

FUNCTIONAL MODIFICATION OF POLY VINYL ALCOHOL/ACRYLIC ACID HYDROGELS PREPARED BY Γ -RADIATION THROUGH SOME AMINE COMPOUNDS

BY

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ABSTRACT

Radiation induced-poly vinyl alcohol/acrylic acid (PVA/AAc) hydrogels were modified through condensation reaction with various aliphatic and aromatic amines to form amine-treated polymers. The amine compounds are 2-amino-3-(4-hydroxyphenyl) propanoic acid (**P1**), propane-1,2-diamine (**P2**), 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (4-aminoantipyrine) (**P3**), 2-aminothiazol (**P4**), 4-amino-*N*-(1-phenyl-1*H*-pyrazol-5-yl) benzene sulfonamide (**P5**) and 4-amino-*N*-(4-methoxy-1,2,5-thiadiazol-3-yl) benzene sulfonamide (**P6**). The degree of swelling of amine-modified polymers increased with increasing AAc contents in the PVA/AAc copolymer and lowered irradiation doses, reaching its maximum at PVA: AAc composition; 50:50 wt%. The characterization of all synthesized polymeric compounds was carried out by using IR, NMR and UV spectral analysis, in addition to thermal studies which predicted by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal studies display that the amine-treated polymers have more thermal stability than untreated ones. All the newly synthesized polymeric compounds were evaluated for their antibacterial and antifungal activities in vitro against two Gram-positive bacteria and two Gram negative bacteria as well as two fungi by the disc diffusion method. In general, the newly synthesized polymeric compounds exhibited higher promising biological activities and can be used in medical applications.

Keywords: Functional modification; polyvinyl alcohol; acrylic acid; amine; hydrogels; γ -radiation

Introduction

Hydrogels consist of a hydrophilic polymer that forms a three-dimensional network, which contains a lot of water. They are one of the most promising materials for biomedical applications and have several advantages for wound dressing, contact lenses, drug delivery systems, etc. because of their biocompatibility with blood, body fluids, and tissue (Das et al., 2012; Benamer et al., 2006; Jayachandran et al., 2014). Hydrogels must sustain their physical strength and contain >75% water. Their water adsorption ability is due to hydration, which is related to chemical groups (such as –

COOH, CONH₂, –CONH–, and SO₃H); capillary effect, and osmotic pressure (Abd El-Mohdy and Abd El-Rehim 2008). These hydrogels also undergo volume change, do not dissolve, and have stable strength, properties that are caused by ionic, hydrophobic, and van der Waals forces. However, the effects of these forces are small; and covalent bonding is prevalent (Aziz et al., 2012; Zhang et al., 2005). In fact, hydrogels have been prepared by chemical methods for a long time. However, in recent years, irradiation techniques to produce hydrogels are being used increasingly around the world. This technology is convenient because the physical properties can be manipulated easily by irradiation (Abd El-Mohdy and Ghanem 2009).

Synthesis of functional polymeric particles and polymers for surface functionalization as well as bio-compatible and bio-degradable polymers is a research focus providing links to the research areas such as hybrid structures and bio-related materials. More research has examined end-functional polymers as a method of preparation of various copolymers (Pernot et al., 2002; Yin et al., 2003). Reactions of functional polymers can most easily be studied if the polymer structure is well-defined, with fixed functional group position and molecular weight, and low polydispersity. Chemical modification of polymers has widespread applications, as the obtained functionalized polymers acquire the reactivity of the introduced functionality while keeping the main features of the base polymeric matrix (Izaoumen et al., 2005). Hence, many functional polymers have been prepared through the reaction of polymers with different chemically reactive species. Functionalization can also be achieved through physical blending of some organic compounds such as amine compounds (Sarhan et al., 2002; Abdel-Bary et al., 1997). However, hydrogels with basic groups, such as amine groups, expand and shrink at lower and higher pH values (Abd El-Mohdy 2007; Abd El-Mohdy et al., 2006; Abd El-Mohdy 2012).

Therefore, the present study is an attempt, to study the functional modification of poly vinyl alcohol/acrylic acid hydrogels prepared by γ -radiation through some amine compounds such as L-tyrosine, 1,2-diaminopropane, 2-aminoantipyrine, 4-amino-*N*-(1-phenyl-1*H*-pyrazol-5-yl) benzene sulfonamide, 4-amino-*N*-(4-methoxy-1,2,5-thiadiazol-3-yl)benzene sulfonamide and thiazol-2-amine. The prepared PVA/AAC hydrogels and amine-modified ones were characterized by FTIR, ¹H NMR TGA, DSC, SEM and swelling behavior.

Experimental

Materials

Poly vinyl alcohol and acrylic acid (purity 99%), 2-amino-3-(4-hydroxyphenyl) propanoic acid, propane-1,2-diamine, 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (4-aminoantipyrine), 2-aminothiazol, 4-amino-*N*-(1-phenyl-1*H*-pyrazol-5-yl) benzene sulfonamide and 4-amino-*N*-(4-methoxy-1,2,5-thiadiazol-3-yl) benzene sulfonamide (Merck, Germany) were used as received, the chemical structures are shown in Figure 1.

Hydrogel preparation

Hydrogel was obtained by ionizing irradiation process of gamma source of 4.25 kGy/h dose rate. Various PVA : AAc ratios of 100 : 0.0, 90 : 10, 80 : 20, 60 : 40 and 50 : 50 wt% were prepared. The mixture was stirred at room temperature for 30 mins.

Chemical modification of PVA/AAc hydrogels

Different amine compounds were used as starting point for the introduction of new functional groups via nucleophilic addition of amino groups containing chemical compounds such as amines to produce the corresponding derivatives. The chemical modification was carried out by refluxing 1g of PVA/AAc hydrogels with PVA : AAc ratio; 50 : 50 wt% and irradiation dose; 30 kGy with an appropriate amount of amine in EtOH/EtONa as a catalyst with few drops of (DMF) at 80°C for 72 h. The treated hydrogels were thoroughly washed in hot DMF followed by ethyl alcohol, dried at 60°C for 6 h and kept in dry place.

FT-IR Spectroscopy

Analysis by Infra-Red Spectroscopy was carried out by using Mattson 1000, Unicam, Cambridge, England in the range from 400-4000 cm⁻¹.

Swelling measurement

Dried hydrogel discs (0.3-0.4 mm thickness, 4 mm diameter) were left to swell in distilled water for 24h. Swollen gel was removed from the swelling medium at regular time intervals and superficially dried with filter paper, and then it was weighed and placed in the same bath. The measurement was continued until a constant weight.

$$\text{Swelling \%} = (W_s - W_d / W_d) \times 100 \quad (1)$$

Where, W_s and W_d represent the weights of swollen and dry samples, respectively.

