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pH-Sensitive Hydrogel from Polyethylene Oxide and Acrylic acid by Gamma Radiation

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Abstract: Hydrogel as a good water absorbent has attracted great research interest. A series of hydrogel based on polyethylene oxide (PEO) and acrylic acid (AAc) was prepared by applying gamma radiation with variation in the concentration of acrylic acid. Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) were used to characterize the PEO/ AAc hydrogel. The properties of the prepared hydrogels such as gel content, swelling behavior, tensile strength, and pH sensitivity were evaluated. The formation of the hydrogels was confirmed from FTIR spectra. SEM images showed the inner porous structure of the hydrogels. The dose of gamma radiation was optimized to get a hydrogel with good swelling property and mechanical strength. The swelling ratio and gel content of the hydrogels were increased with increasing acrylic acid content. The pH of the solutions affected the swelling which indicated the pH-responsive property of the prepared hydrogels. Swelling of the prepared hydrogels in sodium chloride salt solutions decreased with increasing the ionic strength.

Keywords: hydrogel; polyethylene oxide; acrylic acid; gamma radiation; swelling ratio; pH-sensitive hydrogel

1. Introduction

Hydrogels are crosslinked three-dimensional polymer networks with the ability to absorb and retain aqueous fluids without dissolving. The polymeric crosslinking either physical (i.e., entanglement) or chemical (i.e., covalent bond) is the reason behind the network formation of hydrogel. The noteworthy property of hydrogels is their capacity to store water, which makes them very unique materials. Because of hydrophilic interaction between the networks and water molecules, hydrogels imbibe water and swell [1–3]. The properties of these soft materials can be improved by grafting or crosslinking of monomers of various functional groups [4]. These hydrophilic gels exhibit volume changes reliant on external stimuli, such as environmental temperature, pH, ionic strength, mechanical stress, and so on [5–9]. pH-responsive hydrogels are comprised of pendant acidic (e.g., -SO_3H, -COOH) or basic (e.g., –NH_2) groups, so their behavior (e.g., swelling) changes by the influence of ionizable groups, crosslinking density and external pH [10–13]. Many reports have been published about preparation methods; for instance, crosslinking, copolymerization of one or more functional monomers and grafting, etc. [14–16]. Two common methods used for crosslinking are the chemical method and

radiation method. In the radiation method, an initiator, catalyst, and crosslinker are not required because ionizing radiation is highly energetic [17,18]. Moreover, no residue, sterility of the product, and a durable crosslinker are some advantages of radiation-induced polymerization over the chemical method [19,20]. Polyethylene oxide (PEO) is a white thermoplastic, aerobically biodegradable and a unique class of water-soluble polymer. In recent years, PEO has attracted great research interest because of its unique properties in solution and because of those unique properties it is used in the field of drug delivery, tissue implant, and wound healing [21,22]. Acrylic acid (AAc) is a pH-responsive and electrically sensitive material. It forms complexes with polybases [23]. AAc on crosslinking produces high water absorbing hydrogels both as a single component and as part of the multi-component systems. Because of ionizable carboxylic acid, these hydrogels are responsive enough to pH and ionic strength [24]. These monomers have been used as a second component, grafted on polymer surfaces or used as blends to obtain a wide variety of the hydrogels. Because of the high crystallinity Polyethylene oxide (PEO) is not generally used as absorbent [25]. There are many applications of hydrogels such as in agriculture, in the pharmaceutical industry, in food, in personal hygiene, in nanotechnology, in biomedicine, in water remediation, in tissue engineering, in cosmetic and food packaging industry, and in oil spills [26–28]. Based on a literature survey, only a limited amount of information about swelling and characterization of hydrogels synthesized from acrylic acid and polyethylene oxide was found [29]. But there are no studies on hydrogel preparation from partially neutralized acrylic acid grafted on PEO with high water absorbing capacity by gamma radiation.

In this research, a series of pH-sensitive hydrogels have been prepared from high molecular weight polyethylene oxide and acrylic acid monomer by a simple method of radiation polymerization. These hydrogels were characterized by various analytical and microscopic techniques. In addition, the effects of pH-sensitive AAc content on different properties were also investigated in detail.

