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Swelling, Thermal and Mechanical Properties of Poly(vinyl alcohol)/Sodium Alginate Hydrogels Synthesized by Electron Beam Irradiation

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Highly hydrophilic hydrogels composed of various contents of poly(vinyl alcohol) (PVA) and sodium alginate (AG) were produced by exposure to electron beam irradiation. The hydrogels were characterized by IR spectroscopy, mechanical testing and thermogravimetric analysis (TGA). The kinetic parameters of the thermal decomposition were determined by the Kissinger method (different heating rates). In addition, the swelling behavior in different temperatures and pH values was studied. The IR spectroscopic analysis indicates the formation of interpenetrating polymer networks and the presence of hydrogen bonding. The thermal study showed that the PVA/AG hydrogels, over the studied compositions, possess higher thermal stability than pure PVA hydrogel. The kinetic studies of swelling in water showed that pure PVA and PVA/AG hydrogels reaches equilibrium after 4 h. However, PVA/SAG hydrogels show swelling in water greater than pure PVA hydrogel. It was found that the swelling of PVA/AG hydrogels increases greatly within the temperature range 10–25°C, and the pH range 5–7 depending on composition. This behavior was clear in the case of PVA/AG composed of higher contents of AG.

Keywords: electron beam irradiation; thermal stability; mechanical properties; responsive hydrogels; sodium alginate

1 Introduction

Hydrogels are three-dimensional crosslinked polymeric structures, which are 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). 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).

Alginate, the major structural polysaccharides of marine brown algae is a (1–4) linked polyanionic copolymer of β.D-mannuronic (M) and α-L guluronic (G) residue, differing from each other in their relative proportions (M/G ratios) (16–18). Alginate has found biomedical and biotechnology applications mainly as a material for the encapsulation and immobilization of a variety of cells for immunoisolatory and biochemical processing applications. Subject to diffusions limitations, cells can maintain viability within the crosslinked hydrogels (19, 20). In this regard, sodium alginate gels of different compositions were evaluated for bone marrow cell tissue (21). It was found that high purity and G-type alginate retained 27% of its initial strength after 12 days in culture and comparable levels of proliferation were observed on this material and tissue culture plastic. In addition, alginate with different molecular weights and M/G ratios were used as gel matrixes in order to obtain magnetic nonstructural compositions (22). The analyzed magnetic materials subjected to several oxidative cycles showed high magnetic response, absence of hystersis and central paramagnetic behavior.

Although there is extensive work on the responsive hydrogels towards external environments, few researchers have dealt with the synthesis of hydrogels composed of sodium alginate as a constituent. Thermo- and pH-responsive semi-interpenetrating polymer (IPN) networks and comb-type

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graft hydrogels, composed of alginate and poly(N-isopropyacrylamide (PNIPAAm), were synthesized (8, 9). It was found that alginate/PNIPAAm semi-IPN hydrogels exhibited a reasonable sensitivity to temperature, pH and ionic strength of the swelling medium. The present work was undertaken to study the possible formation of hydrogels composed of sodium alginate and poly(vinyl alcohol) by exposing their solutions to electron beam irradiation. Moreover, the effect of temperature and pH on the swelling of these hydrogels is another objective of this study. The durability of these hydrogels was investigated in terms of the thermal and mechanical properties.

2 Experimental

2.1 Materials

Sodium alginate (AG) used in this study was a laboratory grade chemical obtained from Aldrich Chemical Co. (Milwaukee, WI), and used as received. Poly(vinyl alcohol), laboratory grade, was a fully hydrolyzed polymer in the form of a powder, average molecular weight (Mw) of 106,000 g mol^{-1}, obtained from Laboratory Rasayan, Cairo, Egypt.