Thermal gravimetric analysis (TGA)

Perkin Elmar TGA system under Nitrogen atmosphere 10 mL/min was used. The temperature range was from ambient temperature to 600°C.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were performed with a PerkinElmer model DSC-7. A specimen (≈ 5 mg) of the sample was used for DSC measurements. Indium and zinc standards were used to calibrate the temperature and thermal scale. The measurements were carried out in a N₂ atmosphere from 20 to 220°C at a heating rate of 10°C/min.

pH Measurements

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

Scanning electron microscopy (SEM)

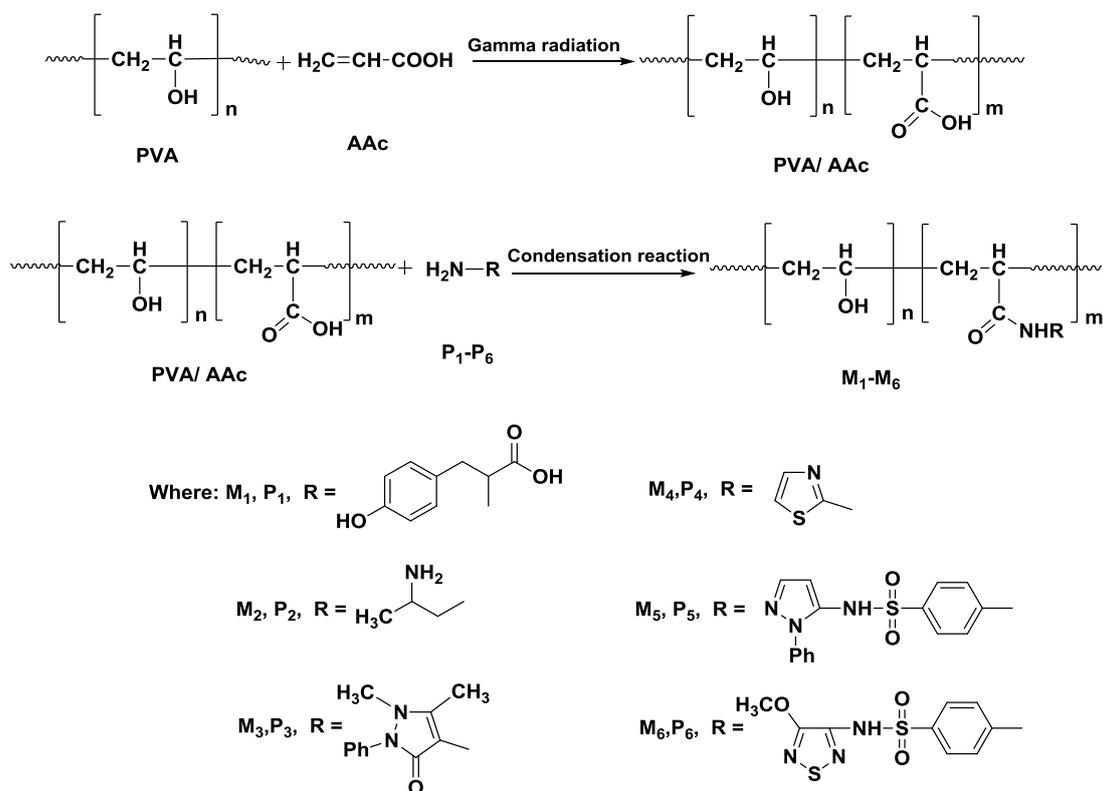
The lyophilized dried hydrogels were examined with a Jeol JSM-5400 SEM microscope. The surfaces of the polymers were sputter coated with gold for 3 min.

Antimicrobial assay

Four bacteria and four fungi were used as test microorganisms in this study. Test fungi included, *Aspergillus fumigatus*, *Geotrichum candidum*, *Candida albicans* and *Syncephalastrum racemosum* on Sabourad dextrose agar plates. Test bacteria included, *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive bacteria) while *Pseudomonas aeruginosa* and *Escherichia coli* (as gram negative bacteria). All strains were supplemented by the Regional Center for Mycology and Biotechnology, Al-Azhar University, Cairo, Egypt. The medium used for growing bacteria were universal nutrient agar while Sabouraud and/or yeast malt extract agar was used for fungi. Antimicrobial activity was determined by agar well-diffusion method. Briefly, agar plates were seeded with test microorganisms and kept for 30 min until medium solidified. Circular pieces of about 5 mm diameters of test hydrogel samples were added. Plates were kept for 2 hs at 4 °C prior to incubating at appropriate temperature for bacteria or fungi. Plates were examined on daily bases for development of growth inhibition zones around the loaded hydrogels.

3. Results and discussion

Scheme 1 shows the radiation-induced crosslinked co-polymerization of PVA and AAc in addition to the interaction between PVA/AAc and different amine compounds for modification of their various properties.



Scheme 1. Synthesis of radiation-induced crosslinked co-polymerization of PVA/AAc and its interaction with different amine compounds.

Gel fraction

The degree of crosslinking of polymers can be studied by an estimation of the mass percentage of the gel fraction. A typical dependence of gel fraction on the PVA/AAc compositions and irradiation doses was given in Fig.1. It can be seen that the gel fraction increased with increasing irradiation dose and interaction between PVA and AAc. It is increased with AAc content in PVA/AAc hydrogel, the composition at 70/30 ratios gave a maximum gel content at different irradiation doses, whereas a further increase in AAc decreased the gel content. The high gel fraction of PVA/AAc hydrogels occurred due to higher degree of cross-linking of the polymer networks at high irradiation doses.

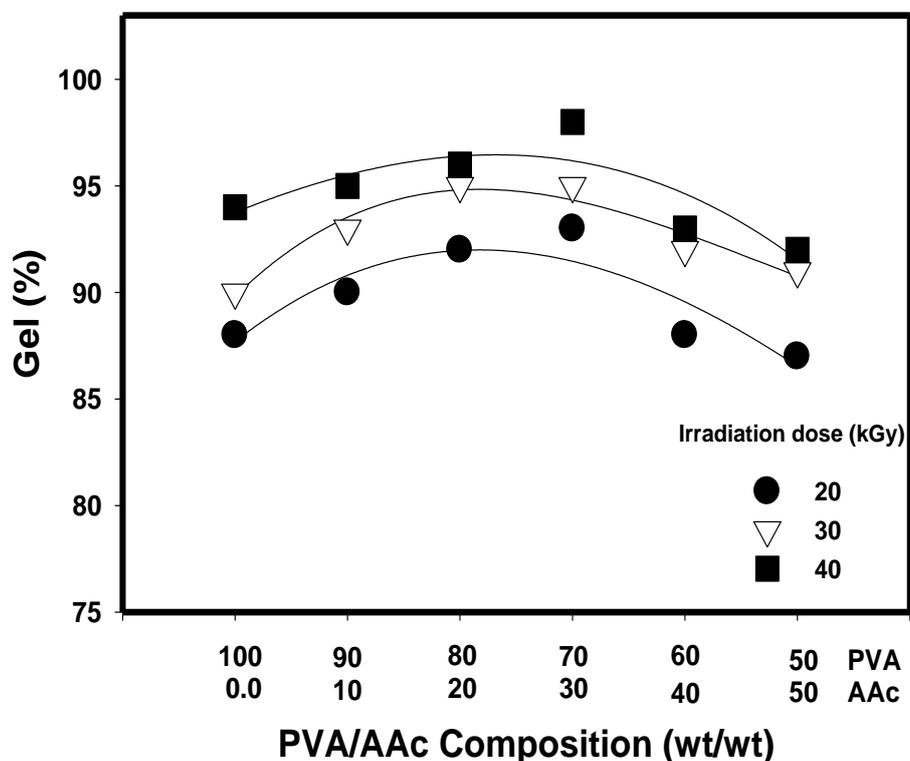


Figure 1. Effect of various PVA:AAc compositions on the gel content of PVA/AAc hydrogels at different irradiation doses.

FT-IR spectroscopy

FTIR spectroscopy and ^1H NMR spectra were carried out here to confirm the chemical structure and interactions products of PVA/AAc polymeric networks with

different amine compounds. FTIR spectra of PVA/AAc, amine compounds (**P1-P6**) and amines-modified PVA/AAc hydrogels (**M1-M6**) are recorded in Figures 2-7. FTIR spectrum of PVA/AAc copolymer showed characteristic bands of both acrylic acid repeating units and PVA unit which appeared at shifted positions as shown in Figure 2a. A very wide broad absorption band was observed within the range 3050–3600 cm^{-1} which may be explained due to O-H stretching H-bonding between the carboxylic groups of AAc and the hydroxyl groups of PVA. A very broad band corresponding to carboxyl groups of acrylic acid has stretched frequency in the region 3000–2500 cm^{-1} . It shows a broad absorption band observed at 1760 cm^{-1} due to C=O stretching of carboxylic acid association in PVA/AAc hydrogel. O-H out of plane bend observed near 860 cm^{-1} . N-H out of a plane band, observed near 800 cm^{-1} . There is a sharp band at about 1720 cm^{-1} characteristic of the carbonyl group of acrylic acid. In addition to this, other characteristic bands related to OH group of the carboxyl group are observed at 1454 and 1119 cm^{-1} indicating the incorporation of acrylic acid units in the copolymer chains. This is supported with ^1H NMR spectra, there are disappearance of both the signals which related to OH group of the carboxyl group for the unit of acrylic acid in PVA/AAc hydrogel units at δ 10.7 ppm and the signals characteristic for NH_2 groups for all amine units.