2. Materials and Methods

2.1. Materials

Acrylic acid (BASF, Ludwigshafen, Germany) and polyethylene oxide of average molecular weight 400,000 (Sigma-Aldrich Co, St. Louis, MO, USA) were used as monomer and polymer respectively. Sodium hydroxide was obtained from BASF, Germany and acetic acid was from Merk, Darmstadt, Germany. All other reagents were of analytical grade and were supplied from Fluka, Buchs, Switzerland.

2.2. Preparation of PEO/AAc (PA) Hydrogels

At first, 5% aqueous solution of PEO (P) (Mw 4.0×10^5) was prepared by dissolving 5 g of PEO in a beaker (250 mL) with 100 mL distilled water at room temperature with a stirrer to have a homogeneous solution. Partially neutralized (pH 6–6.5) AAc was then added with different concentrations (5%, 10%, and 15%, w/w) in 5% PEO solution to prepare PEO/AAC (PA) hydrogels. AAc was treated with 20% NaOH solution for neutralization. To make a homogenous solution the PEO-AAc mixtures were stirred intermittently and cooled it to room temperature. The solutions were then transferred into polyethylene plastic bags, taped up and exposed in gamma rays from ^{60}Co source with radiation doses from 25 kGy to 50 kGy. The obtained hydrogels in square shape were cut into pieces with desired sizes for further analysis. The cross-linked PA hydrogel was dried and weighed.

2.3. FTIR-ATR Spectral Analysis

PerkinElmer Spectrum 2 FT–IR spectrometer, Japan, was used to record Fourier transform infrared (FTIR-ATR) spectra of AAc, PEO, and PA hydrogels using diamond crystal. All spectra were calculated from 4000 to 500 cm^{-1} frequency range.

2.4. Scanning Electron Microscopy (SEM)

The surface morphology of the hydrogels was observed by scanning electron microscope SEM (JCM-5700, Jeol, Tokyo, Japan). Samples at equilibrium state were plunge-freeze in liquid nitrogen and then allowed to keep freeze drier, FRD-mini (IWAKI, Asahi Techno Glass, Tokyo, Japan) at −50°C under vacuum for 2 days to remove water. Finally, the specimen of freeze-dried samples was coated with osmium about 20 nm in osmium plasma coater OPC 60N (Filgen Inc., Aichi, Japan) to examine by SEM to get the interior structural image.

2.5. Measurement of Gel Fraction of Prepared Hydrogel

The prepared non-sticky solid sample was oven dried to obtain constant weight (W_i) at 60 °C. The sol fraction or unreacted components from the sample were removed by immersing in distilled water about 24 h at ambient temperature. The samples were dried and re-weighted until constant weight (W_d) was achieved. The gel fraction was calculated by the following equation proposed by Khoylou et al. [25]:

$$\text{Gel fraction } (\%) \;=\; (W_d / W_i) \times 100$$

where W_d is the weight of dried gel after extraction and W_i is the initial weight of dried gel.

2.6. Measurement of Swelling Ratio in Distilled Water

The measurement of equilibrium swelling, dried samples were dipped in distilled water and kept in that container at same condition until they reached a constant weight. The required data were collected periodically by taking the swollen gel out of the container and drying until it was a constant weight. Before drying, extra surface water of gel was wiped by filter paper very carefully. The calculation for the swelling ratio was done according to the equation proposed by Khoylou et al. [25]:

$$\text{Swelling ratio } (\%) \;=\; (W_t - W_d / W_d) \times 100$$

where W_d is the weight of dried gel before swelling and W_t is the weight of the swollen gel at time t.

2.7. Preparation of Buffer Solutions of Different pH

0.2 M HCl was used to prepare solutions of pH 1 and of pH 2 respectively. 0.1 M (acetic acid/sodium acetate) was used to prepare the solutions for pH 3 to 6 and 0.2 M (potassium dihydrogen phosphate/sodium hydroxide) was used to prepare buffer solutions ranging from 7–8. The sample was then swollen in various pH buffer solutions.

