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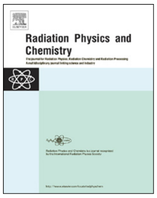

Enhancement swelling properties of PVGA hydrogel by alternative radiation crosslinking route

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ABSTRACT

The development of environmentally friendly materials based on non-toxic absorbent polymers, which can ensure high water absorption for several applications in biomedical or agricultural areas, is one of the most complexes problems. In the literature, the non-toxic biodegradable polymer poly(vinyl alcohol) (PVA) was chemically modified with glyoxylic acid to obtain poly(vinylglyoxylic acid) (PVGA) as a biodegradable super-absorbent hydrogel polymer (SHAP), but in fact, the chemical crosslinking reaction decreases the water absorption capacity. In order to crosslink PVGA without losing its absorbent capacity; an alternative radiation-crosslink route has been studied. Radiation-induced crosslinking in the main C-C chain of PVGA where not all free hydrophilic groups (COOH) are involved in a crosslinking reaction as occurs in a traditional chemical reaction. The aim of this work was not only the chemical modification of 99% hydrolyzed PVA to obtain the linear and non-crosslinked PVGA at certain conditions, but also radiation crosslinking at different doses, at dose rate of $5\,\mathrm{kGy\,h^{-1}}$ attempting to increase the superabsorbent capacity. The samples were characterized by Scanning Electron Microscopy (SEM), Thermo-gravimetrical Analysis (TGA), Nuclear Magnetic Resonance (1H) (NMR) and Infrared Spectroscopy (FTIR). The swelling behavior was measured gravimetrically in different solvents as pure water, buffer pH 3, 7 and 10. Results showed that radiation-crosslink route improves the swelling behavior of PVGA in approximately 215% when compared with PVGA chemically crosslinked, swelled in pure water.

1. Introduction

Commercial superabsorbent hydrogel polymers (SAHP) are crosslinked networks of ionic polymers, capable of absorbing large amounts of water and retaining absorbed water under pressure. The main industrial uses of commercial SAHPs are as absorbents in personal disposable hygiene products, such as baby diapers, adult protective underwear and sanitary napkins, agriculture field and wastewater (Calo and Khutoryansk, 2015; Omidian and Park, 2017; Guilherme et al., 2015; Ma et al., 2017; Saleh et al., 2018). Currently, the most common SAHP employed industrially is sodium polyacrylate (salt of polyacrylic acid), typically crosslinked with a diacrylate or bisacrylamide, such as N,N′-methylene-bisacrylamide (Ahmed and Ali-Syed, 2016; Zheng and Wang, 2008). Various copolymers of acrylamide and ethylene maleic anhydride are also employed as SAHPs, as well as crosslinked carboxymethyl cellulose, starch, polyacrylate-polyvinyl alcohol copolymers, and polyethylene oxide (Athawale and Lele, 2001; Ferreira et al., 2018; Akhtar et al., 2016; Barba et al., 2018; Relleve et al., 2018). Similarly, the acrylic type monomer itaconic acid is known for being useful for making hydrogel-forming polymers. However, sections of polymeric polyelectrolyte chains including a preponderance of repeat units derived from polymerization of acrylic type monomers (e.g. acrylic acid, acrylamide, itaconic acid and their salts) are not biodegradable and thus are persistent in the environment (Pourjavadi et al., 2006; Mahdavinia et al., 2006; Liu and Rempel, 1997). Further, when acrylic copolymers and grafts are used in conjunction with degradable polymer materials, only the non-acrylic polymer segments have been conclusively demonstrated to undergo biodegradation (Wang et al., 2016).

There is an increasing need to develop new “eco-friendly” super-absorbent polymers to cope with the high absorbency materials demands of developing countries. These materials should be based on synthetic biodegradable and natural polymers to achieve high super

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absorbency, modulated biodegradability, and fully biocompatibility. Poly(vinyl alcohol) (PVA) is a hydrophilic, non-toxic, biocompatible polymer that is obtained from polyvinyl acetate by alcoholysis (Slaughter et al., 2009).

PVA has not only high hydrophilicity and water absorption capacity but also has an excellent capacity to be processed in the form of particles, fibers, textiles, sponges, and films (Krissanasaeranee et al., 2010; Cui et al., 2004; Biswas and Ram, 2006). PVA is susceptible to modify due to its high hydrophilicity, excellent chemical properties, thermal stability and low cost (Zhang et al., 2008; Saraf et al., 2014; Salehi et al., 2012). Due to its good solubility in water, was suitable for functioning during hydrophilic modifications (Du et al., 2009). When an aldehyde reacts with PVA, the product is a poly(vinyl acetal). Examples of poly(vinyl acetals) include poly(vinyl formal) (PVF), poly (vinyl butyral) (PVB), and poly(vinyl glyoxylic acid) (PVGA); the chemical synthesis of the last one was described in (Georg and Ulrich, 1940) and in the US. Pat. No. 2,187,570 (Farmer and Jemmott, 1990).