2.2 Preparation of PVA/AG Hydrogels

The hydrogels were prepared by dissolving separately, different ratios of PVA (60–100%) and AG (20–40%) in distilled water. The PVA and AG solutions were then mixed with continuous stirring until complete miscibility was achieved. The ratios of PVA and AG in the mixtures were 80/20, 75/25, 70/30, and 60/40%. The mixtures were then poured into dishes and subjected to electron beam irradiation.

2.3 Electron Beam Irradiation

Irradiation was carried out in the electron accelerator facility (1.5 MeV, 25 kW) of the National Center for Radiation Research and Technology, in which the required doses were obtained by adjusting the electron beam parameters and conveyer speed.

2.4 Determination of Gel Fraction

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

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

2.5 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.

2.6 Thermogravimetric Analysis (TGA)

The thermal decomposition studies were performed over a temperature range from room temperature to 500°C using a Shimadzu–50 instrument (Kyoto, Japan) at different heating rates of 10, 20 and 30°C/min. The TGA thermograms were used to determine the kinetic parameters of thermal decomposition reaction.

2.7 Tensile Mechanical Measurements

Mechanical tests of LDPE/PLST blends including tensile strength and elongation at yield and break points were preformed at room temperature using an Instron Machine (model 1195) employing a crosshead speed of 10 mm/min according to ASTM D-638 standards.

2.8 Swelling Studies of PVA/AG Hydrogels

Swelling studies were conducted on PVA/AG hydrogels as a function of time (0–48 h), temperature (10–50°C) and pH (2–10). A known dry weight of insoluble hydrogel (W_d) was immersed in water under different conditions. The samples were then removed and blotted on filter paper to remove excess water and weighed (W_s), in which the percentage swelling under each condition 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:

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

3 Results and Discussion

3.1 Synthesis and Composition of PVA/AG Hydrogels

In this work, alginate was chosen as a natural polymer to form hydrogels with PVA in solutions after the exposure to electron beam irradiation. This is because this polymers couple/blend may result in a unique combination of properties based on the hydroxyl groups of PVA and the carboxylic group of alginate as ionic hydrogels. Table 1 shows the gel fraction and water uptake of pure PVA and PVA/AG hydrogels at various compositions formed at a constant dose of 25 kGy of accelerated electrons. It can be seen that the gel fraction decreases systematically with increasing the content of alginate. On the other hand, the percentage water uptake increases with increasing the content of alginate to reach ~8 times that displayed by PVA for the hydrogel composed of 40% alginate.

The gel formation of PVA in solution by electron beam irradiation is well known, in which the gelation dose (the

Table 1. Gel fraction and water uptake at equilibrium of PVA/AG hydrogels formed at a dose of 25 kGy of electron beam irradiation

PVA/AG composition (%)	Gel fraction (%)	Water uptake (%)
100/0	89	945
80/20	85	2327
75/25	80	2530
70/30	73	5340
60/40	65	7950

first insoluble fraction of gel appears) was reported to be 3.4 kGy (23). Sodium alginate, on the other hand, is soluble in water but does not form gels under the effect of ionizing radiation. However, it does form stable gels at room temperature in the presence of a certain concentration of divalent cations (i.e., Ba^{2+}, Ca^{2+}) through the ionic interaction between the guluronic acid groups. The mechanism of crosslinking of polymers and the polymerization of monomers in solution by ionizing radiation was studied by Chaprio (24, 25), Saaito (26, 27) et al. (28, 29).

The mechanism of crosslinking of PVA in aqueous solution by accelerated electrons can be briefly outlined as follows: [1] The polymer PVAH and the solvent HOH absorb the accelerated electrons and go to the transient activated states PVAH* and HOH*, which dissociate causing the formation of the radicals $PVA^{\bullet}$, $HO^{\bullet}$, and $H^{\bullet}$. [2] The transfer of radical from water to polymer increases the concentration of PVA radicals and increases the rate of crosslinking and gelation:

$$\mathrm{PVAH} + (\mathrm{H}^{\bullet}\mathrm{or\ HO}^{\bullet}) \longrightarrow \mathrm{PVA}^{\bullet}\mathrm{HOH}$$

