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ORIGINAL ARTICLE

Synthesis, characterization and properties of radiation-induced Starch/(EG-co-MAA) hydrogels

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Abstract Association of poly(carboxylic acids) and non-ionic polymers in solutions via hydrogen bonding results in formation of novel polymeric materials–interpolymer complexes. Starch/(EG-co-MAA) polymeric hydrogels were obtained by γ-initiated radiation copolymerization of ethylene glycol (EG) with methacrylic acid (MAA) which grafted on starch. The gel content of prepared hydrogels was varied with changes in starch content, EG:MAA composition and irradiation dose as well as crosslinking density. The swelling was studied as a function of starch content, EG:MAA composition, irradiation dose, type of soaked liquid, pH and temperature of matrix-surrounding medium. The degree of swelling greatly increased with enhanced MAA content, pH and temperature whereas, it decreased with reduced starch content and irradiation dose. The swelling was varied with the polarity of soaked liquid. The results showed that Starch/(EG-co-MAA) hydrogels reached the equilibrium swelling state in water after 72 h. The structure and surface morphology of prepared polymer were confirmed with FTIR and SEM, respectively. The thermal properties of hydrogels were studied by using DSC and TGA, they cleared that there is miscibility between EG and MAA in copolymer and adding them improve the thermal stability of starch. The results indicate that Starch/(EG-co-MAA) materials may be used in various applications.

1. Introduction

Hydrogels are three-dimensional networks of covalently bound hydrophilic polymer chains able to swell in water to an equilibrium state, they have been investigated since the 1950s (Charlesby, 1953, 1954). Since then, they have been used in number of practical applications starting from diapers, incontinence and feminine products up to biomaterials such as contact lenses, drug-delivery systems, and wound dressings (Hoffman, 2001; Abd El-Mohdy and Hegazy, 2008). Hydrogels are particularly suitable for the latter applications, due

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to their good biocompatibility and ability to mimic the properties of naturals of tissues. Different studies on biomaterials based on classical hydrogels are still being continued over the past 40 years (Abd El-Mohdy and Safrany, 2008; Hea et al., 2008; Liu et al., 2007; Angelopoulos and Tsitsilianis, 2006; Yao and Krause, 2003; Traitel et al., 2000; Kang and Bae, 2003; Alvarez-Lorenzo and Concheiro, 2002; Alarcon et al., 2005). Such gels are able to change their properties (conformational changes of polymer chain segments with change in gel volume and in the volume fraction of the liquid) with external stimuli such as temperature, pH, ionic strength, light, electric field or changes in the concentration of a given chemical species. Due to these properties, stimuli-sensitive gels are tested for applications such as detectors, actuators, chemical valves, controllable or self-regulating drug-delivery systems (Murdan, 2003; Liu et al., 2006; Vihola et al., 2008; Hovgaard and Brondsted, 1995).

Starch is a polysaccharide added to the synthetic polymers due to a renewable, biodegradable, a naturally abundant polysaccharide and low cost material. In recent years, particular attention has been attached to synthesis of starch graft copolymer due to an increasing interest in the synthesis of new cost-effective polymer (Abd El-Mohdy et al., 2006; Mostafa and El-sanabary, 2003). Whereas, ethylene glycol and methacrylic acid are biocompatible monomers with excellent biocompatibility and no-toxicity; they are often blended or compounded with other monomers or polymers to be used in the field of drug-controlled release systems (Dorski et al., 1996; Robinson and Peppas, 2002).

Hydrogen-bonded polymer complexes have been exploited to develop responsive hydrogels, for example, poly methacrylic acid (PMAA) and poly ethylene glycol (PEG) may associate to form hydrogen-bonded complexes under acidic conditions. These complexes may be used to develop responsive polymers since the properties of the complex may be notably different than those of the constituent polymers. For example, the PMAA–PEG complex is considerably less hydrophilic than the individual polymers, therefore a hydrogel containing a backbone of PMAA and grafts of PEG exhibits a relatively low degree of swelling under complex-promoting conditions (low pH when the acid is protonated), and a high degree of swelling when the complex is broken (high pH when the acid is neutralized) (Keun et al., 2004; Xiangen et al., 2008; Vitaliy, 2007; Karybiants et al., 1996; Peppas and Klier, 1991).

Ionizing radiation has long been recognized as a suitable tool for the formation of hydrogels. Easy process control, possibility of joining hydrogel formation and sterilization in one technological step, no necessity to add any initiators, crosslinkers, etc., having no waste, and relatively low running costs, are advantages of ionizing radiation (Nam et al., 2003; Henke et al., 2005; Sung-Eun et al., 2004; David et al., 2011; Zainuddin et al., 2004, 2007; Hossen et al., 2008). These advantages make irradiation a method of choice in the synthesis of hydrogels, especially for biomedical use.

In this paper, we present the synthesis, characterization and investigation of specific features of a series of radiation induced Starch/(EG-co-MAA) hydrogels to use in different applications such as controlled delivery systems for active materials such as drugs and agrochemicals.

2. Experimental

2.1. Materials

Methacrylic acid and ethylene glycol of purity 99%, Merck Germany, were used as received. Water-soluble starch was purchased from El-Nasr Co. for Chemical Industries, Egypt and used without further purification.