Scholten and coworkers disclose solutions of PVA partially acetalized with glyoxylic acid to obtain a SAHP, based on the cyclic acetal reactions products of glyoxylic acid or salt, with two contiguous polyvinyl alcohol repeat units to form an acetal functionalized polymer, but the chemical crosslinking reactions to obtain the SAHP, can decrease gradually the polymer absorption (Scholten et al., 2012).

Polymers can be crosslinked by various techniques. One approach involves crosslinking agents in hydrogel fabrication process, but the purity of final product could be no guaranteed (Ahmed, 2015). Ionizing radiation seems to be an interesting alternative to classical chemical methods for obtaining hydrogels, especially for biomedical applications, when the chemical purity of the product is the critical factor (Alcântara et al., 2012; El-Shamy et al., 2017). The process does not require any low-molecular-weight additives (Rosiak and Ulanski, 1999). Synthesizing hydrogels can be uniformly processed by gamma rays due to its high penetration capability (Rosiak and Ulanski, 1999; Ahmed, 2015) and, Sakurada and Ikada described diluting solutions of PVGA polymers crosslinked by ionizing radiation in the presence of water and sodium chloride solutions (Sakurada and Ikada, 1962).

Thus, the aim of this study was, synthesized a crosslinkable modified PVA derivate (PVGA) and subsequently, exposing the aqueous solution of PVGA under gamma radiation to obtain an absorbent radiation crosslinked hydrogel. The water absorption was characterized by swelling method in different solvents, and the absorption capacity was compared with chemical crosslinking hydrogels.

2. Materials and methods

PVA from Clevol^{MT} Brazil 110,000 Mw 99% hydrolyzed, glyoxylic acid from Exodo Brazil 50% in water solution, sodium hydroxide from Exodo Brazil, hydroclorhidric acid from Labsynth Brazil and acetone from Labsynth Brazil were used as received.

2.1. PVA chemical modification and chemical crosslinking of PVGA

Modification of PVA to obtain PVGA chemical crosslinked hydrogel was carried out as described in US 2013/0065765A1 patent (Selifonov et al., 2013). Modification of PVA and chemical crosslinking occurs in one step by esterification pathway. In a neck flask was added the desired volume of glyoxylic acid (GA) (Table 1) into 150 mL 8% PVA water solution (99% hydrolyzed, Mw 110,000) at 75 °C by 1 h. The hydrogel was washed with distilled water at 40 °C until it loses its color.

2.2. Chemical synthesis of non-crosslinked PVGA

In organic chemistry, it is known that the selectivity of the acetalization over esterification (crosslinking) depends on the pH. Then, for the synthesis of non-crosslinked PVGA, it was used a mixture of sodium glyoxylate and glyoxylic acid (SG/GA) by addition of desired NaOH, which provided an equilibrium in the balance of acid catalysis with selectivity for acetalization over esterification. The procedure to obtain non-crosslinked PVGA was similar to PVGA chemically crosslinked, but the synthesis of the first one was made in three different pH values (2, 4 and 6 of SG/GA instead only GA), time reaction of 2 h and same molar ratio as shown in the Table 1. After synthesis, the non-crosslinked polymer was purified by precipitation in acetone, followed by Soxhlet extraction for 48 h, subsequent washing with ice-cold distilled water for three times and finally dried in vacuum by three days until constant weight. The reaction to obtain non-crosslinked or crosslinked PVGA occurs as follow where is possible to observe that an excess of protons leads to chemical crosslinking (Fig. 1).

Table 1
Molar rate of GA/PVA.

Sample	Molar rate GA/PVA
PVGA-0.25	0.25
PVGA-0.50	0.50
PVGA-0.70	0.70
PVGA-0.80	0.80

2.3. Radiation crosslinking PVGA

Water solutions 8 wt% of non-crosslinked PVGA molar ratio 0.8 (SG/GA)/PVA were exposed to gamma radiation at doses of 15, 20, 25, 30, 35 and 40 kGy at a dose rate of 5.1 ± 0.2 kGy h^{-1} to promote crosslinking via free radicals. The solutions were placed in rectangle PET forms, covered with a PET film and sealed in vacuum plastic bags. Samples of 8 wt% PVA water solution was irradiated at the same conditions for comparison.