2.8. Measurement of Mechanical Properties (Tensile Strength) of Prepared Hydrogels

Mechanical characterization of hydrogels was done by tensile testing. This method involves applying a tensile force to strips of material held between two grips. The specimens were prepared in the desired shape with dimensions of 15 mm × 20 mm × 3 mm of each PA sample. Tensile strength (TS) values of hydrogel samples were conducted with a universal testing machine (Hounsfield Series S, Salfords, UK) with a 5 N load capacity at a crosshead speed of 10 mm/min. Each result represents the mean of 3 measurements performed in the same condition.

3. Results and Discussion

3.1. Optimization of Radiation Dose

The optimal analysis of the γ-absorbed dose for PA hydrogel was performed by using different radiation doses (25 to 50 kGy). The effect of radiation doses was evaluated against the background of gel content, swelling ratio and tensile strength of synthesized hydrogel (PA15). The results are shown in Figures 1–3 respectively. It is observed from the Figure 1 that the gel content increased with increasing

radiation doses because when the radiation dose passed through the polymer/monomer system, the percentage of the free radicals became greater than before in the system [30]. Free radical formation is one of the main reasons for crosslinking; a higher radiation dose leads to higher crosslinking among polymer chains which results in an increasing gel fraction [31]. The outcomes of swelling ratio experiments are shown in Figure 2. From this Figure, the maximum swelling ratio was observed at 25 kGy after which the swelling ratio decreased. This decreasing water swelling tendency of PA gels can be explained by the fact that the densely crosslinked gel was formed at a high radiation dose, which also produced a very compact interior. Crosslinking obstructs the movability of the polymer chain and hence it limits the penetration of water into the hydrogel structure [32]. From Figure 3, the tensile strength of PA15 improved further by raising the radiation level, with significant high value at 30 kGy (5.3 kPa). Therefore, considering the gel fraction, swelling ratio and tensile strength, 30 kGy is chosen as an optimized dose for our further research.

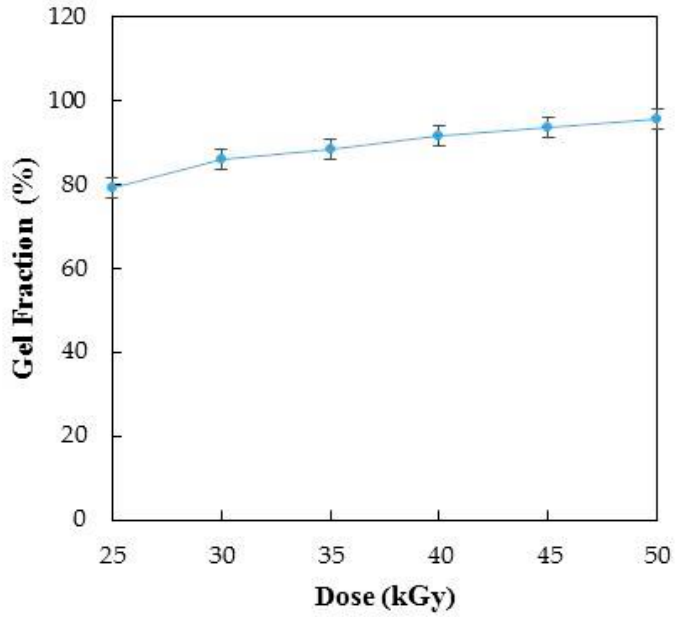

Figure 1. Effect of radiation dose on gel fraction of PA15 hydrogel.