FTIR spectrum of 2-amino-3-(4-hydroxyphenyl) propanoic acid (**P1**) was shown in Figure 2b. It showed a broad band in the range 3600–3200 cm^{-1} , which derived from N–H and –OH stretching vibrations. A very broad band corresponding to carboxyl groups has stretched frequency in the region 3000–2500 cm^{-1} . The sharp band at 2910 cm^{-1} is due to the stretching vibration of backbone aliphatic C–H. The strong absorption peak at 1130 cm^{-1} has been assigned to the C–O in stretching mode and the bands observed at 1355 cm^{-1} have been attributed to combination frequencies of CH–OH. The C=C aromatic stretches appear in a pair of peaks, one at 670 cm^{-1} and the other one at 1475 cm^{-1} . The band observed at 1438 cm^{-1} can be assigned to the C–N stretching vibrations of the amines (Yin et al., 2003). FTIR spectrum of PVA/AAc/**P1** (**M1**) was shown in Figure 2c. There is a shift in absorption bands of C=O stretching of carboxylic acid to lower value which observed at 1748 cm^{-1} . The ^1H NMR spectrum (DMSO- d_6 , 300 MHz) of **M1** was confirmed by the signals at δ 3.1, 4.8 ppm. These were attributed to the methylene (– CH_2 –) adjacent to the phenyl ring and methine (–CH–)

protons in the L-Tyrosine moiety. According to chemical shift rule, other protons in amine moiety which characteristic to phenyl group, imino, hydroxyl and carboxylic groups were appeared at δ 6.7-6.9, 8.4, 9.1 and 12.8 ppm, respectively. In addition to, the presence of characteristic signals at δ 1.2, 1.6 ppm for the two methylene ($-\text{CH}_2-$) protons, 2.3, 3.7 ppm for two methine ($-\text{CH}-$) protons and 4.4 ppm which assigned the OH group in PVA/AAc hydrogel units.

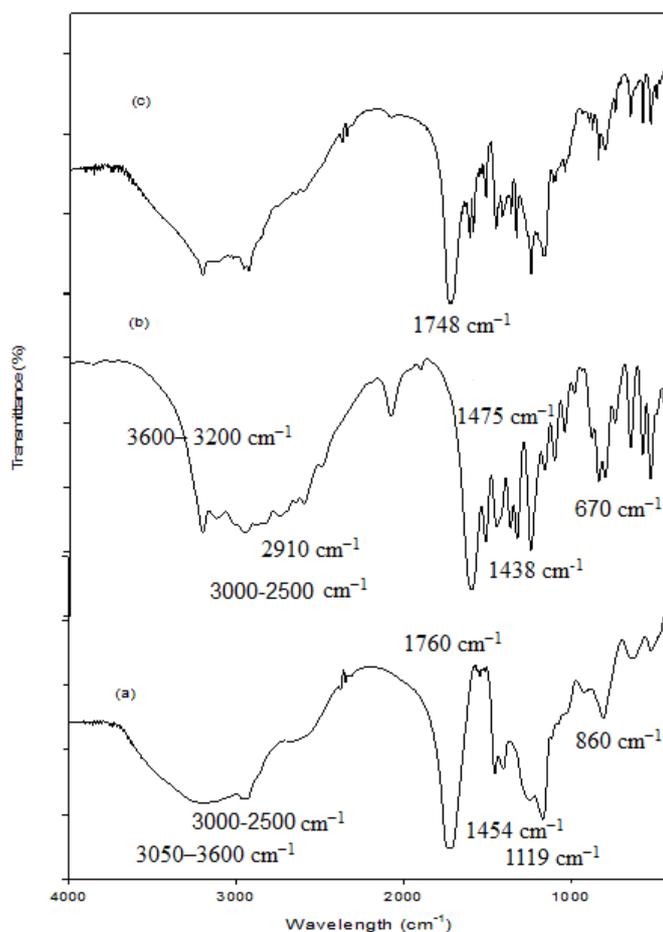


Figure 2. FT-IR spectra of (a) PVA/AAc hydrogel, (b) P1 and (c) M1.

FTIR spectrum of propane-1,2-diamine (**P2**) was shown in Figure 3b. The sharp band at 2910 cm^{-1} is due to the stretching vibration of backbone aliphatic C-H. N-H stretching broad bands appeared at 3300 cm^{-1} . C-N stretch occurred at 1250 cm^{-1} . The band observed at 1438 cm^{-1} can be assigned to the C-N stretching vibrations of the amines (Sanghi and Verma 2009).

FTIR spectrum of PVA/AAc/**P2** (**M2**) was shown in Figure 3c. There is a shift in absorption band of N-H bending to lower value in addition to reduction of the band broadening. The ^1H NMR spectrum (DMSO- d_6 , 300 MHz) of **M2** was established by the absence of the signal for carboxylic group in PVA/AAc copolymer and presence the protons of methyl, amine ($-\text{NH}_2$), methane ($-\text{CHNH}_2-$), methylene ($-\text{CH}_2\text{NH}-$), and

amido (-NH) at δ 1.1, 1.5, 3.2, 3.4 and 8.1 ppm. Also, presence the characteristic signals at δ 1.3, 1.7 ppm for the two methylene (-CH₂-) protons, and 2.2, 3.7 ppm for two methine (-CH-) protons and 4.3 ppm which assigned the OH group.

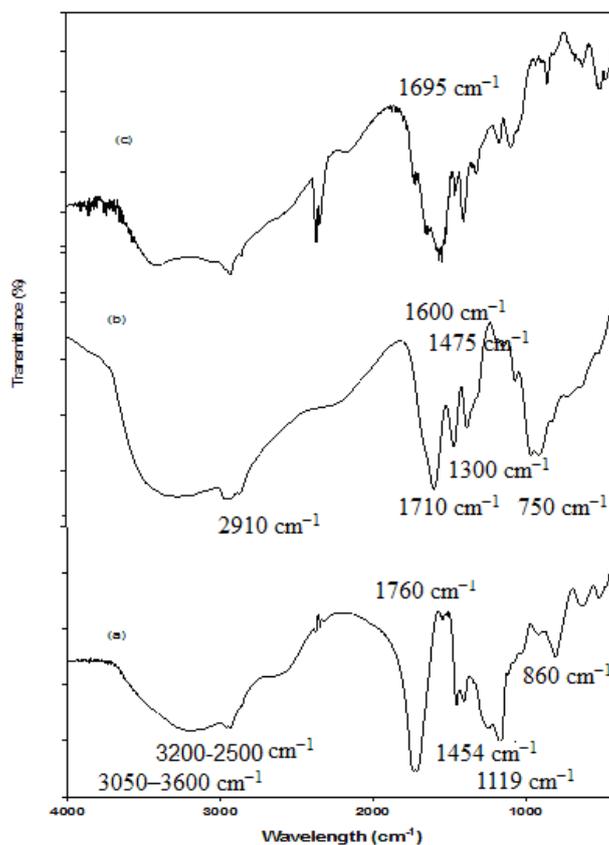


Figure 3. FT-IR spectra of (a) PVA/AAc hydrogel, (b) P2 and (c) M2.