3. Measurements

3.1. FTIR-ATR

FTIR-ATR spectra were recorded on previously dried samples using a spectrometer Nicolet 6700. MCT Detector, Perkin-Elmer Spectrum 100 Instruments, USA fitted with a Universal ATR sampling accessory (DiCompTM crystal, which is composed of a diamond ATR with a zinc selenide focusing element in direct contact with the diamond from 400 to 4000 cm^{-1}).

3.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was performed with a Scanning Electron Microscope from Jeol-JEM 6701F (Tokyo JAPAN) at 1.5 kV.

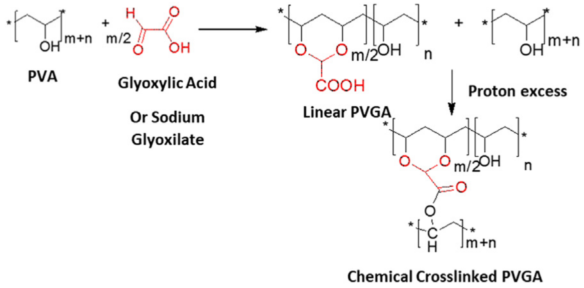

Fig. 1. Synthetic route to obtain non-crosslinked PVGA and chemical crosslinked PVGA.

3.3. Thermogravimetric Analysis (TGA)

TGA of samples was carried out using Mettler-Toledo TGA/SDTA 581 thermobalance in nitrogen atmosphere from 25 to 600 °C and heating rate of 10 °C min^{-1}.

3.4. Nuclear Magnetic Resonance (1H)

NMR for non-crosslinked PVGA measurements were performed on a Bruker Avance III 500 MHz spectrometer under a static magnetic field of 9.4 T. 45° single pulse sequence was used for FID accumulation; pulse repetition delay = 60 s. Samples were dissolved in D_2O.

3.5. Carboxylic group content

The total content of carboxylic groups present in the non-crosslinked PVGA was determined by titration with 0.1 mol L^{-1} sodium hydroxide (NaOH) using phenolphthalein as an indicator.

3.6. Measurement of the percentage of swelling

Aqueous solution of 8 wt% of PVA and non-crosslinked PVGA-0.8 were irradiated at six different doses under gamma radiation, 24 h after irradiation, samples were exposed to air, cut into pieces of 4 cm^2, weighted and put to swell by three times into glass tubes with 200 mL of distilled water by 24 h and 48 h, after that, the samples were dried under vacuum oven for 48 h (Ws).

On the other hand, portions of PVA and PVA-0.8 from samples exposed exactly the same than before exposed samples were cut into pieces of 4 cm^2 and dried under vacuum oven for 48 h (Wo).

Swelling degree was calculated by next equation:

$$S_w(\%) = 100\ \frac{(W_S - W_0)}{W_0} \tag{1}$$

where S_w *(%)* corresponds to swelling degree, W_O and W_S are the weights of the dry and the swollen samples, respectively.

3.6.1. Swelling degree analysis at different pH value

The swelling analysis was carried out by immersion of the previously weighed samples in different solvents as pure water and buffer solution pH 3, 7 and 10. Subsequently, the samples were removed from the solvent at different time intervals, blotted with paper, weighed and immersed again. The swelling percentage was determined gravimetrically by Eq. (1). Solutions of 0.2 M/0.05 M (boric acid/citric acid) and 0.1 M (trisodium orthophosphate $12H_2O$) were used to prepare buffer solutions.

4. Discussion

Scholten and Selifonov employed PVA in the design of SHAP materials due to excellent biodegradable properties using solutions of PVA partially acetalized with glyoxylic acid to obtain PVGA hydrogel. Their results showing that swelling behavior was affected by crosslinking grade because synthesis of chemical crosslinked PVGA use the hydrophilic carboxylic acid group to form covalent bonds in crosslinking process (Scholten et al., 2012; Selifonov et al., 2013). Sakurada and Ikada described the dilute crosslinked solutions of PVGA by ionizing radiation in the presence of water and sodium chloride solutions. They were found that crosslinking by gamma radiation is higher in alpha carbon to OH, in the other words, the increase of crosslinking in PVGA is probably due to the acetal group is not involved in crosslinking process. Although, this study was focus in a degradation analysis by effect of gamma radiation in aerated and air-free low concentration solutions of PVGA.