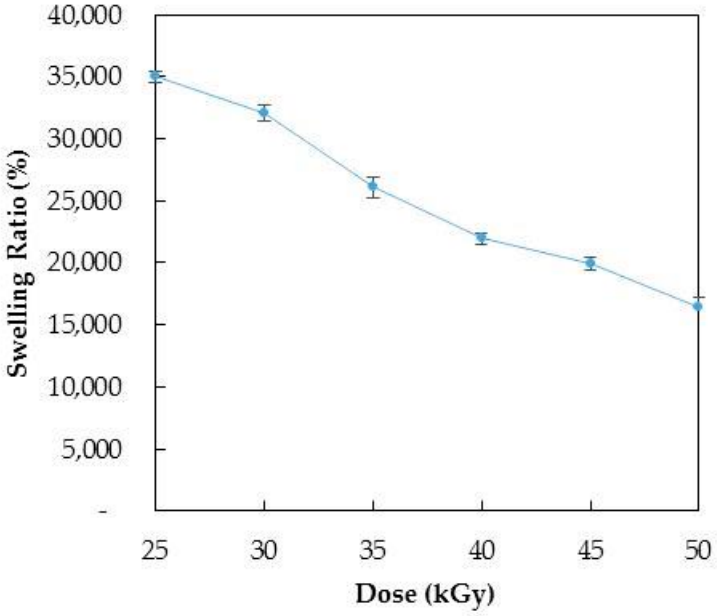

Figure 2. Effect of radiation dose on swelling ratio of PA15 hydrogel.

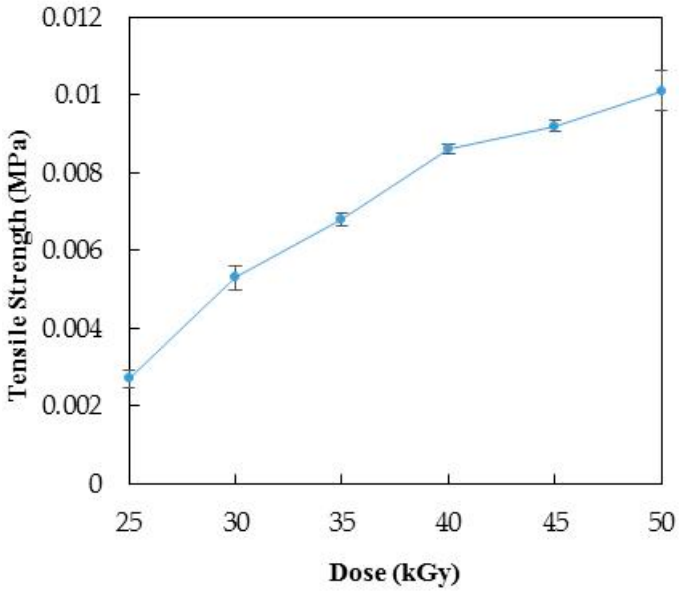

Figure 3. Effect of radiation dose on tensile strength of PA15 hydrogel.

3.2. PEO/AAc(PA) Hydrogels Synthesis at Optimized Dose

We optimized the radiation dose (30 kGy), which was used to prepare the PA hydrogels with different composition of AAc. Table 1 presents the feed ingredients of the prepared hydrogels. Water worked as an initiator for the process of network formation. Moreover, when the aqueous solution of PEO and AAc was exposed by γ-radiation, the water molecules transmuted into reactive intermediates such as $^{\bullet}OH$, $^{\bullet}H$, H_2O_2, H_2, and H^+. These intermediates then reacted with PEO and AAc molecules to generate free radicals of polymer and monomer; further, the gel network configuration was formed as a consequence of graft homo-polymerization, and the crosslinking of monomers and polymers [33].

Table 1. Feed composition and optimized radiation dose for the prepared hydrogels.

Sample	PEO (%)	AAc (%)	Dose (kGy)
PA0	5	0	30
PA5	5	5	30
PA10	5	10	30
PA15	5	15	30

3.3. FT-IR Analysis of Hydrogels

To understand the formation and crosslinking of hydrogel obtained from PEO and partially neutralized AAc monomers, FT-IR spectra of PEO, AAc, and PA hydrogel (PA15) are presented in Figure 4. For pure PEO, the absorption band at 3425 cm^{-1} and 2882 cm^{-1} are due to the result of the stretching frequency of OH group and C-H stretching vibration respectively. For AAc, the absorption bands at 3390 cm^{-1} is for OH stretch, 2971 cm^{-1} is for -CH_2- stretching, 1705 cm^{-1} is for carboxyl acid groups respectively. In PA hydrogel, the absorption band at 1721 cm^{-1} indicates the bond formation between AAc and PEO for the intramolecular hydrogen bond detachment among carboxylic groups. The peak at 1551 cm^{-1} is assigned to the –COONa group in PA hydrogel. Changes in hydroxyl stretching regions are also observed in PA hydrogel. The absorption band of the hydroxyl group in PEO and AAc shifts to lower wave number 3360 cm^{-1}. The shifting in bands indicates the crosslinking between PEO and AAc in PA hydrogel [34–39].