2.2. Hydrogel preparation

Hydrogel was obtained by gamma irradiation-induced copolymerization of 20 wt.% aqueous solutions of hydrogel mixtures with different weight ratio in small glass tubes with stirring at room temperature, and using gamma rays with a dose rate; 4.25 kGy/h. Eight grams of maize starch powder was first mixed with 70 ml of distilled water to form gel-like solution, and the system was stirred and heated at 80 °C (at the same time for 1 h to form paste-like slurry). The gelatinized starch was cooled at room temperature. Different EG:MAA ratios were mixed with the gelatinized starch and the total volume is 100 ml. The mixture was stirred at room temperature for 30 min. The gelatinized starch–comonomer mixture was transferred into a 10 ml glass and then irradiated with gamma rays. After copolymerization, the tubes were broken, the formed polymeric cylinders were removed and cut into disks of 2 mm thickness. The obtained hydrogel was washed with distilled water for removal of unreacted monomers and then dried in vacuum oven at 40 °C.

2.3. Gel content

Dried hydrogels were extracted with distilled water for 24 h at 100 °C to extract the insoluble parts in the hydrogel. The insoluble parts, that is, the gelled parts, were taken out and washed with hot distilled water for the removal of soluble parts and then were dried and weighed. This extraction cycle was repeated until the weight became constant. The gel yield in the hydrogel was determined as follows:

$$\text{Gel}(\%) = (W_e/W_d) \times 100 \quad (1)$$

where W_d and W_e represent the weights of the dry hydrogel and the gelled part after extraction, respectively.

2.4. Swelling measurement

Dried hydrogel disks (0.3–0.4 mm thickness and 4-mm diameter) were left to swell in water, organic solvents or phosphate buffer solutions of desired pH (3, 5, 7, 9 and 11). Swollen gels were removed from the swelling medium at regular time intervals and dried superficially with filter paper, weighed and placed in the same bath.

$$\text{Swelling}(g/g) = (W_s - W_d/W_d) \quad (2)$$

where W_s and W_d represents the weights of swollen and dry samples respectively.

2.5. Water retention

The weight loss of the wet gel of known weights against time interval was calculated with different gel compositions and various temperatures. The following equation was used to determine the percentage of water retention.

$$\text{Water retention}(\%) = W_t/W_i \times 100 \qquad (3)$$

where W_t and W_i are the weights of gel at certain time and initial weight, respectively.

2.6. FT-IR Spectroscopy

Analysis by FTIR spectroscopy, using Mattson 1000, Unicam, Cambridg, England, was carried out in the 400–4000 cm^{-1} range.

2.7. pH Measurements

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

2.8. Thermogravimetric analysis (TGA)

Shimadzu TGA-50 TGA system was used to study the thermal stability of the prepared copolymers under a nitrogen atmosphere. The temperature range was from ambient temperature to 600 °C at heating rate of 10 °C/min.

2.9. Differential scanning calorimetry (DSC)

The thermal parameters of the hydrogel, melting temperature (Tm) and heat of melting (ΔH_m), were determined by DSC on a PerkinElmer apparatus equipped with a DSC-7 data station. About 5 mg specimen of the hydrogel was used for DSC measurement. The measurement was carried out in an N_2 atmosphere at heating rate of 10 °C/min.

2.10. Scanning electron microscopy (SEM)

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

3. Results and discussion

Using radiation for initiation of the polymerization has some advantages in comparison with chemical initiation: obtained polymers are highly pure, easily regulated dose rate, safe control of reaction, possibility to interrupt irradiation process, low temperature of reaction proceeding etc. In the present work the hydrogels containing complementary chains in their structure which are able to form interpolymer complexes were obtained by γ-initiated radiation graft copolymerization of EG and MAA on starch. Influence of irradiation dose, initial monomer content, etc. onto the yield and various physical and chemical characteristics of the Starch/(EG-co-MAA) gels was studied. The mechanism of crosslinking of polymer components in aqueous solution by gamma radiation can be briefly outlined as follows:

1. MAA, EG monomers, Starch and the solvent (HO—H) absorb the gamma radiation and go to the transient activated states which dissociate causing the formation of MAA, EG, Starch radicals, HO. and H.
2. The transfer of radicals from water to polymer increases the concentration of polymer radicals of MAA, EG, Starch:

$$\text{MAA, EG, Starch} + \text{HO}^{\cdot} \text{ or } \text{H}^{\cdot}$$
$$\rightarrow \text{PMAA}^{\cdot}, \text{PEG}^{\cdot}, \text{Starch}^{\cdot} + \text{HO} - \text{H or H–H}$$

3. PMAA, PEG, Starch polymer radicals repeat units combine to form a crosslinked point and increase the rate of crosslinking and gelation:

$$\text{PMAA}^{\cdot} + \text{PEG}^{\cdot} + \text{Starch}^{\cdot}$$
$$\rightarrow \text{PMAA-PEG-Starch (Crosslinked networks)}$$

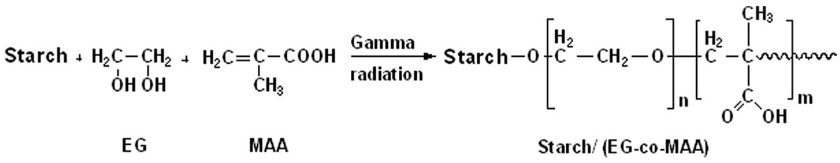
The previous mechanism of preparation of Starch/(EG-co-MAA) hydrogels by using radiation can be concluded in Scheme 1.