In comparation with degradation study of Sarakuda and Ikada, our is based on the study of the influence of gamma radiation in the increase of swelling proprieties of PVGA through unaltered carboxylic groups during irradiation crosslinking in comparison with chemical crosslinking proposed by Scholten and Selifonov method. The maximum acetalization grade formulation obtained by Scholten and Selifonov (maximum swelling) was reproduced and compared with both maximum acetalization grade formulation obtained at pH 4 and PVGA crosslinked by gamma radiation. As a result, the hydrophilic carboxylic acid groups were preserve and was possible improve the enhancement swelling behavior in different pH aqueous solutions.

5. Results

5.1. Chemical crosslinking and non-crosslinked PVGA

After 1 h of reaction under acidic conditions, PVA was turned into chemically crosslinked PVGA hydrogel. Moreover, it was observed that the best pH value to synthesize non-crosslinked PVGA was 4 because it provides the best equilibrium to acetalization over esterification. Above this, an excess of sodium glyoxylate salt is generated and does not react with PVA. Meanwhile, in a pH 3, the excess of protons favors the chemical crosslinking of PVGA.

5.2. PVA modification grade

Fig. 2 shows the modification grade of PVA (linear PVGA) calculated from titrimetric carboxylic group content, considering that every two OH groups from PVA where transformed into a one cyclic acetal group from PVGA. The modification content increased as a molar ratio (SG/GA) increased. The maximum modification grade for PVA was 90% from molar rate 0.8 synthesized at pH 4. Above molar ratio 0.8, PVGA turns on a crosslinking gel due to an excess of SG/GA and subsequently proton excess.

5.3. Nuclear Magnetic Resonance (NMR) 1H of PVGA

Fig. 3 shows characteristic NMR (1H), spectrum of pure non-crosslinked PVGA was carried out using D_2O as a solvent, and it was possible to assign the most important peaks values as follows: 1.2–1.9 ppm (C-H_2 linear and C-H_3 terminal protons), 2–2.4 ppm (C-H glycol) associated to different possible structures of 1–2 and 1–3 glycol, 4 ppm (O-H alcohol) and finally 5.1 (C-H acetal) as a result of the formation of cyclic acetals in synthesis of non-crosslinked PVGA. PVA/D_2O spectrum reported in literature, showed the same peaks values that PVGA RMN spectrum. At 4 ppm of O-H alcohol group, C-H_2 at 1.9 ppm, 2–2.4 ppm of C-H glycol associated to different possible structures of 1–2 and 1–3 glycol, but the peak in 5.1 that corresponds to (C-H acetal) is no present in PVA structure (Amiya et al., 1990),

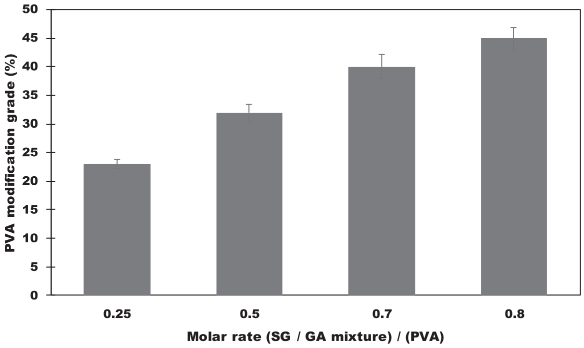

Fig. 2. Modification grade of PVA as a function of the molar rate of sodium glyoxylate-glyoxylic acid mixture (SG/GA)/PVA at pH 4.

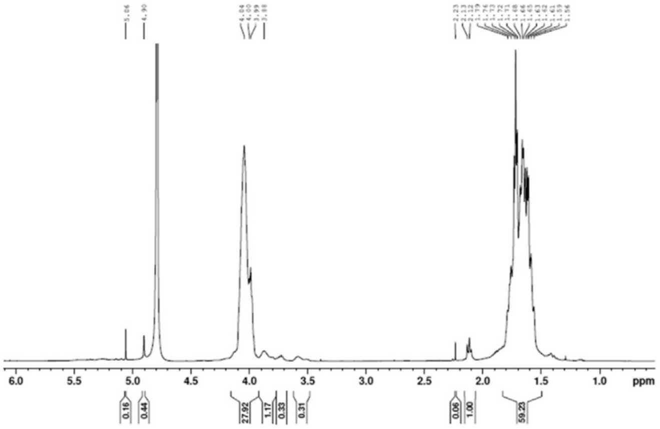

Fig. 3. NMR (1H) spectrum of PVGA-0.8 8 wt%.