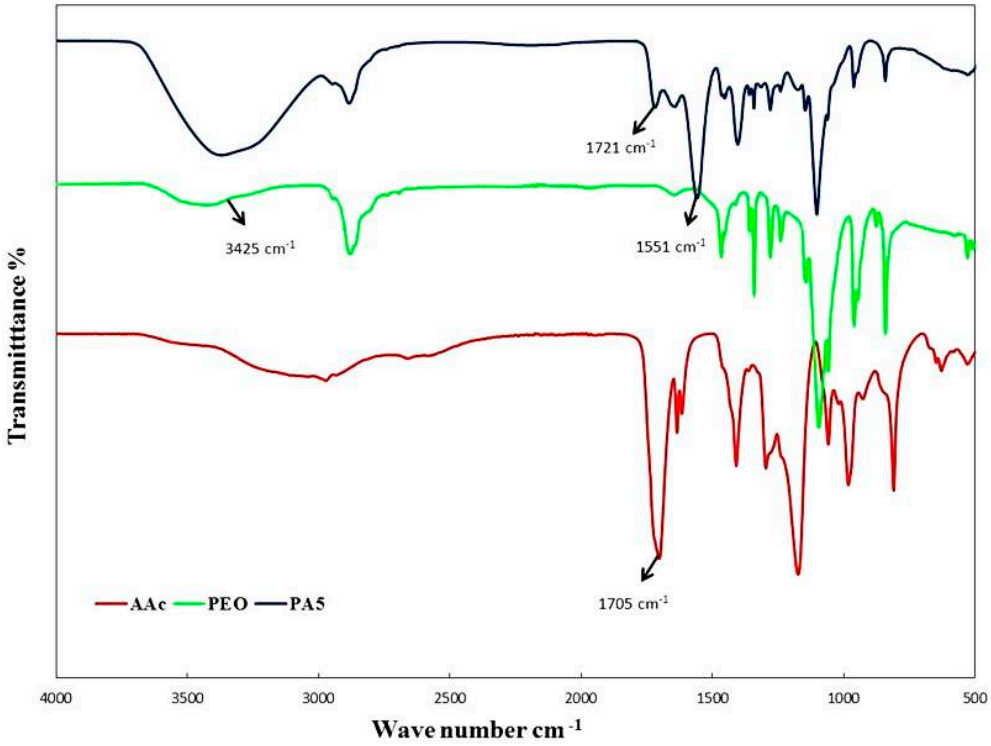

Figure 4. FT-IR spectra of pure AAc, pure PEO, and PA5 hydrogel blend prepared at 30 kGy radiation dose with ranges 4000–500 cm^{-1}.

3.4. Morphological Analysis by Scanning Electron Microscopy

The prepared sample (PA5) was freeze-dried and then evaluated by a scanning electron microscope (SEM) to observe its internal morphologies. The SEM micrographs of the hydrogel are presented in Figure 5. From the Figure, it is quite clear that the inner structure is porous and sponge-like, which implies that the hydrogel mostly contained water. Hence, this is a possible explanation behind the high water absorbing capacity of hydrogel.