[3] Two polymer radicals $PVA^{\bullet}$ with m and n repeat units combine to form a crosslinked point:

$$\mathrm{PVA}^{\bullet}_{m} + \mathrm{PVA}^{\bullet}_{n} \longrightarrow \mathrm{PVA}_{m} - \mathrm{PVA}_{n}$$

The depression in the gel fraction from ~90% for pure PVA to 65% for PVA/AG hydrogel prepared from initial composition containing 40% of alginate means that 25% of the insoluble fraction part is lost in the extraction process. Meanwhile, the gel fraction of PVA was decreased by the factors 5, 10, 18, and 27 by introducing 20, 25, 30, and 40% in the preparing solutions, respectively. In order to determine the actual composition of the final product, the hydrogels were subjected to acid-base analysis because alginate is the only component containing carboxylic groups. The results showed that this fraction was lost from the starting weight of alginate and not from PVA. This finding may be explained as due the existence of alginate in a non-crosslinked state inside the network structure of PVA. However, a part of alginate forms an interpenetrating polymer network within the PVA matrix. Thus, the free end polymer chains of alginate and the highly hydrophilic properties will results in a higher water uptake by PVA/AG hydrogels compared to pure PVA.

IR spectroscopic analysis was used to illustrate the structure and nature of bonding and to confirm the composition of hydrogels. Figure 1 shows the IR spectra of pure PVA and PVA/AG hydrogels of various compositions formed by the exposure to a constant dose of 25 kGy of electron beam irradiation. The spectrum of pure PVA showed an absorption peak around $2950\,cm^{-1}$, with a weak shoulder arising from C-H stretching. In addition, an absorption peak at $1287\,cm^{-1}$ is assigned for vinyl groups. The characteristic absorption peaks of alginate can be seen at $3500\,cm^{-1}$to the hydroxyl groups and at $1620\,cm^{-1}$ and $1410\,cm^{-1}$ for the asymmetric COO^{-} stretching vibration and symmetric COO^{-} stretching vibration, respectively (9). As the ratio of AG to PVA increases, the intensity of these absorption bands increases. In addition, the IR spectra of PVA/AG hydrogels showed that the broadness of these absorption bands due to the hydroxyl to decrease with increasing alginate content indicating formation of hydrogen bonding. Hydrogen bonding in this case might be formed between the hydroxyl groups of PVA and the carboxylate of alginate. Accordingly, it seems reasonable to presume that the evolved heat during electron beam irradiation will accelerate the reaction to occur between the COO^{-} of alginate, and the OH of PVA to form a network structure of alginate inside the PVA network structure.

3.2 *Swelling Behavior of PVA/AG Hydrogels*

Figure 2 shows the swelling kinetics in water at 25°C for PVA/AG hydrogels at various compositions, formed at a constant dose of 25 kGy of electron beam irradiation. It can be seen that the percentage swelling of all the hydrogels increases linearly within the initial time of swelling up to 4 h, and then reaches equilibrium. The swelling of PVA/AG hydrogels displayed a systematic trend in accordance with composition, in which the percentage swelling increases with increasing the content of alginate. This behavior is due to the higher hydrophilic character of AG compared to PVA. The calculated initial rate of swelling was found to be 0.07, 1.22 and 2.22 g water/g gel · min for PVA(80)/AG (20), PVA(70)/AG (30), and PVA(60)/AG (40) hydrogels, respectively.

The equilibrium water content (EWC) is an important quantitative factor to represent the water absorbed rather than the 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/AG hydrogels having 20, 30, and 40% AG equilibrated at 25°C was found to be 0.9583, 0.9816 and 0.9875, respectively. The EWC values of PVA/AG hydrogels (0.9583–0.9875) are greater than the percentage content of living tissues. The PVA/AG hydrogels exhibited fluid contents greater than that for living tissues by ~0.60 (or 60%) (30).