3.1. FT-IR spectroscopy

The IR spectra of both pure and grafted starch are shown in Fig. 1. It shows a broad absorption band at 3200–3650 cm^{-1} due to OH stretching and glucosidic ring in starch (Fig. 1A) which diminished to 3426.3 cm^{-1} in Starch/(EG-co-MAA) hydrogel (Fig. 1D). In addition, absorption band at 1690 cm^{-1} due to C=O stretching of carboxylic acid association in pure MAA (Fig. 1C) has been observed apart from usual peaks in starch and shifted to 1718.1 cm^{-1} in Starch/(EG-co-MAA) due to interaction among starch and monomer components, Fig. 1D. In Fig. 1B for PEG, strong and broad absorption band at 3450 cm^{-1} refers to the O—H stretching. The bands at approximately 1344 and 1471 cm^{-1} are ascribed to the —CH_2 wagging vibration. The peak at ~1109 cm^{-1} is due to C—O—C stretching vibration and the band at 1965 cm^{-1} due to the characteristic vibration of the PEG crystallization state. The bands were shown at 2931 and 2927 cm^{-1} for C—H stretching and at 960 cm^{-1} is assigned to C—O vibration.

3.2. Gel content

The formation of hydrogels using high-energy radiation can be simply explained as a result of the reciprocal recombination of macroradicals. These, in turn, are generated as a



Scheme 1 Suggested equation for preparation of Starch/(EG-co-MAA) hydrogel.

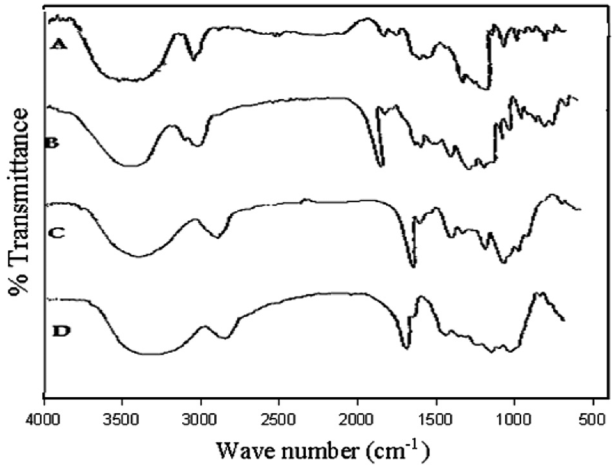


Figure 1 FTIR of (A) Starch, (B) Ethylene glycol, (C) Methacrylic acid and (D) Starch/(EG-co-MAA) hydrogel.

consequence of the direct interaction of radiation with polymer or with radicals generated during water radiolysis. If radicals located on different polymer chains are favorably positioned, their recombination results in covalent bonds between polymer chains. If bond-formation processes are faster than concurrent degradation reactions, then an insoluble gel fraction is formed. Gel content measurement is an effective method for evaluating the degree of crosslinking of the polymeric hydrogel. Gel content and crosslinking network density of prepared polymer have a great influence on its swelling character. There are many factors affecting the polymer gel content among them, polymer compositions and irradiation doses (Slawomir et al., 2010; Abd El-Mohdy and Abd El-Rehim, 2009). The gel content of Starch/(EG-co-MAA) hydrogels of different starch concentrations and EG:MAA contents that prepared at various irradiation doses is shown in Figs. 2 and 3, respectively. It is clear that the gel content of hydrogel increases with increasing the MAA content and irradiation dose as well as crosslinking density and reduced with increasing starch content in the graft copolymer. The decrease observed in the gel fraction caused by increasing the ratio of EG may be due to its lower sensitivity toward gamma irradiation compared to MAA monomer. The maximum gel content occurred for hydrogels has EG:MAA of 20:80 wt.% and prepared at irradiation dose; 30 kGy. These regularities can be induced by formation of hydrogen bonds in copolymer which play an important role as additional cross-links in the structure of the formed gel and therefore enhance the polymerization process (Mun et al., 2007).

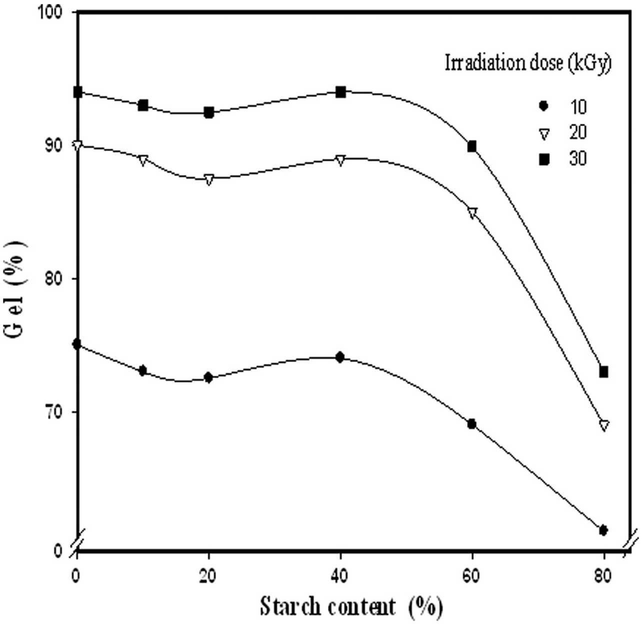


Figure 2 Effect of starch content on the gel (%) of Starch/(EG-co-MAA) hydrogels at different irradiation doses and EG:MAA composition; 50:50 wt.%.