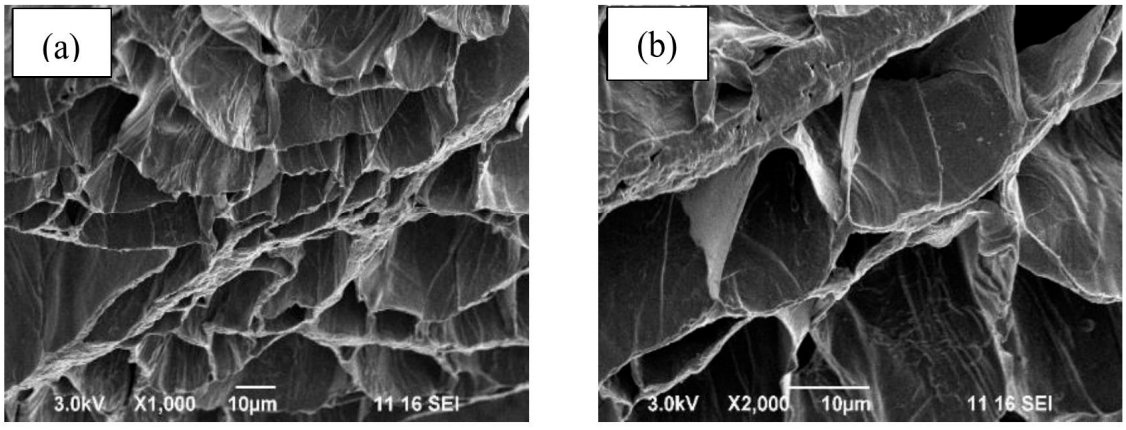

Figure 5. Scanning electron microscope images of PA blend hydrogel (PA5) surface at various magnifications (**a**) ×1000, (**b**) ×2000.

3.5. Gel Fraction of PA Hydrogel

The fabrication of the network is appearing in an escalation in the insoluble part and reduction in the soluble part in the polymeric system. This matter depends on a number of parameters, such as weight average functionality, molecular weights of polymer and monomers and the reaction conditions

(e.g., concentration of monomers) [40]. The influence of AAc concentration (wt %) on the gel content of PEO/AAc hydrogels is shown in Figure 6. It was found that this high radiation dose increased the gel portion of the hydrogels with an increased percentage of AAc. Gel fractions increased from 71.56% to 85.95% for acrylic acid concentration 5% to 15% at 30 kGy. This might be due to an accelerated tendency of free radical formation with increasing concentration of monomer or polymer [31]. The free radical was liable for crosslinking. Random reactions of these radicals are accountable for the conception of crosslinking, graft copolymerization, and homopolymerization of AAc. When two connected radials were nearby, their co-ordination measures increased crosslink of macromolecules. Polymer free radicals produced by ionization radiation came closer in polymer solution of higher concentration than in the lower concentrated solution, and, hence, more crosslink form in network structure. Moreover, high crosslinking density in network depicted the higher percentage of gel content and be responsible for a rigid structure of hydrogel [32].

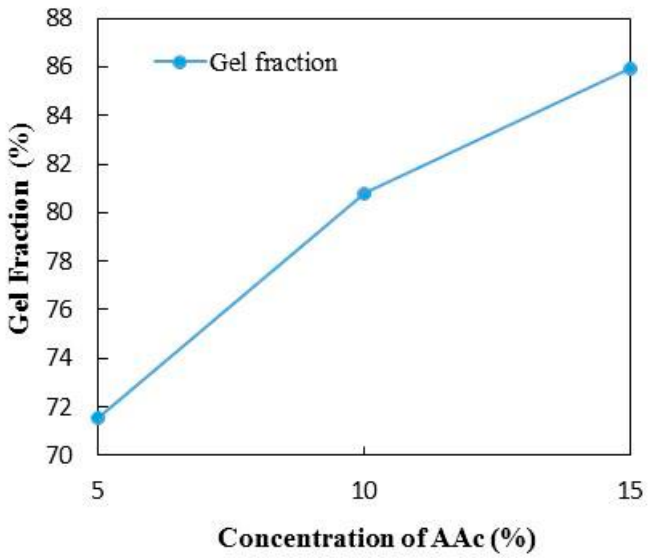

Figure 6. Effect of AAc concentrations on gel fraction of PA hydrogels prepared at radiation dose 30 kGy.