FTIR spectrum of 4-aminoantipyrine (**P3**) was shown in Figure 4b. The sharp band at 2910 cm^{-1} is due to the stretching vibration of backbone aliphatic C-H. The C=C aromatic stretches appear in a pair of peaks, one at 1600 cm^{-1} and the other one at 1475 cm^{-1} . It shows a broad absorption band observed at 1670 cm^{-1} due to C=O stretching of amide groups. N-H stretching broad band appeared at 3340 cm^{-1} . C-N stretch occurs at 1300 cm^{-1} . FTIR spectrum of PVA/AAc/**P3** (**M3**) was shown in Figure 4c. There is a shift in absorption band of C=O stretching of carboxylic acid to lower value which observed at 1695 cm^{-1} . The new synthetic polymer **M3** was supported by ¹H NMR spectrum (DMSO-d₆, 300 MHz) in which signals of NH₂ protons in the antipyrine moiety, carboxylic group in PVA/AAc copolymer disappeared and presence the signal assign amido proton at δ 9.3 ppm. Also, 1.3, 1.6 for (2-CH₂), 2.2(-CH₃), 2.4, 3.6 (2-CH), 3.0 (-NCH₃), 4.4 (OH), 7.1-7.5 ppm (m, Ar-H).

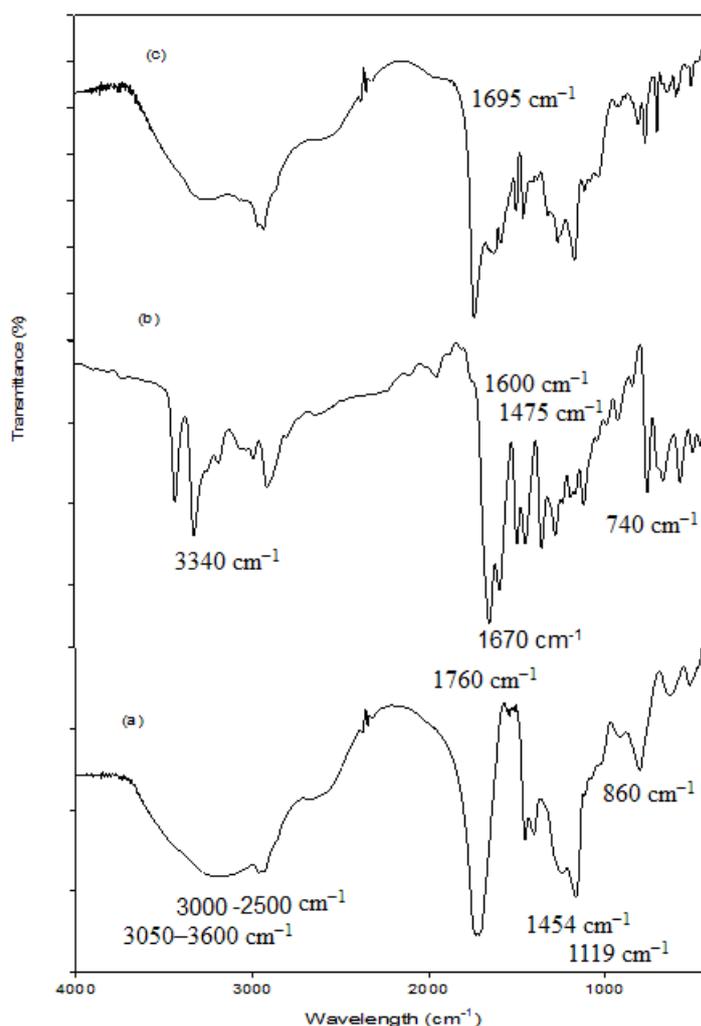


Figure 4. FT-IR spectra of (a) PVA/AAc hydrogel, (b) P3 and (c) M3.

FTIR spectrum of 2-aminothiazol (**P4**) was shown in Figure 5b. The sharp band at 2910 cm^{-1} is due to the stretching vibration of backbone aliphatic C-H. The C=C stretches appear in a pair of beaks, one at 1600 cm^{-1} and the other one at 1475 cm^{-1} . N-H stretching broad bands appeared at 3340 cm^{-1} whereas, N-H out of a plane band observed near 740 cm^{-1} . C-N stretch occurred at 1250 cm^{-1} .

FTIR spectrum of PVA/AAc/**P4** (**M4**) was shown in Figure 5c. There is a shift in absorption band of C=O stretching of carboxylic acid to lower value which observed at 1695 cm^{-1} . The ^1H NMR spectrum of **M4** in DMSO- d_6 revealed the presence signals at $\delta = 1.3$ and 1.6 ppm characteristic for two methylene ($-\text{CH}_2-$) proton groups with two signals at $\delta 2.4$, 3.7 ppm characteristic for methine ($-\text{CH}-$) protons and 4.3 ppm for OH group of PVA/AAc copolymer moiety, in addition to the signals at $\delta 7.1$, 7.4 and 12.6 ppm attributable to thiazole -H and NH protons.

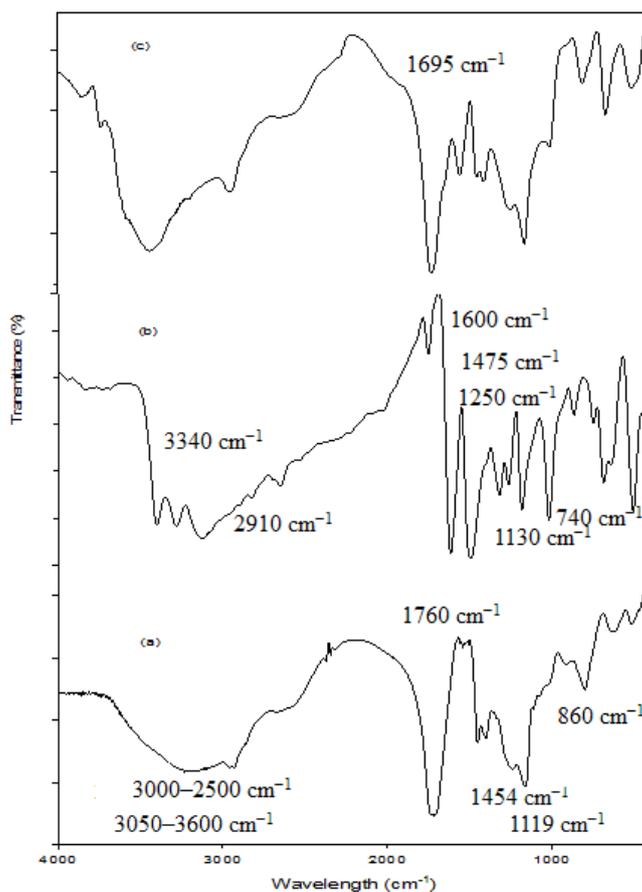


Figure 5. FT-IR spectra of (a) PVA/AAc hydrogel, (b) P4 and (c) M4.

FTIR spectrum of 4-amino-*N*-(1-phenyl-1*H*-pyrazol-5-yl)benzene sulfonamide (**P5**) was shown in Figure 6. A very broad band corresponding to carboxyl groups has stretched frequency in the region 3000–2500 cm^{-1} . The sharp band at 2910 cm^{-1} is due to the stretching vibration of backbone aliphatic C-H. The strong absorption peak at 1130 cm^{-1} has been assigned to the C-O in stretching mode and the bands observed at 1355 cm^{-1} have been attributed to combination frequencies of CH-OH. The C=C aromatic stretches appear in a pair of peaks, one at 1600 cm^{-1} and the other one at 1475 cm^{-1} . N-H stretching appeared at 3300 cm^{-1} . C-N stretch occurred at 1300 cm^{-1} whereas, S=O stretching appeared at 1400 cm^{-1} . FTIR spectrum of **M5** was shown in Figure 6c. There is a shift in absorption band of C=O stretching of carboxylic acid to lower value which observed at 1748 cm^{-1} . On the other hand, the ^1H NMR spectrum of **M5** in DMSO- d_6 revealed the signals at δ 1.4, 1.7, 2.6 and 3.6 ppm. These were attributed to the two methylene (-CH₂-) protons and two methine (-CH-) protons and 4.4 ppm for OH group in PVA/AAc copolymer moiety. The other protons in amine polymers which characteristic to pyrazol-H, benzene rings, imino and NHSO₂ groups were appeared at δ 6.7, 7.1, 7.5-7.7, 10.1 and 11.3 ppm, respectively.