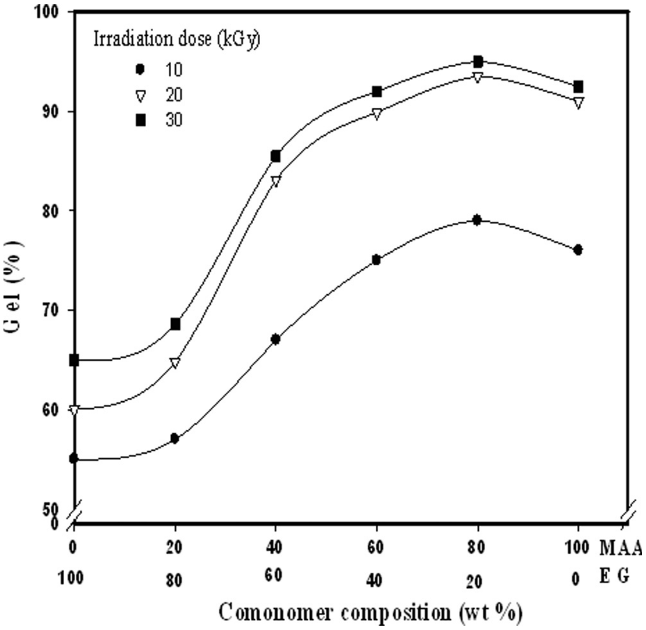


Figure 3 Effect of EG:MAA composition on the gel (%) of Starch/(EG-co-MAA) hydrogels at different irradiation doses and starch concentration; 40 wt.%.

3.3. Swelling of Starch/(EG-co-MAA) hydrogels

Swelling characteristics and diffusion behavior of hydrogels are key features for their usefulness in various applications. Swelling influences solute diffusion coefficient, surface wettability, mobility and mechanical properties. Environmental parameters, such as pH, temperature, solvent concentration, ionic strength, electrostatic forces, thermodynamic activity and nature of the polymer define the equilibrium swelling and deswelling, in addition to substantially affecting polymer–solvent interactions. These properties, either singly or in combination, have led to widespread interest in the different uses of hydrogels. The swelling of Starch/(EG-co-MAA) hydrogels of different starch contents and various irradiation doses was investigated and was shown in Fig. 4. It reveals that the swelling ratio continuously decreases with increasing the

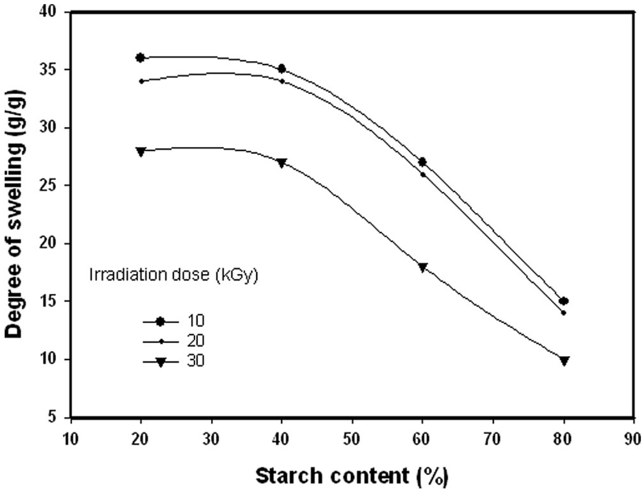


Figure 4 Effect of starch content on the degree of swelling of Starch/(EG-co-MAA) hydrogels at different irradiation doses and EG:MAA composition; 20:80 wt.%.

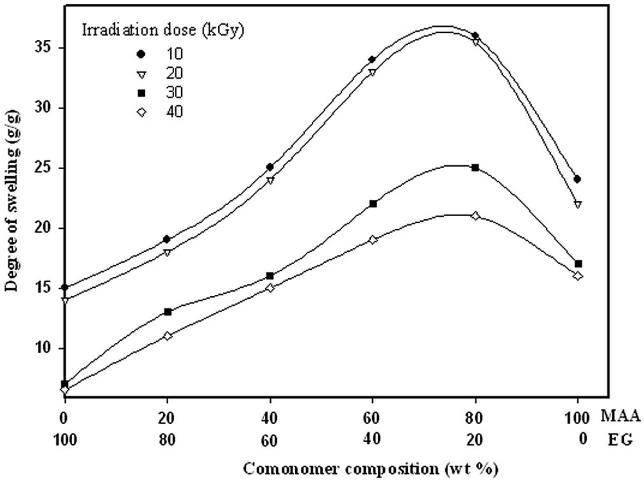


Figure 5 Effect of EG:MAA composition on the degree of swelling of Starch/(EG-co-MAA) hydrogels at different irradiation doses and starch concentration; 40 wt.%.

irradiation dose as well as starch content in the graft copolymer, but it increased with enhanced MAA content in the polymer matrix, Fig. 5. The results can be explained by the fact that the increasing of MAA content in the feed solution resulted in high –COOH content in the hydrogel network that expand the polymeric chains as a result of repulsive forces among it which increases the swelling and water diffusion into the polymeric matrix. Peppas and co-workers prepared the complexing networks based on graft-copolymers of PEG and PMAA (Peppas and Klier, 1991; Madsen and Peppas, 1999). These networks were synthesized by copolymerizing poly(ethylene glycol) methacrylate macromonomers with methacrylic acid in the presence of tetraethylene glycol dimethacrylate as cross-linking agent. Interactions between PEG and PMAA within these networks strongly influenced their equilibrium swelling. The degree to which complexation occurred varied with the copolymer composition and the molecular weight of the PEG chains grafted to the polymer backbone.