3.6. Swelling Ratio of PA Hydrogel in Distill Water

PA hydrogels of different acrylic acid composition (Table 1) were synthesized to investigate the impact of AAc on water imbibing capacity and presented in Figure 7. It was observed from the figure that the swelling ratio of obtained hydrogels was reliant on monomeric composition. Moreover, the swelling ratio of PA gels increased with increasing quantities of acrylic acid in feed composition. For instance, it increased from 20,915% to 32,096% for the increased concentration of acrylic acid from 5% to 15% in the hydrogels. This can be explained by the fact that the high water affinity and ionization tendency of -COOH group in AAc [41]. This caused a significant expansion in the crosslinking network and resulted in higher swelling of gels. Moreover, it is clear that for PA hydrogels (Figure 5) there are many open pores with different size, which have a channel-like interconnected structure in them. It seems that water molecules are able to enter into the hydrogel structure more easily and hence increase the swelling ratio. The equilibrated swelling ratio was reached within 24 h; maximum water absorption occurred within the initial 15 h and then the absorption rate increased slowly with a tendency to be constant.

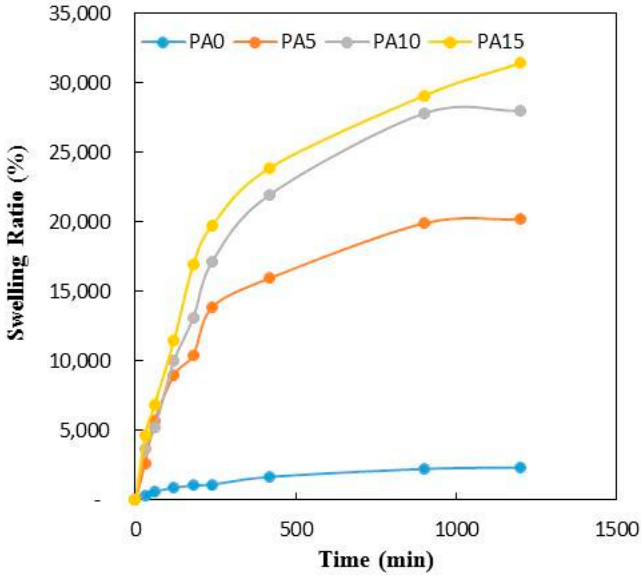

Figure 7. Swelling ratio of PA hydrogels with various concentrations of AAc as a function of time at radiation dose 30 kGy.

3.7. Effect of pH on Swelling Ratio of PA Hydrogels

As expected, pH had an effect on the swelling ratio of PA blend hydrogels (Figure 8). The presence of carboxylate groups in acrylic acid changed the swelling ratio with an increase or decrease of acrylic acid concentration. At low pH value, the swelling capacity of the hydrogels reduced and, in the case of high pH, the opposite result was seen. The highest swelling was observed for pH 8. Because the acidic pendant group was on the polymer chains when the pH value was raised, the ionization of carboxylic acid groups caused the fixation of negative charges (COO^-) on the polymer chains and mobility of positive charges (Na^+) in the surrounding medium. This phenomenon caused electrostatic repulsion between carboxylate ions and increased free spaces that caused more hydrophilicity and, thus, enhanced the swelling of the hydrogels. On the other hand, in the case of low pH, the declination of the negative charge (carboxylate groups) on the polymer chains due to protonation by HCl caused the hydrophobicity of the polymer. Therefore, the swelling capacity falls at low pH [12,33,42,43].

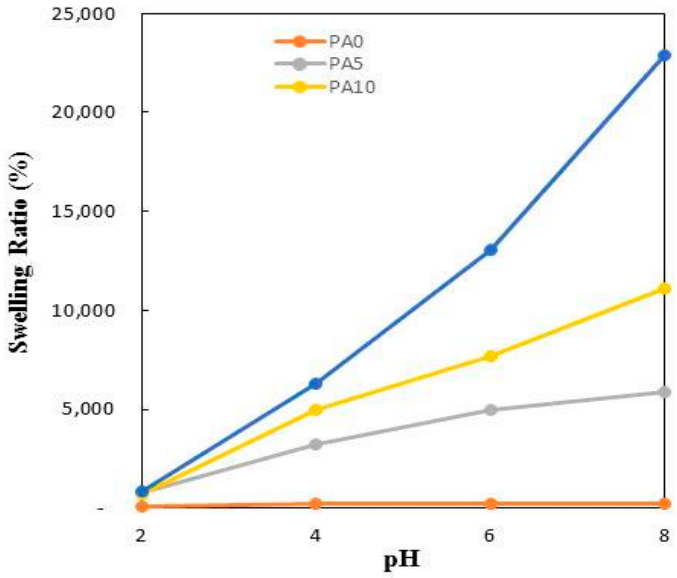

Figure 8. Effect of pH on swelling ratio PA hydrogels prepared at radiation dose 30 kGy.