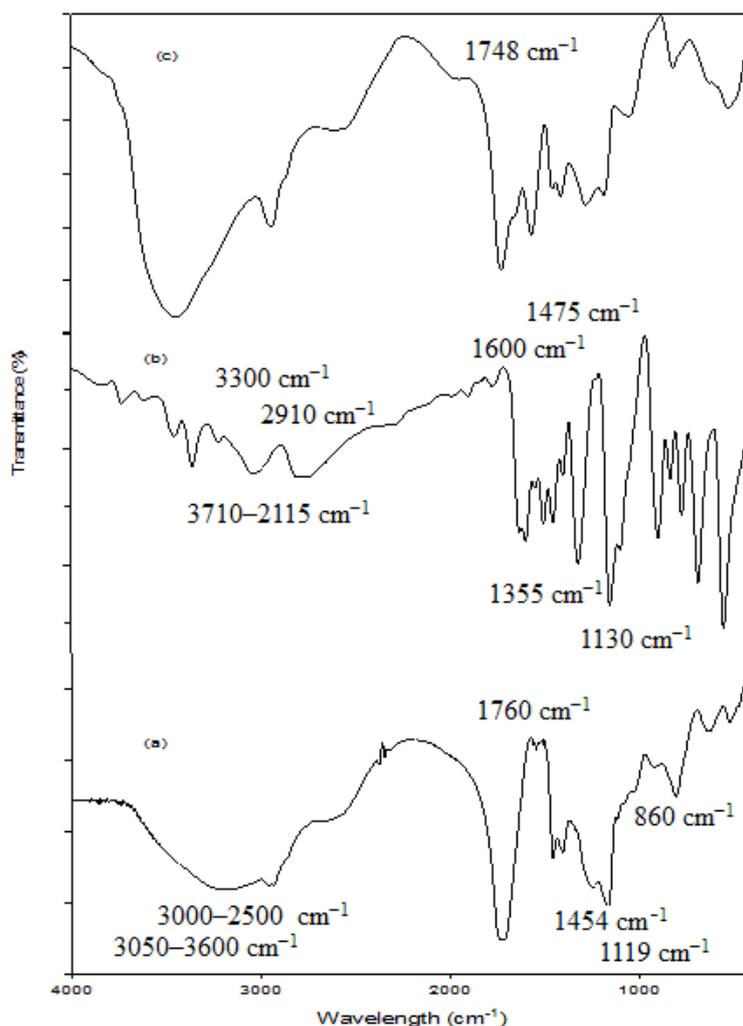


Figure 6. FT-IR spectra of (a) PVA/Ac hydrogel, (b) P5 and (c) M5.

FTIR spectrum of 4-amino-*N*-(4-methoxy-1,2,5-thiadiazol-3-yl) benzene sulfonamide (**P6**) was shown in Figure 7b. It showed a characteristic broad band at 3220 cm^{-1} that corresponds to O-H stretched vibration. A very broad band corresponding showed to carboxyl groups has stretching frequency in the region $3000\text{--}2500\text{ cm}^{-1}$. The sharp band at 2910 cm^{-1} is due to the stretching vibration of backbone aliphatic C-H. The strong absorption peak at 1130 cm^{-1} has been assigned to the C-O in stretching mode and the bands observed at 1355 cm^{-1} have been attributed to combination frequencies of CH-OH. The C=C aromatic stretches appear in a pair of peaks and the other one at 1600 cm^{-1} and one at 1475 cm^{-1} . N-H stretching appeared at 3300 cm^{-1} and C-N stretch occurred at 1300 cm^{-1} whereas, S=O stretching appeared at 1400 cm^{-1} . FTIR spectrum of PVA/Ac/**P6** (**M6**) was shown in Figure 7c. There is a shift in absorption band of C=O stretching of carboxylic acid to lower value which observed at 1748 cm^{-1} . Finally, the structure of **M6** was conformed by the ^1H NMR spectrum in $\text{DMSO-}d_6$ which revealed the presence of signals at $\delta = 1.2$ and 1.5 ppm characteristic for two methylene ($-\text{CH}_2-$) protons group with two signals at $\delta 2.7$, 3.8 ppm characteristic for methine ($-\text{CH}-$) protons and 4.0 , 4.5 ppm for methoxy and hydroxyl groups in the product amine polymer, in addition to the signals at $\delta 7.6$, 7.7 , 10.3 and 11.2 ppm attributable to aromatic protons, imino and NHSO_2 protons.

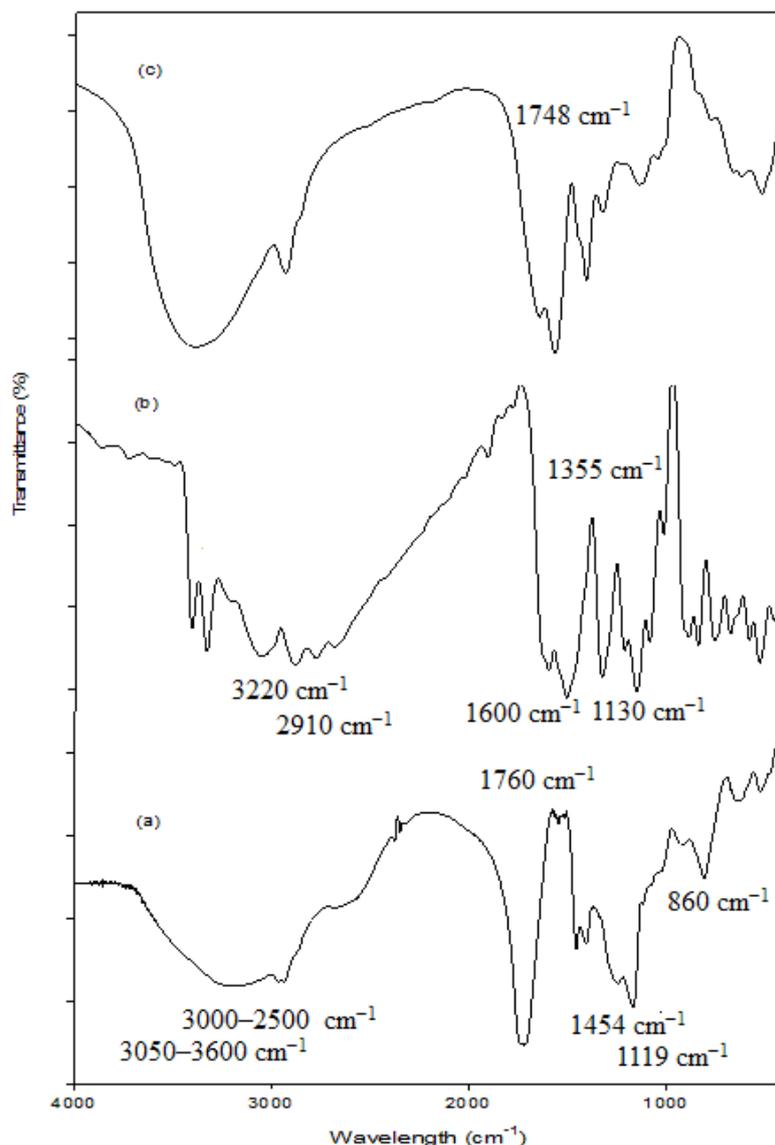


Figure 7. FT-IR spectra of (a) PVA/Ac hydrogel, (b) P6 and (c) M6.

