dw/dt) against temperature for PVA and PAM polymer hydrogels and their copolymer hydrogels at different compositions, formed at a dose of 20 kGy of gamma radiation.

decomposition of these hydrogels does not depend on the residual mass but on temperature and follows a zero order reaction. In this case, $\log(dw/dt)$ is plotted against $1/T$ and the slope is equal to $E^*/2.303R$, from which the activation energy can be calculated, as shown in Figure 4. However, when $\Delta \log(dw/dt)$ was plotted against $\Delta \log w$ for PVA/AM hydrogels, the data points fall on a straight line as shown in Figure 5. The calculated activation energies for all the hydrogels are presented in Table 2.

Based on the thermal decomposition study, few conclusions may be made: (1) the thermal stability of PVA/AM hydrogels is relatively lower than that of individual PAM and higher than pure PVA hydrogel. However, the thermal stability increases with increasing the content of AM in the initial solutions composition suggesting that the composition of the final composition corresponds to the initial preparing solutions. (2) The thermal decomposition of pure PVA or PAM goes through one maximum, while those of PVA/AM copolymer hydrogels go through three maxima. These findings may give supports to the IR spectra, which suggest the formation of interpenetrating

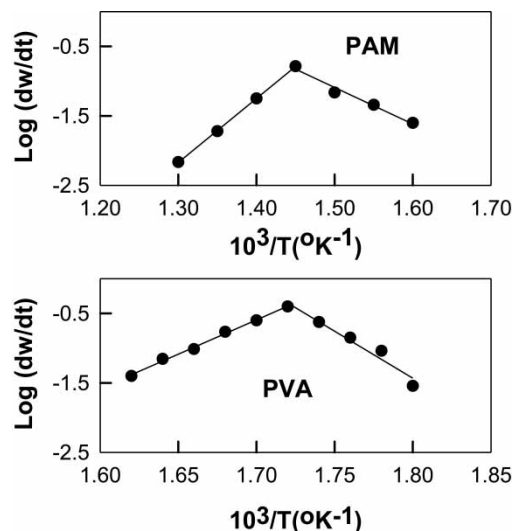


Fig. 4. Temperature dependency of the logarithm of the rate of reaction for PVA and PAM hydrogels formed at a dose of 20 kGy of gamma radiation.

polymer network. (3) The activation energy calculations of PVA/AM hydrogels showed clearly that the thermal decomposition stability increases with increases the content of PAM component.

3.4 Swelling Behavior of PVA/AM Hydrogels

Figure 6 shows the swelling kinetics in water at 25°C for pure PVA, PAM and PVA/AM hydrogels at various compositions formed at a dose of 20 kGy of gamma radiation. It can be seen that the percentage swelling of all the hydrogels increases linearly within the initial time of swelling up to 6 h, and then reached the equilibrium state after 8 h. The swelling of PVA/AM hydrogels displays a systematic trend in accordance with composition. This behavior is due to the higher hydrophilic character of PVA than that of PAM. The calculated initial rate of swelling was found to be 1.51, 1.21, and 0.67 g water/g gel. min for PVA(50)/AM (50), PVA(30)/AM (70) and PVA(20)/AM (80) hydrogels, respectively.

Equilibrium water content (EWC) is an important quantitative factor to represent the water absorbed rather than the

Table 2. Temperatures of the maximum rate of reaction and activation energy of the thermal decomposition for Pure PVA and PVA/AM hydrogel at various compositions formed at a constant 20 kGy dose of gamma radiation

PVA/AM composition (%)	Temperature of the maximum rate of reaction			Activation energy (kJ/mol)
	1st T_{max}	2nd T_{max}	3rd T_{max}	
PAM (100)	—	—	410°C (60.9%)	149.9 (Zero order)
PVA/AM (20/80)	142°C (11.1%)	275°C (18.3%)	396°C (57.6%)	125.0 First order
PVA/AM (30/70)	159°C (7.2%)	279°C (19.4%)	396°C (57.6%)	122.5 First order
PVA/AM (50/50)	180°C (7.6%)	260°C (17%)	381°C (47.4%)	106.3 First order
PVA (100)	—	—	306°C (65.7%)	94.4 (Zero order)

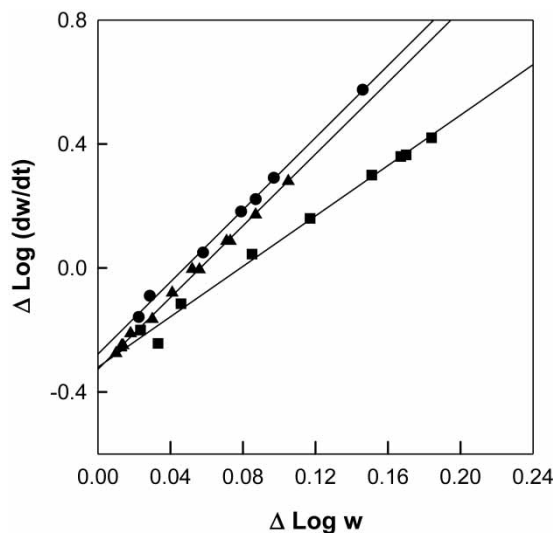


Fig. 5. Anderson-Freeman plots to calculate the activation energy of the thermal decomposition reaction for pure PVA homopolymers and PVA/PAM hydrogels at different ratios formed at a dose of 20 kGy of gamma radiation. (●) PVA/PAM (50/50), (■) PVA/PAM (30/70), (▲) PVA/PAM (20/80).