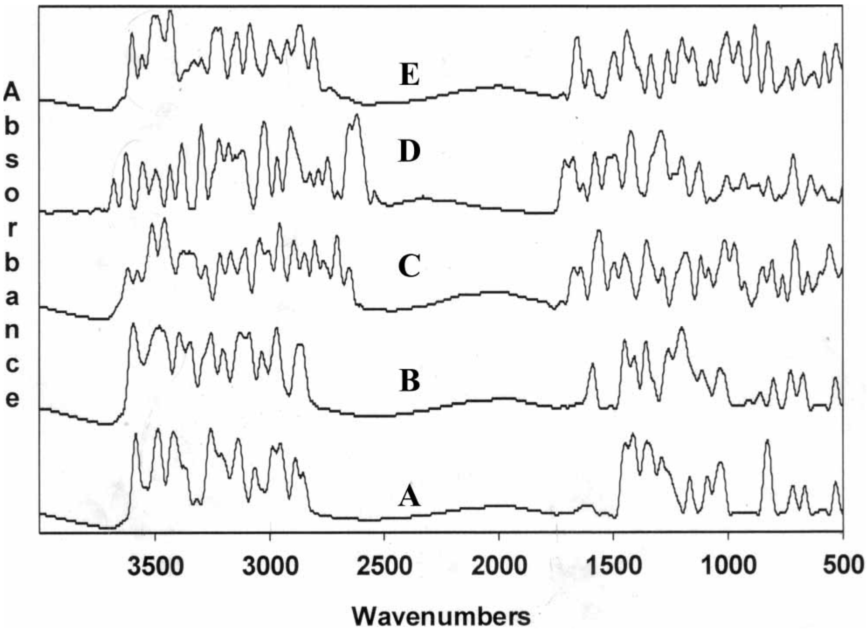

Fig. 1. IR Spectra of : (A) Pure PVA, (B) PVA/AG (80/20), (C) PVA/AG (75/25), (D) PVA/AG (70/30), (E) PVA/AG (60/40).

3.3 *Sensitivity of PVA/AG Hydrogels for Temperature and pH Environments*

The swelling behavior at equilibrium of PVA/AG hydrogels at various compositions was investigated as a function of temperature, as shown in Figure 3. It can be seen that the swelling of PVA/AG hydrogels changes significantly over the temperature range 10–25°C. This sensitivity depends greatly on the alginate content. In this regard, the increase in swelling with increasing the temperature from 10 to 25°C for the hydrogels, containing 20, 25, 30, and 40% of alginate, was ~250, 270, 630, and 840%, respectively. The thermo sensitivity of the swelling is probably due to the formation of interpenetrating polymer networks and definitely not due to pure polymers. Thus, it can be concluded that the

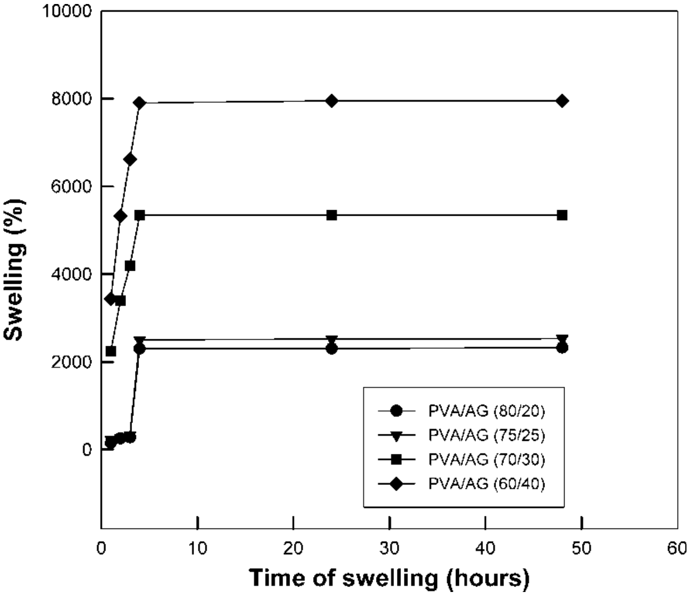

Fig. 2. Kinetics of swelling of PVA/AG hydrogels at various compositions formed at a constant dose of 25 kGy of electron beam irradiation.