5.4. Radiation crosslinking of PVGA

In order to compare, samples of an aqueous solution of PVA 8 wt% and non-crosslinked PVGA-0.8, 8 wt% were exposed to gamma radiation at different doses. Fig. 4. shows the appearance of irradiated PVA. As expected, the crosslinking increased as a function of dose and samples turn into a gel at all tested doses. Samples of PVGA irradiated at 10 kGy showed a visible increase in the viscosity when compared with no irradiated solution. Samples irradiated at 15 and 20 kGy turned into a jelly solution and samples irradiated at 25, 30, 35 and 40 kGy showed a similar appearance to PVA samples irradiated at 20 kGy (Fig. 4B).

5.5. Crosslinking of PVGA by gamma radiation

Gamma radiation produces free radicals with superior probability in saturated carbon than in carboxylic acid groups. The most probable radical formation when PVGA is exposed to gamma radiation based in comparison with exposed PVA presented in literature is shown in Fig. 5 (Sakurada and Ikada, 1962; Charlesby, 1960; Zainuddin et al., 2001).

The highest value of radiochemical yield (G) for PVA under gamma radiation exposure corresponds to radical group OH analyzed by Zainuddin with ESR studies (Zainuddin et al., 2001). Then, the site in the PVGA with the highest probability to crosslink is in alpha carbon to OH with no modification. The final probable structure is shown in Fig. 6.

5.6. FTIR analysis

Fig. 7 shows FTIR spectra of PVA, non-irradiated PVGA, radiation-crosslinked PVGA (25 kGy) and chemical crosslinked PVGA. At 3350 cm^{-1} is located the characteristic OH very abroad band of PVA and at 3000 cm^{-1} corresponding to stretching band of CH_2 and CH_3 signals. Non-irradiated PVGA spectrum shows characteristics bands of PVA, plus a band at 1612 cm^{-1} that corresponds to carboxylic acid from substituted cyclic acetal group. For this spectrum, is possible to see that the carboxylic acid groups in its majority were no crosslinked and are free groups because the OH vibration from COOH signal in 3230 cm^{-1} not disappears. It was not possible to identify the tenuous bands of acetal formation under 1200 cm^{-1}, possibly overlapped by

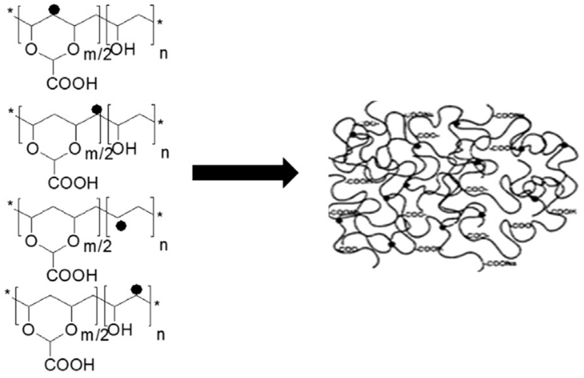

Fig. 5. Probability to induce free radicals in PVGA due to gamma radiation exposition.

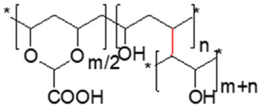

Fig. 6. Probable final structure of radiation-crosslinked PVGA after gamma irradiation.

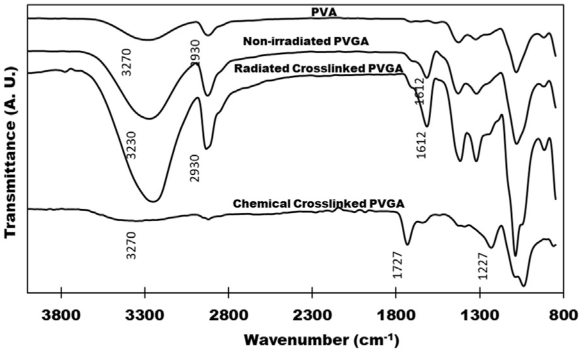

Fig. 7. FT-IR spectra of PVA, non-irradiated PVGA-0.8, chemically crosslinked PVGA and radiation crosslinked PVGA 8 wt%.