Table 1 Swelling of Starch/(EG-co-MAA) hydrogels in different solvents at EG:MAA composition; 20:80 wt.%, starch concentration; 40 wt.% and irradiation dose; 20 kGy.

Solvent	Swelling (g/g)
Methanol	43
Water	36
Ethanol	18
Benzene	0.007
Toluene	0.0004

The variation in swelling behavior of Starch/(EG-co-MAA) hydrogel in water against different organic solvents such as Methanol, Ethanol, Benzene and Toluene is shown in Table 1. The highest swelling was observed in the hydrogen bond accepting Methanol, Water, and Ethanol 43, 36, and 18 g/g, respectively (Savest et al., 2007). It was observed that the degree of swelling can be arranged in the following order: Methanol > Water > Ethanol > Benzene > Toluene. It can be seen that Starch/(EG-co-MAA) hydrogels have no tendency to swell in non-polar solvents such as benzene, toluene and they have a great tendency toward polar solvent such as methanol, water and ethanol.

3.4. Swelling rate of Starch/(EG-co-MAA) hydrogels

The comparative study among the swelling rates of Starch/(EG-co-MAA) hydrogels, having various EG:MAA compositions, in distilled water was investigated and was shown in Fig. 6. It can be seen that the swelling rate is significantly influenced by the MAA content into the hydrogels. The swelling rate for prepared hydrogels enhanced at high MAA and reduced with adding EG. The results showed that Starch/(EG-co-MAA) hydrogels with different compositions reached the equilibrium swelling state in water after 72 h. These results can be supported by studying the morphology of the hydrogel surface at different MAA contents by elucidating the pore structure of the copolymer, the surface morphology of the

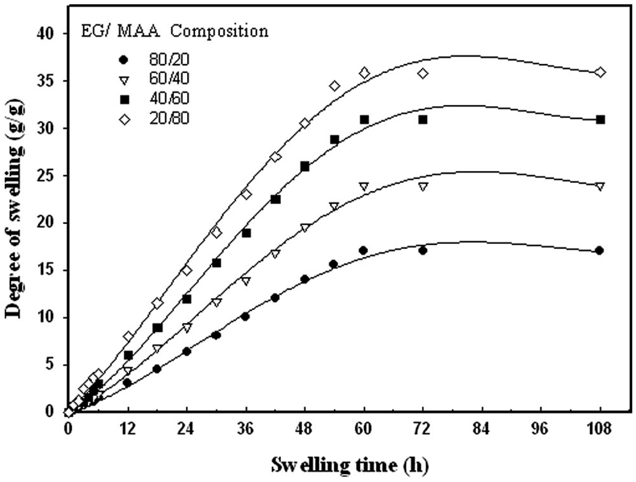


Figure 6 Swelling rate of Starch/(EG-co-MAA) hydrogels at different EG:MAA compositions. Irradiation dose; 20 kGy and starch concentration; 40 wt.%.

Starch/(EG-co-MAA) hydrogels was examined by SEM, which was used to observe the micromorphology on fresh cross sections of hydrogel samples dehydrated by freeze-dryer technique. The micromorphology of the prepared hydrogel as well as its pore diameter mainly depends on those factors affecting the swelling properties of hydrogels such as the sample dehydration methods, the type of copolymer, and its crosslinking density (Nishi and Kotaka, 1985). In other words, polymer compositions and irradiation doses seriously affect the copolymer crosslinking degree and micromorphology of the polymer. The pore size and morphological structure of polymeric surface may be studied by scanning electron microscopy. The morphological structure of both Starch/EG and Starch/(EG-co-MAA) hydrogels with different EG:MAA compositions were investigated and were shown in Fig. 7. The EG:MAA composition at 20:80 wt.% shows a larger pore structure than other compositions due to the high hydrophilicity of —COOH group in MAA which lead to accelerate the swelling rate.

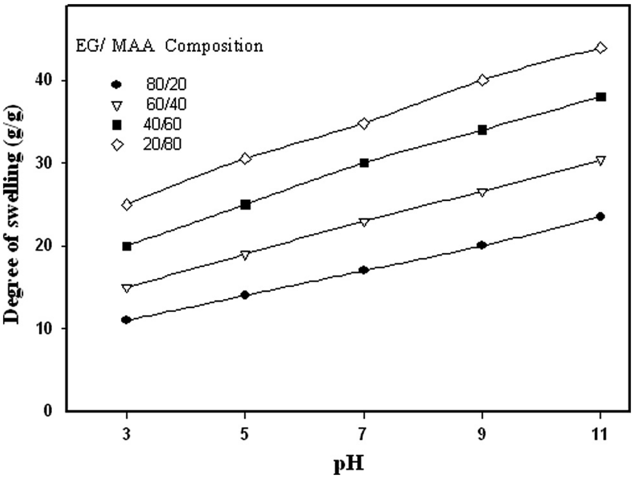


Figure 8 Effect of pH on the degree of swelling of Starch/(EG-co-MAA) hydrogels at different EG:MAA compositions. Irradiation dose; 20 kGy and starch concentration; 40 wt.%.