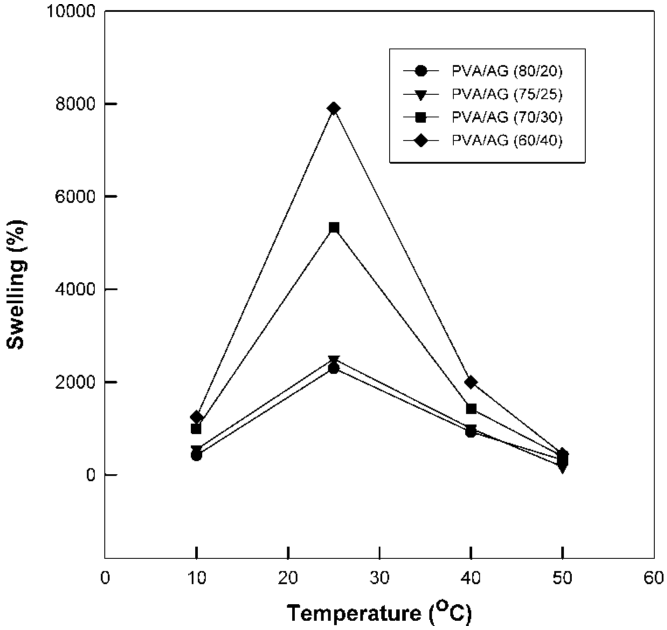

Fig. 3. Kinetics of swelling as a function of temperature of PVA/AG hydrogels at various compositions formed at a constant dose of 25 kGy of electron beam irradiation.

temperature range 10–25°C is the lower critical solution temperature (LCST) for those hydrogels showing a positive sensitive systems, in which they swell by heating above the LCST (8). Usually, LCST behavior is driven by changes in water bonding accompanied by inter-chain bonding enhancement. Therefore, it would be expected that the temperature sensitivity of PVA/AG is due to the formation of hydrophobic inter-chain bonding and/or interpenetrating polymer network between PVA and AG and this type of bonding will eventually increase with increasing the AG ratio as shown in Figure 3.

Figure 4 shows the percentage swelling as a function of pH values for PVA/AG hydrogels at various compositions. It should be noted that the hydrogel samples were immersed in different buffer solutions at 25°C for the equilibrium. The pH sensitive swelling behavior can be observed, in which the swelling was shown to increase by increasing the pH value from 5 to 7, and then suddenly decreases within the pH range 7–10 depending on hydrogel composition. The percentage swelling of the PVA/AG hydrogels with AG ratios of 20, 30, 40% was increased by 4.2, 4.7, and 5 times (based on the values at pH 5) by increasing the pH value from 5 to 7, respectively. Thus, it can be concluded that the pH-sensitivity increases with increasing the AG ratio in the hydrogel. The pKa of alginate was about 3.2 and 4 for guluronic and manuronic acid, respectively (9). At low pH, most carboxylic acid groups in alginate are in the form of COOH. As the pH of the medium increases, the carboxylic groups become ionized, and the resulting electrostatic repulsion in the network causes the hydrogel to swell. These changes in pH values would cause states of contraction and expansion, i.e., cause the hydrogels to swell and shrink.

3.4 Thermal Decomposition Behavior

Thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of pure PVA and PVA/AG hydrogels formed at a dose of 25 kGy of electron beam irradiation as shown in Figure 5 and Table 2. Up to 5% wt loss, the hydrogel containing 40% AG displayed the highest thermal stability (higher temperature).