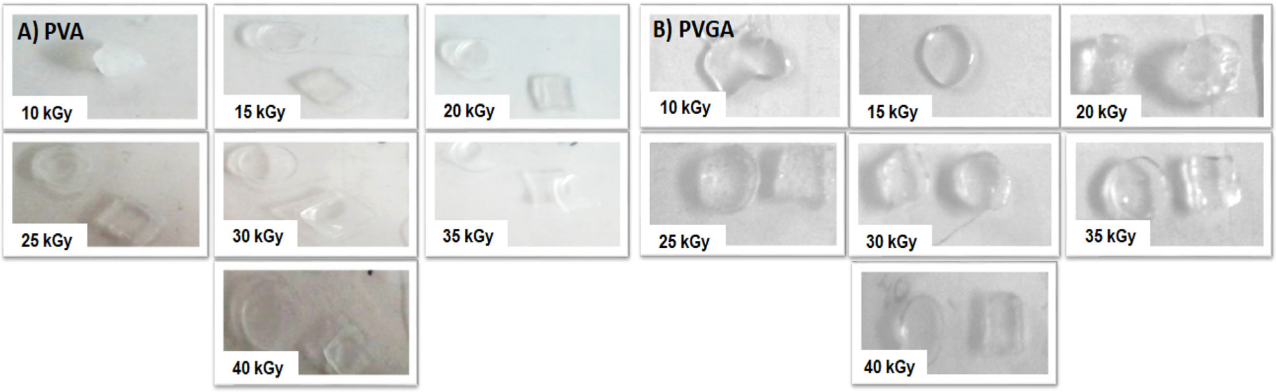

Fig. 4. Physical appearance of PVA A) and PVGA-0.8 B) 8 wt% irradiated at different doses.

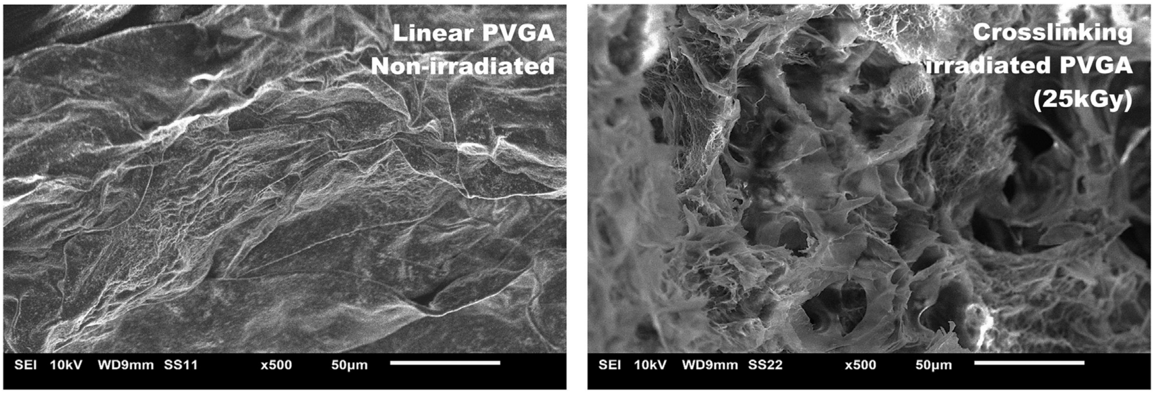

Fig. 8. SEM microscopy of irradiated and non-irradiated PVGA-0.8 8 wt%.

bands of groups of CH_3.

Irradiated PVGA spectrum indicated that no any band changed after radiation crosslinking process when compared with non-crosslinked PVGA, confirming that crosslinking via gamma radiation does not use acetal groups to form chemical bonds instead the crosslinking is via free radical in the main chain and COOH group from acetal is not involved. Finally, the infrared spectrum of chemical crosslinking of PVGA synthesized in acidic conditions, showed a decrease in the intensity of OH band indicating a modification of PVA. The chemical crosslinking was confirmed by a band at 1727 cm^{-1} that correspond to the carbonyl of the ester group and its two confirmation bands at 1227 cm^{-1} and 1170 cm^{-1}. It is possible to observe a weak band at 1612 cm^{-1} that showed that no all carboxylic acid groups were crosslinked.

5.7. *SEM analysis of irradiated and no irradiated PVGA*

The irradiated and no-irradiated linear PVGA were dried under vacuum oven for 24 h and then swollen in distilled water for 24 h. The samples were immediately frozen by immersion in liquid nitrogen and fractured. Frozen samples were lyophilized for 48 h and reserved for SEM microscopy in vacuum (Jeol-JEM 6701F (Tokyo JAPAN) at 1.5 kV). Fig. 8 shows cross-section of SEM microscopy of irradiated at 25 kGy and non-irradiated linear PVGA. Irradiated crosslinked PVGA cross-section showed different pore sizes, due to the water retention in the net structure due to the hydrogel formation. No irradiated linear PVGA polymer did not show porosity and present a homogenous surface. The differences between two morphologies is based on the formation of interconnected porous structures by radiation crosslinking of PVGA while linear PVGA did not present porous structures because absence of polymer networks.