3.5. Swelling variation with pH

Since the Starch/(EG-co-MAA) hydrogels comprise of carboxylic groups, so they may act as pH-sensitive hydrogel which may exhibit sharp swelling changes at a wide range of pH values. Therefore, the equilibrium swelling of hydrogel was measured at various buffer solutions with pH ranging from 3 to 11 (Fig. 8). At low pH values, hydrogen bonds were formed between ether and carboxyl groups to promote polymer collapse which can restrict the water absorption by the carboxylic groups which lead to reduce the degree of swelling. Meanwhile, there are no significant variations in the swelling values for different compositions at moderate pH (pH 4 and 5) which may be due to the balance between the number of carboxylic groups and its degree of dissociation. At high pH values, carboxylic groups ionize and the polymer swells and behaves as a polyelectrolyte, so the swelling increases as the MAA content in the copolymer hydrogel increases. The results could be explained as follows in the light of the ionization of ionic groups present in the network structure that the swelling in ionic

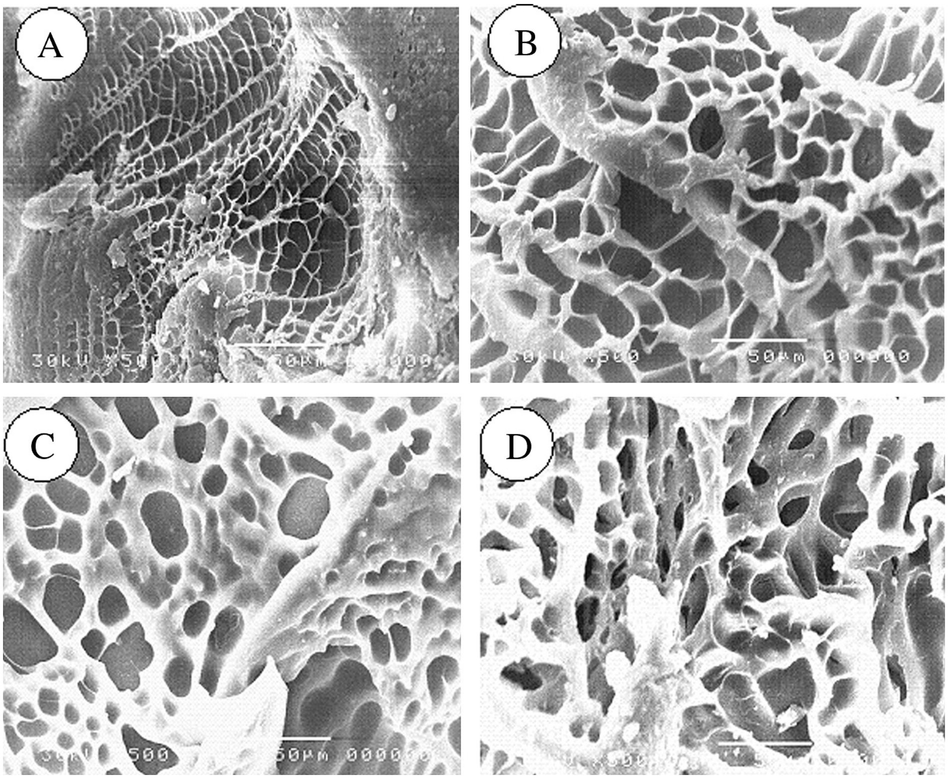


Figure 7 Scanning electron microscopy of (A) Starch/EG, (B) Starch/(EG-co-MAA) (EG:MAA; 80:20 wt.%), (C) Starch/(EG-co-MAA) (EG:MAA; 60:40 wt.%) and (D) Starch/(EG-co-MAA) (EG:MAA; 20:80 wt.%).

hydrogels is significantly affected by ionization of the functional groups of the polymer. Increase in ionization of functional groups at pH greater than MAA pKa (4.66) causes electrostatic repulsion among the ionized —COO$^-$ groups, leading to chain expansion, which in turn affects chain relaxation. At higher pH values, the rich MAA copolymer gel possesses high swelling degree that the carboxylic groups became progressively more ionized. That is because, at pH higher than pKa of MAA, the carboxylic groups became completely dissociated. In these cases, the swelling value reaches its maximum value because of the intermolecular repulsion between the ionized acid groups. A similar phenomenon has been observed for interpenetrating networks prepared by polymerizing acrylic acid inside the crosslinked PEG networks (Nishi and Kotaka, 1985). Again, a charge screening effect of the counter ions (cations) limit the swelling at higher basic pH values ($pH > 8$) (Abd El-Mohdy and Ghanem, 2009).

3.6. Effect of temperature on the hydrogel swelling

The influence of temperature on the swelling of Starch/(EG-co-MAA) hydrogels which prepared with various EG:MAA compositions was studied in the range of 30–70 °C, the results are shown in Fig. 9. It indicates that the swelling ratio increases with increasing the temperature of the surrounding solution as well as MAA content. The observed increase in the swelling ratio can be interpreted as the fact that on raising temperature, both segmental mobility and diffusion of water molecules increase, which leads to an enhancement in the degree of swelling.