However, pure PVA hydrogel displayed higher thermal stability than the other PVA/AG hydrogels containing AG content less than 40%. Meanwhile, up to 50% wt loss, the PVA/AG hydrogels displayed higher thermal stability than pure PVA hydrogel. In addition, it can be seen that the thermal stability of PVA/AG hydrogels constantly increases with increasing the alginate contents, based on the temperatures at which certain weight loss occurs.

The derivative of the rate of reaction (DTGA) curves for pure PVA and PVA/AG hydrogels is shown in Figure 6. In addition, the temperatures at which the maximum values of the rate of reaction (T_{max}) and the percentage weight loss at these maxima are shown in Table 2. It should be noted that these curves were taken over the T_{max} corresponding to the range of temperatures at which the major decomposition occurs. However, the rate of reaction decomposition of pure PVA hydrogel showed a single T_{max}, while those for PVA/AG hydrogels showed multiple stage thermal decomposition. Based on these T_{max}, it may be conclude that PVA/AG hydrogels possess relatively higher thermal stability than pure PVA polymer hydrogel.

The activation energy E_a for the thermal degradation was confirmed by applying the Kissinger method, which depends on different heating rates according to the following

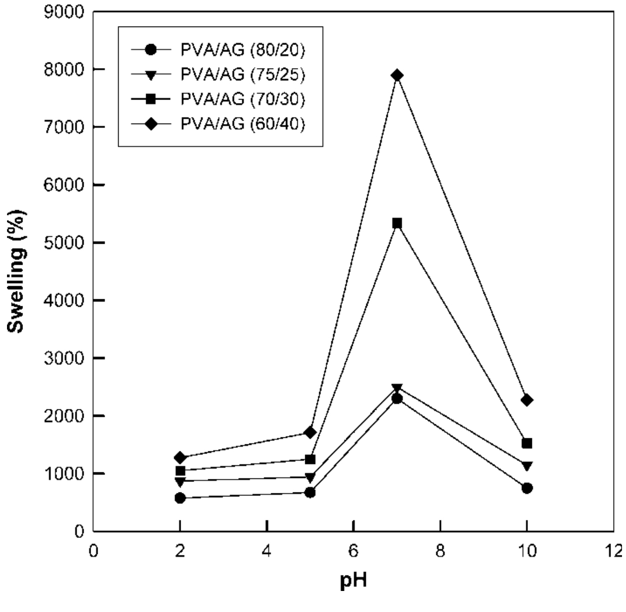

Fig. 4. Kinetics of swelling as a function of pH of PVA/AG hydrogels at various compositions formed at a constant dose of 25 kGy of electron beam irradiation.

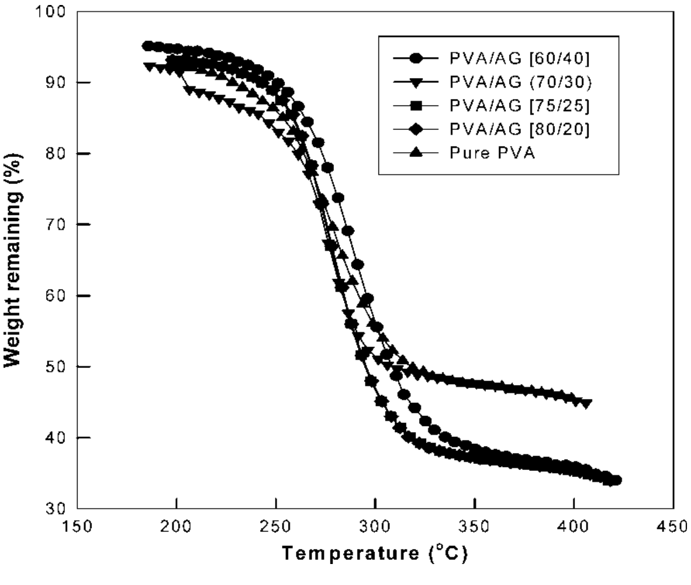

Fig. 5. TGA thermograms of PVA/AG hydrogels at various compositions formed at a constant dose of 25 kGy of electron beam irradiation.