5.8. *Thermogravimetric Analysis TGA*

Fig. 9 shows TGA analysis PVA, two formulations of non-irradiated PVGA and radiation-crosslinked PVGA. In PVA thermogram the first degradation close to 300 °C corresponds to the decomposition of pendant alcohol groups in the main chain; above 450 °C decomposition of the main chain starts. Samples of PVGA ratios 0.25 and 0.80 (SG/GA)/PVA exhibited three different temperature degradation changes. The first one at 280 °C occurs due to decomposition of no reacted alcohol groups present in pendant groups in the main chain. Thermogram shows that at higher modification degree, more alcohol groups were transformed into acetal groups. This result is according to the chemical modification curve, where ratio 0.8 corresponds to approximately 50% of PVA pendant alcohol modification and 0.25 corresponds to around 20% (see Fig. 2). At 420 °C and 550 °C, both curves suffer a decomposition of the CH_2 group followed by decomposition of acetal cyclic groups present in the main chain. Irradiated and non-irradiated non-crosslinked PVGA samples shown identical degradation behavior but thermal resistance at 10% of decomposition increased in 50 °C for irradiated PVGA because of radiation crosslinking.

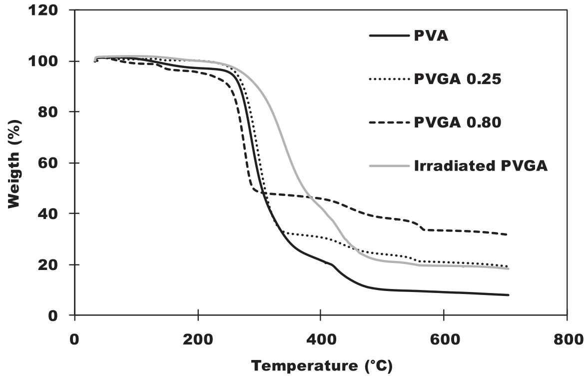

Fig. 9. TGA analysis of PVA and PVGA at different modification ratios.

5.9. *Swelling degree analysis*

5.9.1. *The effect of dose and time in swelling degree analysis*

Fig. 10 shows swelling degree as a function of dose. Results of PVGA irradiated at 15 kGy were omitted due to poor sample manipulation to determine swelling weight. In comparison with PVA, PVGA samples have a notable swelling increase. It was observed that samples of PVA stopped swelling in 24 h and PVGA samples continue to swell after this time. As expected, swelling degree decreases as the dose increases due to higher crosslinking. Irradiated hydrogels at 15 kGy and 25 kGy showed a sticky consistency that made it difficult to handle.

A comparative swelling degree (g water/g polymer) study from PVA and PVGA samples is shown in Fig. 11. Swelling degree for chemical crosslinked PVGA was 7.8 g higher than PVA hydrogel that means an

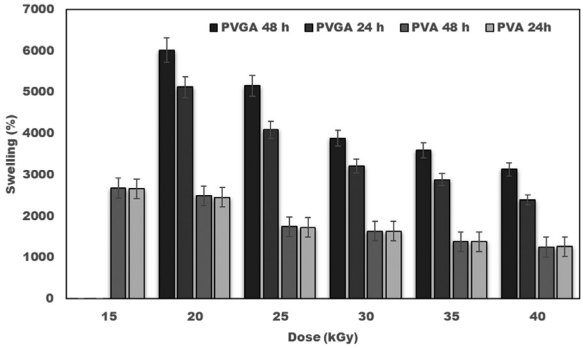

Fig. 10. Swelling as a function of dose for PVA and PVGA-0.8 after gamma irradiation.

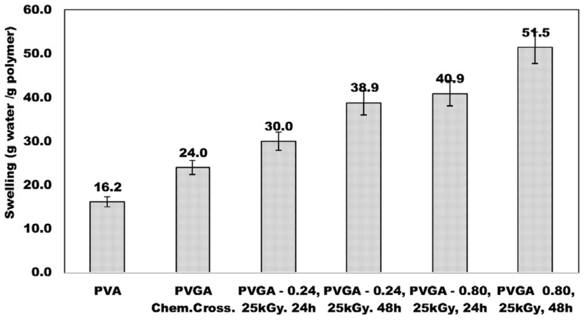

Fig. 11. Swelling degree (g water/g polymer) as a function of swelling response for PVA hydrogel 8% w/v and 25 kGy, chemical crosslinked PVGA, 0.8 GA/PVA molar ratio, PVGA-0.24 and PVGA-0.8, pH 4, obtained at 25 kGy and 8% w/v.