3.8. Effect of Ionic Strength on Swelling Ratio of PA Hydrogels

Figure 9 shows the effect of ionic strength on the swelling ratio of PA blend hydrogel prepared at 30 kGy. The swelling assessment of the prepared hydrogels in the sodium chloride salt solutions indicated that the increased ionic strength of the salt solutions leads to a decrease in the swelling ratio of the hydrogel. The swelling loss might be related to electrostatic repulsion between ionic mobile ions (Na^+). The mobile sodium ions had a weak attraction to negative carboxylate groups of polymer networks. They were trapped in a semipermeable membrane and this resulted in the osmotic pressure difference between inside the gel and outer solution. When the free mobile ion concentration in the outer solution increased, osmotic pressure decreased, and, thus, decreased the gel volume and reduced swelling [43,44].

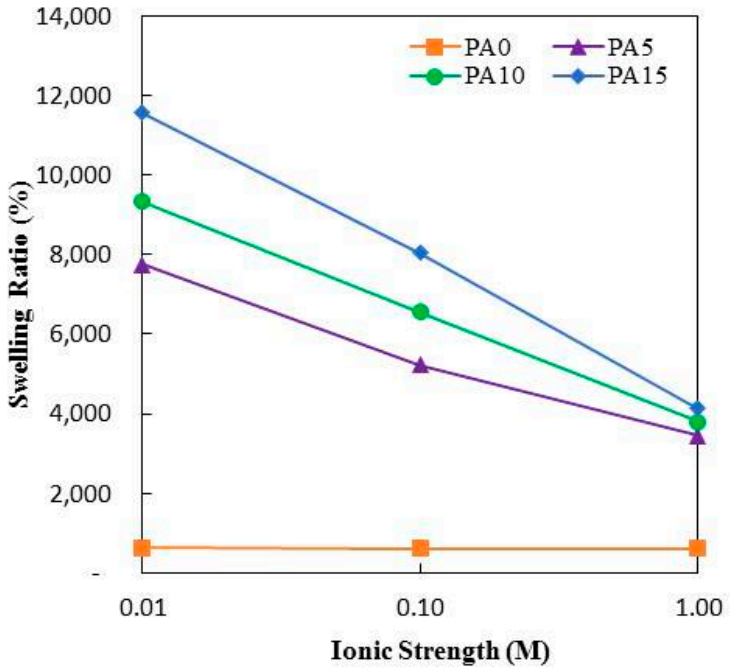

Figure 9. Effect of ionic strength on swelling ratio of PA hydrogels prepared at radiation dose 30 kGy.

4. Conclusions

pH-sensitive hydrogels with excellent swelling properties were successfully prepared from acrylic acid and polyethylene oxide by the application of gamma radiation without any chemical additives. The radiation method is very advantageous to other chemical preparation processes. The structure of the prepared hydrogel was investigated by FTIR spectroscopy. SEM analysis gave the porous structural information about the hydrogel morphology. There were remarkable impacts of radiation doses and monomer concentrations on the basic structure and properties (e.g., swelling behavior, gel fraction, and tensile strength) of hydrogels. The swelling property of the hydrogels was dependent on the acrylic acid content. Gel fraction, swelling ratio, and mechanical strength were increased with increasing acrylic acid content. For example, the gel fraction, swelling ratio, and mechanical properties (tensile strength) increased from 71.56% to 85.95%, 20,915% to 32,096%, and 3.1 KPa to 5.3 KPa, respectively, for the concentration of acrylic acid in the range 5% to 15%. High swelling properties with improved mechanical strengths of these prepared hydrogels might be a suitable candidate for many applications like aquatic fields in pharmacy, agriculture, environmental, biomedical applications, and water purification.

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Conflicts of Interest: The authors declare no conflict of interest.

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