3.3. Swelling behavior

The swelling behavior of hydrogel depends on the nature of polymer network such as the presence of hydrophilic groups, crosslinking density and elasticity of polymer networks, pH and temperature of the swelling medium (Abd El-Mohdy et al., 2006). As such, any variation of the PVA/Ac hydrogel network structure should directly influence its swelling behavior. The ionic charge content of PVA/Ac copolymer, which affects its swelling property, is related to the ratio between the PVA and Ac in the feed solution. Therefore, the swelling of PVA/Ac copolymers of different PVA: Ac compositions, was investigated at different irradiation doses and the results are shown in Figure 8. It is clear that swelling increased with increasing Ac content in the PVA/Ac copolymer and lowered irradiation doses, reaching its maximum at PVA: Ac composition; 50:50 wt%. The results were discussed as follows: the swelling increased with enhanced Ac content due to the hydrophilic

characters of AAc as well as COOH groups that enhance the water uptake (Abd El-Mohdy and Abd El-Rehim 2009).

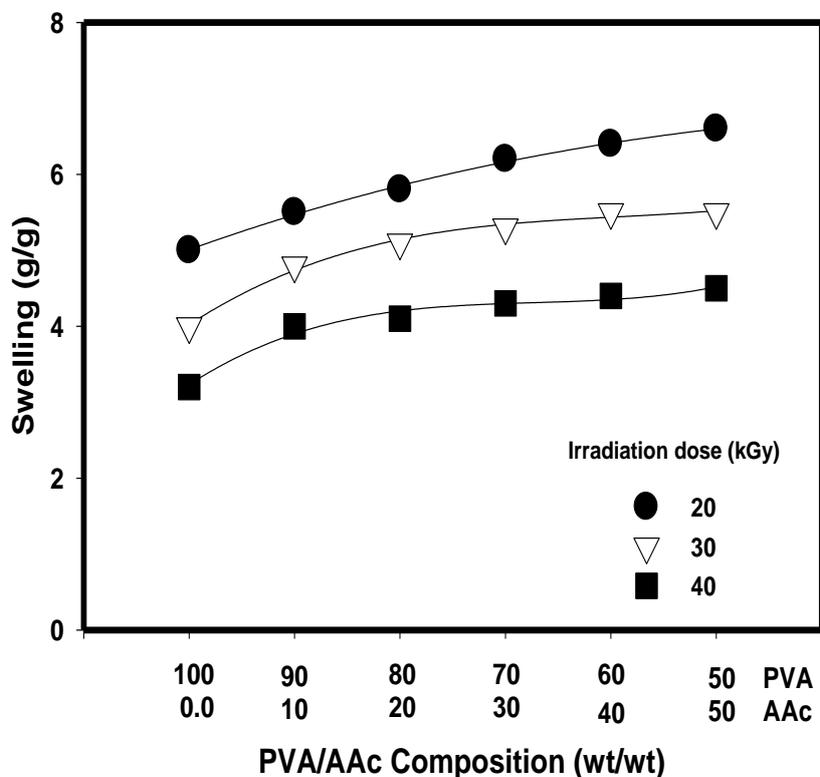


Figure 8. Effect of various PVA : AAc compositions on the equilibrium swelling of PVA/AAc hydrogels at different irradiation doses.

Figure (9) shows the swelling of the different amine-based PVA/AAc hydrogels (**M1-M6**) in compared with neat PVA/AAc. It is cleared that **M1** and **M2** have high swelling values in compared with PVA/AAc hydrogel and the other amine-polymeric compounds. This may be due to the presence of hydrophilic groups such as -COOH in **M1** and NH_2 in **M2**. The swelling of **M3-M6** reduced in compared with PVA/AAc hydrogel due to absence of hydrophilic groups. The swelling characters of prepared polymeric compounds were supported by their morphological structure as well as hydrogel surfaces which were shown in Figure 10. One of the most important properties that must be considered is hydrogel microstructure morphologies. The morphological structure of hydrogels is identified by scanning electron microscopy (SEM). SEM can provide information on the surface of a material. It was used here to detect the topography of PVA/AAc and PVA/AAc/amines hydrogel surfaces. The SEM

photographs of hydrogel surfaces, which prepared at irradiation dose; 30 kGy showed that the porous structure and pore size increased in case of amine polymers in compared with neat PVA/AAc. The images verify that PVA/AAc polymers have porous structure. It has been observed that PVA/AAc has smooth and homogeneous morphology whereas it has structural heterogeneity with interaction of amine compounds to it. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups in the PVA/AAc and amine compounds. Therefore, the porous structure is the predominant reason for the higher swelling ratios (Abd El-Mohdy 2007).

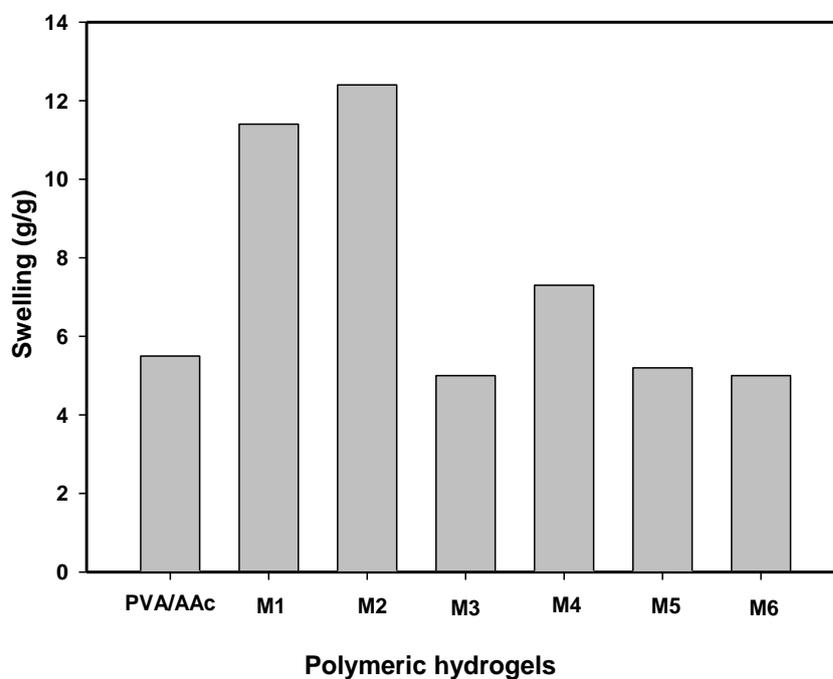


Figure 9. Equilibrium swelling of different PVA/AAc/amines (M1-M6) in compared with neat PVA/AAc.

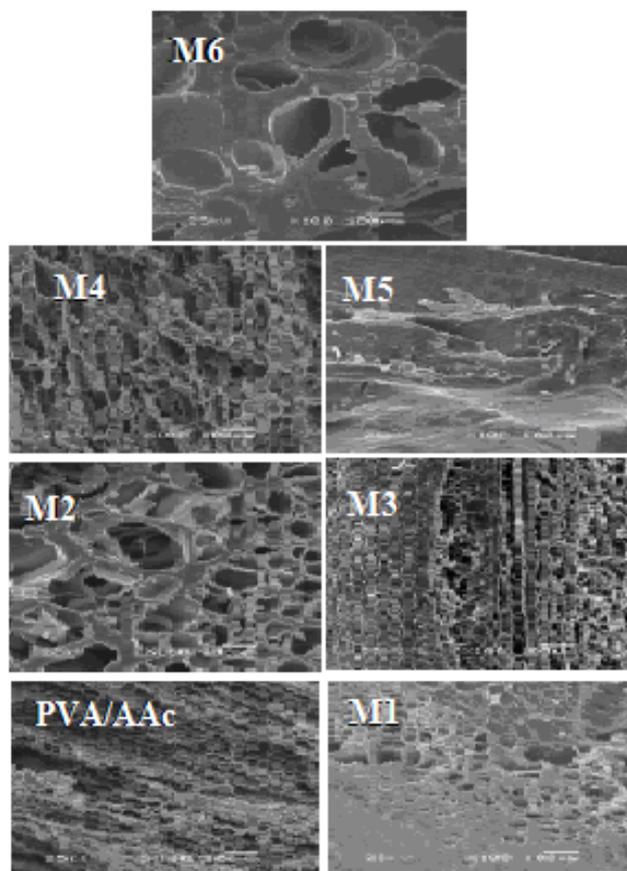


Figure 10. SEM images for PVA/AAc and PVA/AAc/amines (M1-M6).