3.7. Water retention

The water retention of Starch/(EG-co-MAA) hydrogels with different EG:MAA compositions was investigated with time at 25 °C, it is clear that the water loss increased at low MAA and high EG contents, Fig. 10. In other words, the water retention is higher for hydrogels have high MAA content. External parameters such as temperature may affect the water retention of the polymer; the relation between the ability of the prepared hydrogels to keep water against time at different temperature degrees is represented in Fig. 11. As the temperature increases, the deswelling rate of gel imbibed water increases, and results in decreasing polymer water retention (Abd El-Rehim et al., 2006).

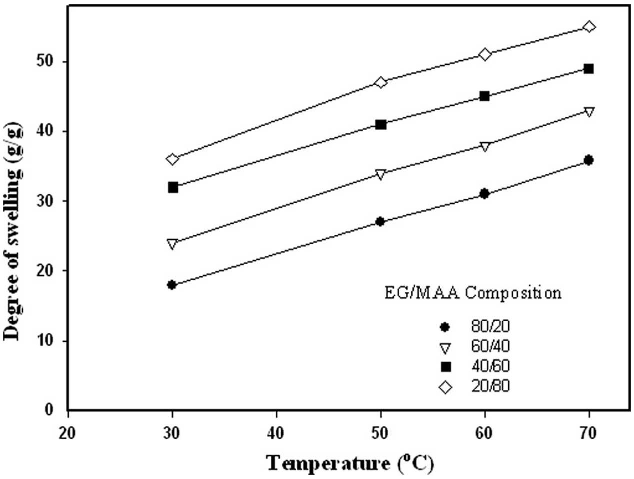


Figure 9 Effect of temperature on the degree of swelling of Starch/(EG-co-MAA) hydrogels at different EG:MAA compositions. Irradiation dose; 20 kGy and starch concentration; 40 wt.%.

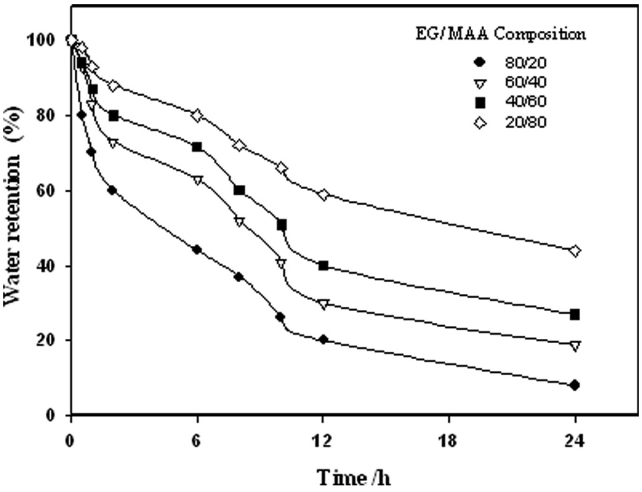


Figure 10 Water retention of Starch/(EG-co-MAA) hydrogels at different EG:MAA compositions. Irradiation dose; 20 kGy and starch concentration; 40 wt.%.

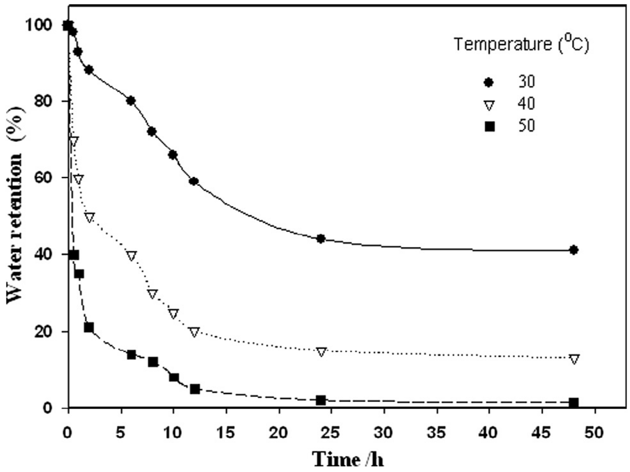


Figure 11 Effect of temperature on the water retention of Starch/(EG-co-MAA) hydrogels at EG:MAA composition; 20:80 wt.%, irradiation dose; 20 kGy and starch concentration; 40 wt.%.

3.8. Thermal properties and stability

One of the unique characteristics of starch-based polymers is their thermal processing properties, which are much more complex than conventional polymers, due to the multiple chemical and physical reactions that may occur during processing. Native starches are non-plastic due to the intra- and intermolecular hydrogen bonds among the hydroxyl groups in starch molecules, which represent their crystallinity.

Thermal processing is used to disrupt and transform the semi-crystalline structure of starch granules to form a homogeneous and amorphous material. The thermal processing of starch-based polymers involves multiple chemical and physical reactions, e.g. water diffusion, granule expansion, gelatinization, decomposition, melting and crystallization. The thermal processes can be detected by differential scanning calorimetry (DSC) (Yu and Christie, 2001). The compatibility among the various components of Starch/(EG-co-MAA) hydrogel can be determined by measuring the change in the thermal properties such as melting temperature (*Tm*) and heat of fusion (ΔH) of hydrogel. Fig. 12 shows the thermal diagram of pure starch and Starch/(EG-co-MAA) hydrogels with different EG:MAA compositions, it showed that the *Tm* of starch increased by grafting with EG and MAA, while its ΔH value decreased. The thermal parameters are shown in Table 2, the obtained results reflect the miscibility and hydrogen bonding interactions between the polymeric components.