Table 2. Temperatures at which different percentage weight loss and temperatures of the maximum rate of reaction for pure PVA and PVA/AG hydrogels at various compositions. Dose as in Table 1

Hydrogel composition (%)	T 5 wt%	T 10 wt%	T 20 wt%	T 50 wt%	T_{max}	Wt loss at T_{max}
PVA (100)	191	206	261	295	278	35.6
PVA/AG (80/20)	134	228	161	303	278	35.4
PVA/AG (75/25)	147	243	266	311	279	34.4
PVA/AG (70/30)	148	243	274	311	284	33.2
PVA/AG (60/40)	208	251	286	319	291	33.1

equation (31):

$$\ln(\beta/T^2_{max}) = E_a/R(1/T_{max}) + \ln[nAR(1-\alpha_m)^{n-1}]/E_a$$

A is the pre-exponential factor, E_a is the apparent activation energy of the degradation reaction, R is the universal gas constant, β is the heating rate. In this method, the activation energy is calculated from the T_{max}, the temperature at which the maximum degradation occurs for different heating rates by assuming that α_m or weight loss percentage at T_{max} is constant. Thus, the activation energy can be computed from the linear dependence of the $\ln \beta/T^2_{max}$ vs. $(1/T_{max})$ for the various heating rates as shown in Figure 7. The activation energy can be calculated from the relationship of $E_a = R \times$ slope. The activation energies of the hydrogels pure PVA, PVA/AG (80/20), PVA/AG (75/25), PVA/AG (70/30), and PVA/AG (60/40) were found to be 255.3, 306.4, 330.0, 370.0, and 656.6 kJ/mol, respectively.

Based on the thermal decomposition study, several conclusions may be made: [1] the thermal decomposition of pure PVA goes through one maximum, while those for PVA/AG hydrogels go through three maxima. These findings may give supports to the IR spectra, which suggest the formation of interpenetrating polymer network; [2] The kinetic parameters showed clearly that the thermal decomposition reaction of pure PVA and PVA/AG hydrogels is a first order according to the Kissinger method, in which the activation energy increases with increasing the ratio of AG component.

4 Mechanical Properties of PVA/AG Hydrogels

The formation of copolymer hydrogel between PVA and alginate is expected to improve in mechanical properties, as shown in Table 3. It can be seen that the hydrogels of pure PVA and PVA/AG (80/20) showed the stress-strain behavior of brittle polymer with no yielding properties. By increasing the content of alginate above 20%, the hydrogels showed the stress-strain behavior of tough polymers with yielding properties. The yield and break stress values were

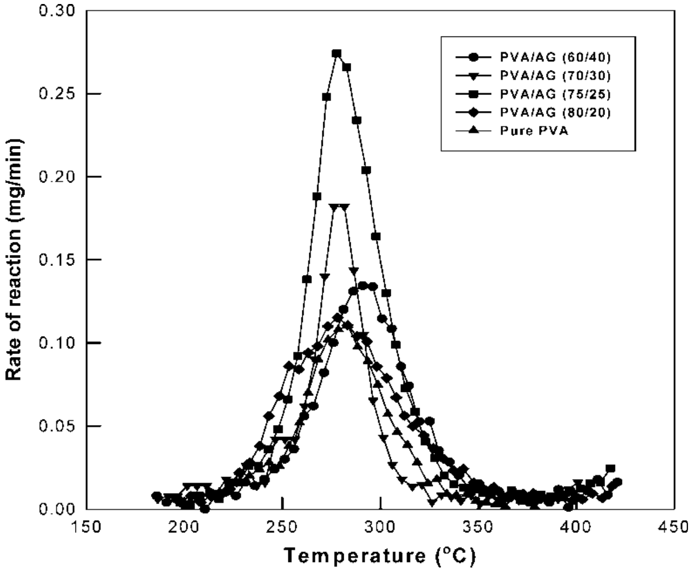

Fig. 6. Rate of reaction curves of the thermal decomposition for PVA/AG hydrogels at various compositions formed at a constant dose of 25 kGy of electron beam irradiation.