percentage swelling and it is defined as the mass of absorbed water at equilibrium with respect to the mass of swollen gel at equilibrium. The value of EWC for PVA/AM hydrogels having 50, 70, and 80% AM equilibrated at 25°C was found to be 0.8112, 0.8773, and 0.8889, respectively. The EWC values of PVA/AM hydrogels (0.8112–0.8889) are greater than the percentage content of living tissues. The PVA/AM hydrogels exhibited fluid contents greater than that for living tissues by 60% (30).

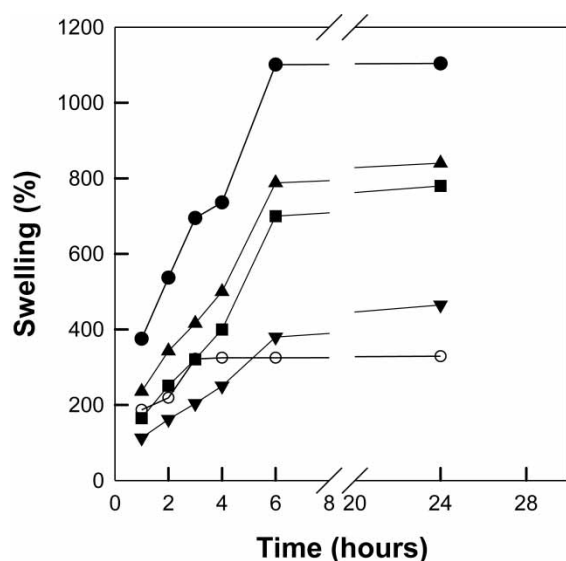


Fig. 6. Swelling kinetics in water at 25°C and (pH = 7) for: (○) pure PAM, (●) pure PVA, (▲) PVA/AM (50/50), (■) PVA/AM (30/70), (▼) PVA/AM (20/80) hydrogels formed at a dose of 20 kGy of gamma radiation.

3.5 Sensitivity of PVA/AM Hydrogels for Temperature and pH Environments

The swelling behavior of PVA/AM hydrogels was investigated as a function of temperature as, shown in Figure 7. It can be seen that the PVA/AM hydrogels displayed changes in the percentage swelling over the temperature range 40–50°C. This sensitivity was greatly dependent on time of swelling and on AM content. In this regard, the sensitivity of the hydrogel initially formed from binary mixture of PVA and AM is clear during the initial time of swelling (1–2 h) and then starts to disappear after 3 h, up to the equilibrium swelling state. In addition, it can be seen that the swelling temperature sensitivity decreases with increasing PVA content. Thus, it can be concluded that 40°C is the lower critical solution temperature (LCST) for those hydrogels, in which they shrink by heating above the LCST (12, 13). In an aqueous solution, the chains hydrate to form expanded structures when the temperature is below the LCST, but become compact by dehydration when heated up above LCST. Therefore, it would be expected that the temperature sensitivity of PVA/AM is due to the formation of hydrophobic inter-chain bonding and/or interpenetrating polymer network between PVA and AM and these bondings will increase with increasing AM contents, as shown in Figure 7.

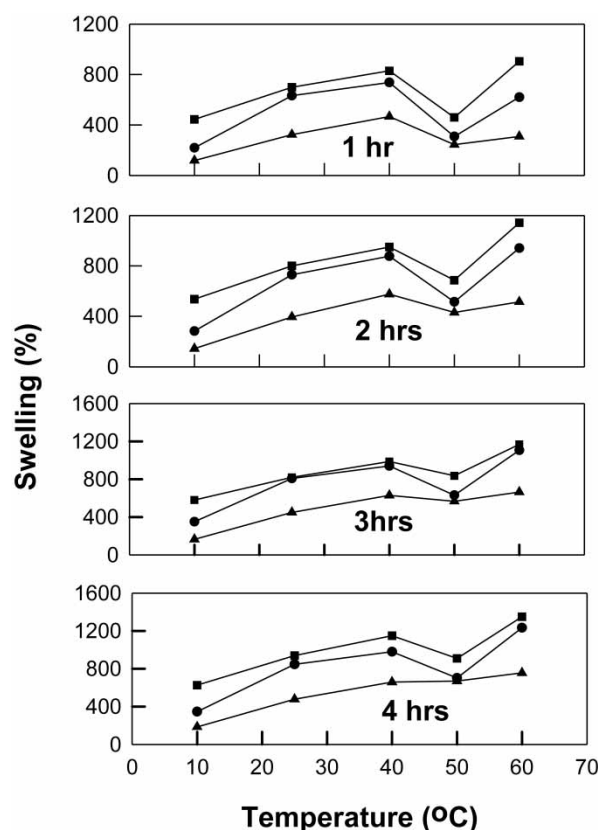


Fig. 7. Swelling in water at different times as a function of temperature for PVA/AM hydrogels at various compositions formed at dose of 20 kGy of gamma radiation. (■) PVA (20)/AM (80), (●) PVA (30)/AM (70), (▲) PVA (50)/AM (50).