Thermal properties

Thermogravimetric analysis (TGA).

TGA curves of different PVA/AAc/amines (**M1-M6**) hydrogels in compared with neat PVA/AAc hydrogel in nitrogen atmosphere are shown in Fig. 11. It was cleared that, the prepared polymers had three decomposition regions. The first region started from 50°C and ended at about 200°C with loss in weight about 5%; in case of PVA/AAc whereas, it was about 5-10% for PVA/AAc/amine polymers. This loss may be due to the evaporation of the moisture and untreated amine or trapped monomer present in the sample. At the second region which started after 200°C, the weight loss was increased by increasing the heating temperature. This loss in weight was attributed to the actual pyrolysis by minor decomposition reaction. The third decomposition region for PVA/AAc which gave the suddenly major decomposition reaction, started at 335°C and finished at 370°C with weight loss from 60-100 wt.% whereas the decomposition of other amine polymers delayed to 600°C. The decomposition took place due to occurring depolymerization with formation of H₂O, CO, CO₂ and CH₄.

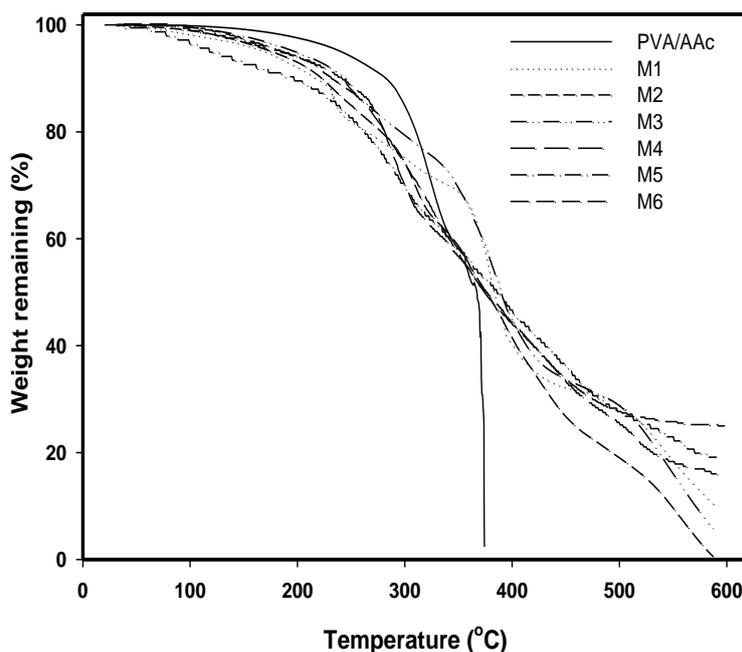


Figure 11: Thermo-gravimetric analysis of PVA/AAc hydrogels and modified hydrogels.

3.4.2. Differential scanning calorimetry (DSC)

Due to the high percentage of water content in the hydrogel samples, DSC scans failed to detect any thermal transitions of the polymer present in the swollen polymers. Therefore all samples were dried at 37°C for 48 h before testing. Fig. 12 shows the thermal parameters of both PVA/AAc and amine-modified PVA/AAc compounds. They are determined by measuring the change in thermal properties such as melting temperature (T_m) and heat of fusion (ΔH) of these polymers using DSC. The thermal diagram of prepared hydrogels showed that T_m of amine-modified polymers reduced to lower values in compared with PVA/AAc whereas ΔH values were changed to different values, Table 1. This decrease in melt temperature is possibly due to morphological changes within the polymer matrix. These may involve changes in the size of the crystallites and the degree of crystallinity. Also, this occurred due to the interaction that occurred between PVA/AAc hydrogel and amine compounds.

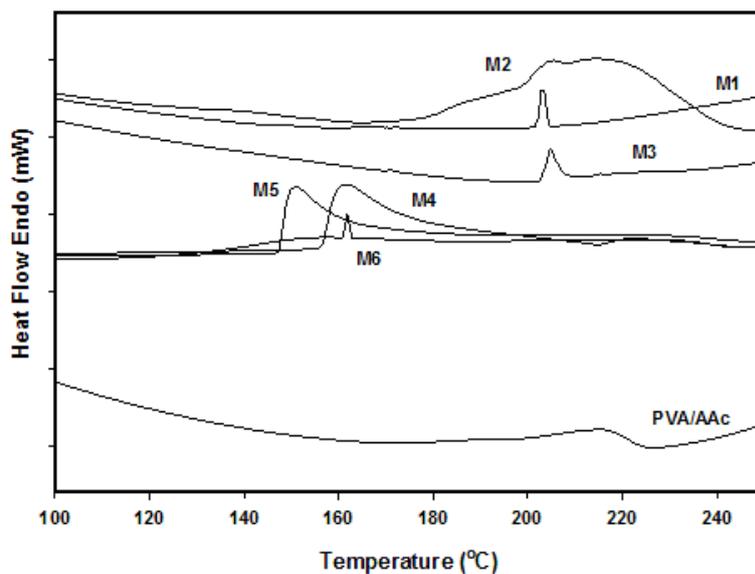


Figure 12. DSC analysis of PVA/AAc hydrogels and modified hydrogels.

Table 1. Thermal parameters for PVA/AAc and PVA/AAc/amines hydrogels.

Hydrogels	Thermal parameters	
	T _m (°C)	ΔH _m (J/g)
PVA/AAc	215.5	17.6
M1	203.1	0.065
M2	214.6	160.1
M3	204.6	8.2
M4	162	96.8
M5	151	78.2
M6	161.5	106.5

UV-vis spectroscopy

To prove the formation of the amine-modified PVA/AAc polymers in compared with PVA/AAc gel, UV-vis absorption studies were carried out. With trapping of amine compounds with PVA/AAc gel, the absorbance peaks increased in compared with neat

gel. As shown in Fig.13, both the intensity and the value of absorbance changed with differing in the structure of polymeric gels. On the other hand, plasmon absorption increments in the UV–vis spectra represent the changes in the structure of polymeric gels.

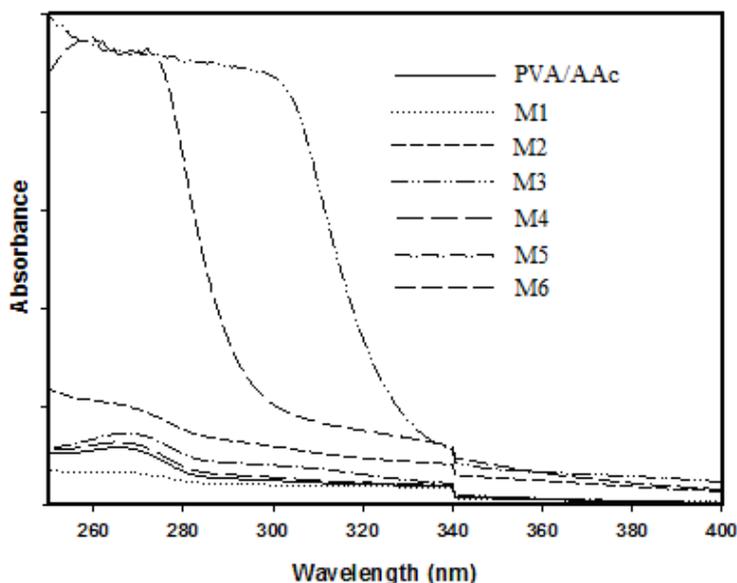


Figure 13 UV–vis spectroscopy of PVA/AAc hydrogels and modified hydrogels.