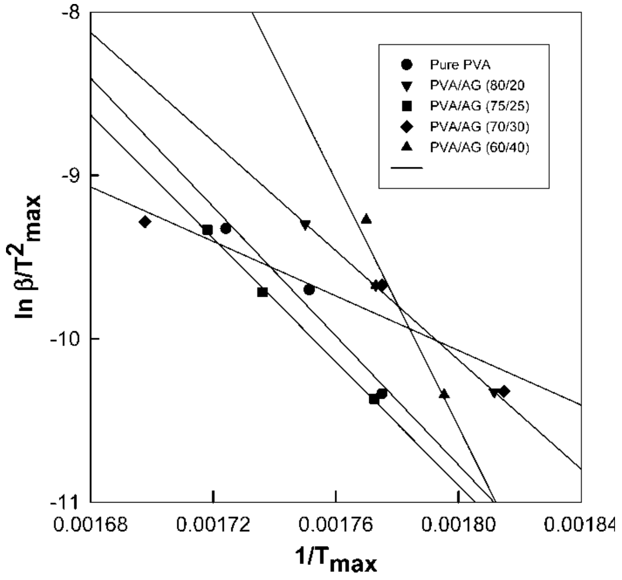

Fig. 7. Kinetics of the determination of thermal decomposition of PVA/AG hydrogels at various compositions formed at a constant dose of 25 kGy of electron beam irradiation.

Table 3. Tensile mechanical properties of PVA/AG hydrogels formed at dose of 25 kGy of electron beam irradiation

Hydrogel composition (%)	Yield stress (MPa)	Yield strain (%)	Break stress (MPa)	Break strain (%)
PVA	Non	Non	4.55 ± 0.17	2.90 ± 0.21
PVA/SAG (80/20)	Non	Non	7.15 ± 0.17	3.06 ± 0.35
PVA/SAG (75/25)	0.656 ± 0.02	3.15 ± 0.22	7.40 ± 0.15	3.40 ± 0.11
PVA/SAG (70/30)	6.31 ± 0.69	4.66 ± 0.06	6.023 ± 0.19	5.41 ± 0.18
PVA/SAG (60/40)	6.87 ± 0.17	4.53 ± 0.13	7.00 ± 0.52	10.62 ± 0.72

found to increase with increasing the content of alginate up to 40% in the hydrogel (PVA/AG) (60/40). The introduction of alginate in the composition with PVA improves the tensile strength only by using alginate content above 20%. This can be attributed to the strong interfacial adhesion between PVA and alginate phases (miscibility), which converts the hydrogels from brittle to tough materials.

5 Conclusions

In this study, hydrogels based on the radiation crosslinkable poly(vinyl alcohol) (PVA) and the non-crosslinkable sodium alginate (AG) were successfully produced by exposing various compositions in aqueous solutions to electron beam irradiation. In this regard, the contents of AG did not exceed 40%; otherwise no homogeneous films could be obtained. These hydrogels may find applications in the biomedical field due to the super swelling in water as well as the pH and temperature responsive character. IR spectroscopic analysis, which was initially used to illustrate the nature of bonding, showed that the hydrogel formation was through an interpenetrating polymer network. In addition, hydrogen bonding was formed. The TGA studies have led us to conclude that the PVA/AG hydrogels possess a higher thermal stability than that of the individual PVA hydrogel. We observe that the hydrogels composition is an effective parameter in determining the responsive character, in which the hydrogel initially prepared from 60% of PVA and 40% of AG clearly showed temperature or pH responsive behavior. However, the PVA/AG hydrogels containing less than 40% AG still displaying these characters within the temperature range 10–25°C, and within the pH range 5–7.

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