Figure 8 shows the relationship between the percentage swelling of water and pH values for PVA/AM hydrogels at various compositions formed at a dose of 20 kGy of γ -irradiation. It should be noted that the hydrogel samples were immersed in different buffer solutions at 25°C for the equilibrium time specific for each hydrogel. The pH sensitive swelling behavior can be observed, in which the swelling was shown to increase by increasing the pH value from 2 to 5, and then suddenly decreases within the pH range 5–7. Furthermore, a slight increase in the percentage swelling can be observed by increasing the pH values from 7 to 10. The hydrogel initially prepared from equal contents of PVA and AM does not exhibit this oscillatory swelling behavior against the change in the pH range from low to high values. The percentage swelling of the PVA/AM hydrogels with PVA ratios of 20, 30, 50% was decreased by 2.4, 1.7, and 1.3 times (based on the values at pH 5) by increasing the pH value from 5 to 7 after a swelling time of one hour, respectively. Meanwhile, after a swelling time of 4 h, the decrease in the percentage swelling of the same hydrogels was found to be 2, 1.4 and 1.2 times, respectively. Thus, it can be seen that the pH-sensitivity increases with increasing the AM contents in the hydrogels, whereas this sensitivity

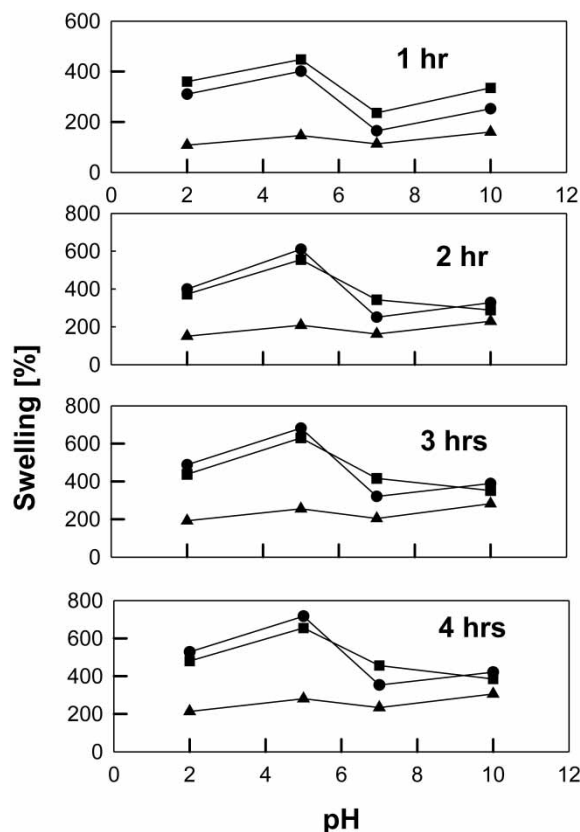


Fig. 8. Swelling dependency on pH at different times for PVA/AM hydrogels at different compositions formed at a dose of 20 kGy of gamma radiation at 25°C. (●) PVA (20)/AM (80), (■) PVA (30)/AM (70), (▲) PVA (50)/AM (50).

decreases with increasing time of swelling. Amides may be hydrolyzed in either acidic or alkaline solutions, and neither type of hydrolysis is reversible. Hydrolysis of amines, in acidic solution, proceeds by the protonation of the carbonyl groups and, hence the release of free acids. As the pH increases, they became ionized with the formation of carboxylate salts. These changes result in the states of contraction and expansion, thus causing the hydrogels to shrink and swell.

4 Conclusions

This study was carried out to illustrate the synthesis of hydrogels based on various compositions of poly(vinyl alcohol) (PVA) and acrylamide monomer (AM) under the effect of γ -irradiation. It was suggested that formation of these hydrogels depends essentially on the radiolysis products, due to radiation absorption and hence, the crosslinking. These hydrogels may find applications in the biomedical field due to the super swelling in water as well as the pH and temperature responsive characteristics. The IR spectroscopic analysis, which was initially used to illustrate the nature of bonding, showed the formation of hydrogen bonding and interpenetrating polymer network. The TGA investigation has led us to the conclusion that the PVA/AM hydrogels possess lower thermal stability compared to that of the individual PAM polymer hydrogel. The composition of hydrogels composition is an effective parameter in determining the responsive character, in which the hydrogel initially prepared from binary mixture of PVA and AM does not show clearly temperature or pH responsive behavior. On the other hand, the PVA/AM hydrogels contain 70 and 80% of PAM showed these characteristics within the temperature range 40–50°C, and within the pH range 5–7 at any time of swelling in water. It was interesting to find that the PVA/AM hydrogels shrink upon either change in temperature or pH value.

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