Antimicrobial activity

The biological activity of the seven investigated hydrogels (PVA/AAc and PVA/AAc-amines; **M1-M6**) was tested against a representative number of pathogenic organisms. Test fungi included, *Aspergillus fumigatus*, *Geotrichum candidum*, *Candida albicans* and *Syncephalastrum racemosum*. Test bacteria included, *Staphylococcus aureus* and *Bacillus subtilis* as gram positive bacteria, whereas *Pseudomonas aeruginosa* and *Escherichia coli* as gram negative bacteria. It is known that the structural variables that alter the properties of polymers would affect their biological activity against microorganisms (Abd El-Mohdy and Ghanem 2009). The properties of polymeric materials would be influenced by the chemical nature, molecular weight and configuration structure of the polymer. Therefore, the effect of chemical composition and molecular weight of PVA/AAc copolymers as well as the presence of pharmacological active moieties such as sulpha-drugs introduced to PVA/AAc copolymers on their activity against pathogenic microorganisms, were investigated. *Clotrimazole* and *Itraconazole* were used as references to evaluate the potency of the tested compounds under the same conditions. Zones of inhibition were determined for compounds PVA/AAc, **M1**, **M2**, **M3**, **M4**, **M5** and **M6**, the results of antifungal and antibacterial activities were summarized in both Table 2, and Table 3, respectively. The results obtained showed that, as the amine compounds entrapped in the polymeric matrix, their biological activity against the investigated pathogenic microorganisms increases.

Table 2. Antifungal activity of the tested hydrogels.

Compound No.	Inhibition zone diameter (mm)			
	<i>Aspergillus fumigatus</i> (RCMB 002003)	<i>Geotrichum candidum</i> (RCMB 052006)	<i>Candida albicans</i> (RCMB 005002)	<i>Syncephalastrum racemosum</i> (RCMB 005003)
PVA/AAc	11.2 ± 0.03	13.4 ± 0.04	10.2 ± 0.03	NA
M1	15.2 ± 0.06	18.4 ± 0.04	15.4 ± 0.1	NA
M2	NA	NA	NA	NA
M3	NA	NA	NA	NA
M4	19.3 ± 0.03	17.2 ± 0.07	16.4 ± 0.08	16.8 ± 0.05
M5	21.6 ± 0.09	18.6 ± 0.08	17.3 ± 0.02	18.9 ± 0.07
M6	14.2 ± 0.08	21.4 ± 0.05	17.8 ± 0.03	20.1 ± 0.07
<i>Itraconazole</i>	28 ± 0.05	27 ± 0.10	26 ± 0.02	22 ± 0.09
<i>Clotrimazole</i>	26 ± 0.10	23 ± 0.03	18 ± 0.10	20 ± 0.20

Mean zone of inhibition in mm ± Standard deviation beyond well diameter (6 mm) produced on a range of environmental and clinically pathogenic microorganisms using (10mg/ml) concentration of tested samples and standard using (30mg/ml).

The test was done using the diffusion agar technique, Well diameter: 6.0 mm (100 µl was tested).

NA: No activity, data are expressed in the form of mean ± SD

Table 3. Antibacterial activity of the tested hydrogels.

Compound No.	Inhibition zone diameter (mm)			
	Gram positive bacteria		Gram negative bacteria	
	<i>Staphylococcus aureus</i> (RCMB 000106)	<i>Bacillus subtilis</i> (RCMB 000107)	<i>Pseudomonas aeruginosa</i> (RCMB 000102)	<i>Escherichia coli</i> (RCMB 000103)
PVA/AAc	14.4 ± 0.50	16.4 ± 0.10	NA	NA
M1	17.2 ± 0.01	18.3 ± 0.03	11.4 ± 0.09	9.2 ± 0.02
M2	13.2 ± 0.01	14.3 ± 0.03	NA	NA
M3	15.2 ± 0.08	13.5 ± 0.2	NA	NA
M4	21.6 ± 0.09	23.9 ± 0.07	16.9 ± 0.02	18.7 ± 0.03
M5	23.4 ± 0.06	25.7 ± 0.07	18.2 ± 0.06	21.3 ± 0.08
M6	26.4 ± 0.08	27.1 ± 0.06	21.2 ± 0.06	24.9 ± 0.08
Penicillin G	29.4 ± 0.08	32.5 ± 0.05	28.3 ± 0.10	33.5 ± 0.07
Streptomycin	25.0 ± 0.20	29.0 ± 0.04	24.0 ± 0.10	25.0 ± 0.03

Mean zone of inhibition in mm ± Standard deviation beyond well diameter (6 mm) produced on a range of environmental and clinically pathogenic microorganisms using (10mg/ml) concentration of tested samples and standard using (30mg/ml).

The test was done using the diffusion agar technique, Well diameter: 6.0 mm (100 µl was tested).

NA: No activity, data are expressed in the form of mean ± SD

Conclusions

PVA/AAc hydrogels that prepared by using γ -irradiation, were modified to produce new PVA/AAc/amines. The swelling of gels was varied with changes in PVA:AAc contents as well as amine structure. Swelling of prepared polymers increased with AAC content. Amine-modified polymers, **M1** and **M2**, have high swelling values in compared with PVA/AAc hydrogel and the other amine-polymeric compounds, whereas the swelling of **M3-M6** reduced due to absence of hydrophilic groups. PVA/AAc has smooth and homogeneous morphology whereas; it has structural heterogeneity at interaction with amine compounds. DSC-TGA scans proved that the

modified PVA/AAc hydrogels are thermally less stable than unmodified one. Biological activity of synthesized amine-modified PVA/AAc exhibited higher promising biological activities and can be used in medical applications.

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تحضير هيدروجيلات مكونة من البولى فينيل الكحولى وحامض الأكريليك والمحضرة بالإشعاع ومعالجتها ببعض مركبات الأمين المختلفة وذلك لتحسين خواصها الكيميائية والبيولوجية.

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في هذه الدراسة تم استخدام الاشعاع الجامى لتكوين هيدروجيلات مكونة من البولى فينيل الكحولى وحامض الأكريليك PVP/AAC. ثم معالجه الهيدروجيلات المحضرة ببعض مركبات الأمين المختلفة وذلك لتحسين خواصها الكيميائية والبيولوجية لاستخدامها فى المجال الطبى وهذه المركبات تشمل:

L-tyrosine (P1), 1,2-Diaminopropane (P2), 2-Aminoantipyrine (P3), 4-Amino-N-(1-phenyl-1H-pyrazol-5-yl) benzenesulfonamide (P4), 4-Amino-N-(4-methoxy-1,2,5-thiadiazol-3-yl) benzenesulfonamide (P5), and Thiazol-2-amine (P6).

تم دراسة تأثير كلا من النسب التركيبية للبوليمر والجرعة الإشعاعية المستخدمة على كلا من نسبة تكوين الجيل ودرجة الانتفاشية للهيدروجيلات المحضرة. أيضا تم دراسة الخواص الحرارية مع تغير النسب التركيبية للبوليمر. تم توصيف الهيدروجيلات المحضرة باستخدام الأجهزة المختلفة مثل:

FT-IR, NMR spectroscopy & DSC and TGA

أيضا تم دراسة الفعالية الميكروبية للمركبات البوليمرية المحضرة بعد ادخال مركبات الأمين عليها وذلك بالمقارنة مع المركبات الغير معدلة للتأكد من مدى تحسن فعاليتها لاستخدامها فى المجال الطبى.