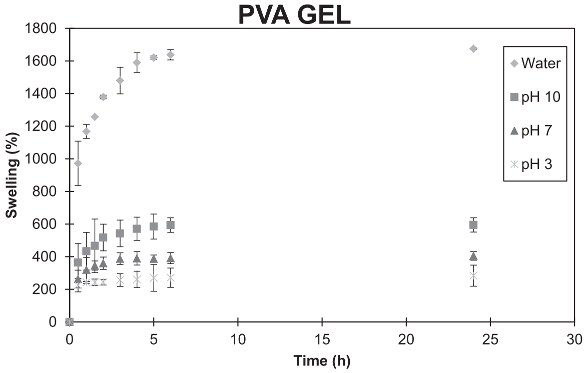

Fig. 12. Swelling behavior of radiation crosslinked PVGA-0.8 Gel 0.8 wt% in different media.

increase of 48.1%; while PVGA-0.24 showed a difference of 21.8 (g water/g polymer) equivalent to a swelling increase of 134%. However, the highest swelling degree was presented by radiation crosslinked PVGA-0.8, when compared with PVA it has an increase of 35.3 (g water/g polymer) that it represents an increase of 217.9%, and when compared with chemical crosslinked PVGA there is an increment of 27.5 (g water/g polymer) that represents an increment of 46.6% almost the double than chemical crosslinked PVGA Scholten and Selifonov method.

5.9.2. The effect of pH in swelling degree analysis

Fig. 12 shows the effects of pH values of buffer solution on the water-swelling ratios radiation crosslinked PVGA-0.8 hydrogel. The swelling degree of PVGA hydrogels have an abruptly increase to 4000% in pure water. In the case of buffer solution with pH values from 3 to 10, the swelling degree depends on interaction with ionic salts; there was a competition between functional groups of PVGA and dissolved salts for water molecules reducing the swelling capacity of the hydrogel. In buffer solution with pH 3, a strong hydrogen bonding was easily generated by the AcCOOH groups in the PVGA-0.8 hydrogel network structure. Thus, the PVGA-0.8 hydrogel network was in a contraction state that had a small swelling ratio. As the pH of the buffer solution increased, the concentration gradients of hydrogen ions inside and outside the hydrogel network increased too. At pH 7, the dissociation amount of the AcCOO$^-$ + H$^+$ groups increased as the pH value increased outside the hydrogel and AcCOO$^-$ ions were generated. Electrostatic interaction played a small role in swelling action. The dissociation degree of the network structure increased, which increased the overall hydrophilicity of PVGA-0.8 hydrogels. The resulting electrostatic interaction also exhibited a certain role in the swelling property of hydrogels. Therefore, the growth rate of the swelling ratio of hydrogels was significantly higher during this period than in the previous period. At pH 10, most AcCOOH groups in the PVGA-0.8 hydrogel were dissociated. The dissociation degree of the network structure rapidly increased. The electrostatic interaction was obviously enhanced, which resulted in a rapid increase in the swelling ratio of PVGA-0.8 hydrogels.

6. Conclusions

A cyclic acetal-COOH derivative of PVA (PVGA) was synthesized. FTIR and NMR spectroscopy verified the chemical structure of obtained non-crosslinked PVGA and confirmed the high efficiency to obtain it at pH 4. Irradiation of aqueous solution of PVGA-0.8 at 8%, in absence of low-molecular-weight additives (crosslinkers), resulted in the formation of macroscopic hydrogels even at doses as low as 15 kGy. Thus, obtaining hydrogel of this PVA derivate using ionizing radiation, i.e. crosslinking through unsaturated C-C bonds of the main chain of PVGA where the absorbent groups (COOH) are not involved, seems to be an interesting alternative in comparison to the commonly used chemical method. The main advantage of radiation as an initiating factor for previously PVGA it allows thorough purification of still linear, soluble polymer prior the network formation, and also the swelling is still improved to obtain an absorbent hydrogel. The swelling ratio in PVGA hydrogels is time-dependent. and increased exponentially in comparison with no treated PVA and traditional chemically crosslinked PVGA; due to the COOH cyclic acetals group's are not involved in a crosslinking reacts as shown in FTIR and TGA analysis. The maximum swelling degree ratios for PVGA and PVA hydrogels were 4000% and 1600% respectively at first 48 h, which represents an increment of 320% in pure water with respect to not treated PVA. The maximum swelling was obtained for PVGA-0.8 at 25 kGy 8 wt% and 48 h, where almost 5000% that represents an increment of 215% when compared with chemical crosslinked PVGA. Swelling ratios of PVGA hydrogels generally increase in basic conditions when AcCOOH groups are dissociated and decrease in acidic conditions when compared with swelling in pure water. Crosslinking using gamma radiation technique could be used to crosslink polymers without losing their functionalities.

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