The occurrence of intermolecular associations between EG and MAA can be estimated by using TGA to show to what extent the addition of EG and MAA affects the thermal stability of starch. Fig. 13 shows the thermo-gravimetric diagram of starch and Starch/(EG-co-MAA) hydrogels with different EG:MAA compositions at temperature interval from 30 to 600 °C. The TGA curves of starch essentially involved two distinct zones of weight loss. The initial weight loss is at 30–280 °C. This is due to the traces of moisture present. The second zone (280–330 °C) was due to degradation of the starch backbone (Sumit et al., 2011). Also, the hydrogels cleared two distinct zones of weight loss, initial weight loss is at 30–350 °C whereas, the second zone is at (350–450 °C). The rate of thermal decomposition of Starch/(EG-co-MAA) hydrogels with respect to temperature was slower than pure starch. It is clear that the decomposition temperature required for the pure starch is lower than that required for different hydrogel compositions. The two decomposition stages for hydrogels can be due to the presence of MAA chains in its structure. The first weight loss of hydrogels is mainly due to anhydride formation reaction and the second-decomposition of polymer is followed by decarboxylation reaction (Ramakrishna et al., 1988; Janevieve et al., 2005). It is concluded that the thermal stability of starch was improved with adding both MAA and EG.

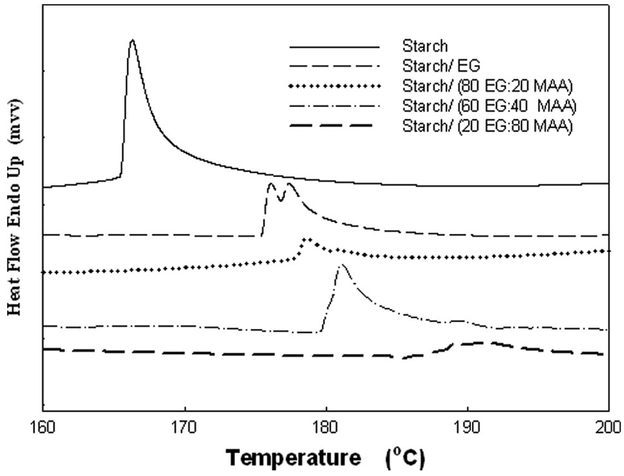


Figure 12 Differential scanning calorimeter (DSC) diagram of starch and different EG:MAA compositions of Starch/(EG-co-MAA) hydrogels at starch conc.; 40 wt.% and irradiation dose; 20 kGy.

Table 2 Thermal parameters for starch and different Starch/(EG-co-MAA) compositions at starch conc.; 40 wt.%.

Thermal parameters	Thermal parameters	
	Tm (°C)	ΔH_m (J/g)
Starch	166	62
Starch/EG	177	25
Starch/(80 EG-co-20 MAA)	178	19
Starch/(40 EG-co-60 MAA)	181	15
Starch/(20 EG-co-80 MAA)	190	12

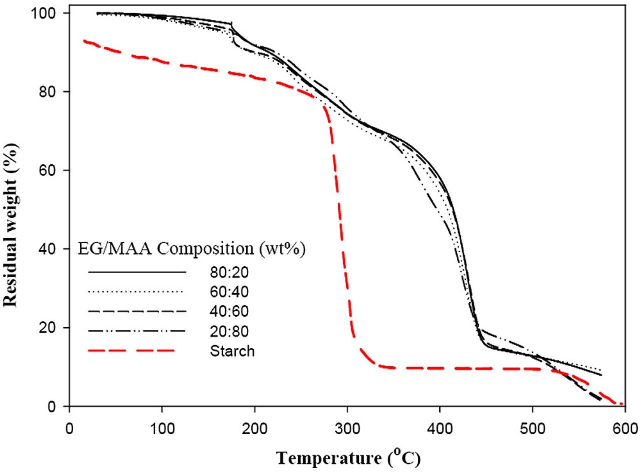


Figure 13 TGA diagram of starch and different EG:MAA compositions of Starch/(EG-co-MAA) hydrogels at starch conc.; 40 wt.% and irradiation dose; 20 kGy.

4. Conclusions

The synthesis of hydrogels by ionizing radiation offers technical advantages, in which the crosslinking occurs in the absence of initiators. In this work, gamma radiation was utilized successfully to form graft copolymer hydrogels based on different ratios of starch, EG and MAA. The gel content of prepared hydrogels was varied with changes in starch content, EG:MAA composition and irradiation dose as well as crosslinking density. The swelling behavior clearly depends on the capability of the samples to form hydrogen bonds arrangements, it greatly increased with MAA content, pH and temperature whereas, it decreased with starch content and irradiation dose. The Starch/(EG-co-MAA) hydrogels with different compositions reached equilibrium swelling state in water after 72 h, the use of MAA as a component in these hydrogels leads to decreasing the time of equilibrium, which may represent an advantage in some applications. It was found that the swelling of hydrogels was affected by the pH values near the pKa of MAA. There is a variation in swelling behavior of hydrogels in water in comparison with different organic solvents, the degree of swelling was arranged in the following order: Methanol > Water > Ethanol > Benzene > Toluene. The water retention of hydrogel reduced with raising temperature and low MAA content. The thermal stability of starch was modified with adding both EG and MAA, the obtained results reflect the miscibility and hydrogen bonding interactions between the polymer components. It is concluded that Starch/(EG-co-MAA) hydrogels can potentially be used in various applications.

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