Synthesis and Characterization of Chitosan/Polyvinyl Alcohol Crosslinked Poly(N-Isopropylacrylamide) Smart Hydrogels Via γ-Radiation

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Submission date: 08-Jan-2023 06:51AM (UTC+0700)
Submission ID: 1989603978
File name: MATPR-Barleany-Template_edit_07012023_tanpareferensi.docx (1.49M)
Word count: 3433
Character count: 18628

<ICChEAS 2022_barleany>

Materials Today: Proceedings

Synthesis and Characterization of Chitosan/Polyvinyl Alcohol Crosslinked Poly(N-Isopropylacrylamide) Smart Hydrogels Via γ-Radiation

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Abstract

Chitosan-based smart hydrogels with stable mechanics and good flexibility have many desirable qualities and broad applications. In this study, novel smart hydrogels of chitosan crosslinked with poly(N-Isopropylacrylamide) (pNIPAAm) and polyvinyl alcohol (PVA) were synthesized through freezing and thawing procedures followed by gamma (γ)-radiation at room temperature. The effect of γ-irradiation dose on the gel fraction and water absorption characteristics of chitosan/pNIPAAm hydrogels was investigated. In addition, the structure-property behaviour of the hydrogels was characterized using Fourier Transform Infra-Red (FTIR) spectroscopy and thermogravimetric analysis (TGA). The experimental results revealed that the hydrogels synthesized with a 15- kGy total dose showed a higher gel content (83.73%) compared to 5-kGy and 10-kGy total doses, while the appropriate dose of γ-radiation to achieve the highest absorption in water (484.146%) was 5-kGy. The hydrogel characterization test confirmed that cross-linking occurred between pNIPAAm, PVA, and chitosan. A higher the radiation dose resulted in more cross-links in the hydrogel and resulted in better thermal stability. This study confirmed that chitosan/PVA cross-linked pNIPAAm hydrogel with dual pH/temperature stimuli-responsiveness holds promise for various applications.

Keywords: Chitosan; Dual-Responsive; Hydrogel; Radiation; Smart Material;

1. Introduction

Hydrogels are three-dimensional cross-linked polymeric networks having the capability to hold a large amount of aqueous solvents and biological fluids within their structures [1]. Hydrogels have emerged as smart materials and have shown great potential in many applications because of their features which are responsive to various external stimuli [2]. Hydrogels as stimuli-responsive polymers display a sharp transition in physicochemical characteristics under a small change in environmental conditions, such as pH, temperature, ionic strength, light exposure, magnetic field, electrical field, ultrasound, etc [3]. With an array of triggering mechanisms, these stimuli-responsive hydrogels allow precise control over basic material properties, such as physical structure, porosity, swelling, and modulus [4]. Their ability to change their conformation and properties when stimulated at different conditions causes them to be used prominently in wastewater treatment [5], sustained release of agrochemicals [6], food science [7], and biomedical field [8].

Smart hydrogels prepared from polysaccharides have many advantages because of their attractive characteristics including biocompatibility, biodegradability [9], self-healing, and responsiveness to environmental stimuli [10]. Among them, chitosan is an excellent excipient because it is an abundant and natural polysaccharide which has many amazing properties such as low toxicity, high biocompatibility, desirable biodegradability [11], and antimicrobial activity [12]. Chitosan which is a derivative of chitin, a natural polymer extracted from crab and shrimp shells, exhibits pH sensitivity and polycationic properties. The external and environmental pH affects the swelling and shrinking behaviour of chitosan-based hydrogel derived from the protonation/deprotonation of the primary amine group (NH_2)

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[13]. Because of its responsive properties, chitosan is to become an advanced biopolymer in the development of smart polymeric delivery systems [3].

Chitosan has hydrophilic (-OH) and hydrophobic (-NH_2) groups which can be easily modified with other natural or synthetic polymers through physically or chemically cross-linked reactions [14] to produce hydrogels with different stimulus responses. In addition to the pH, the temperature is also one of the most exploited stimuli in 3-dimensional networks because it is easy to measure, set and use in testing [13], so the dual responsive chitosan-based hydrogel (pH and temperature) has become a tremendous development in recent years [15; 16; 17]. To improve its performance, chitosan can be modified by crosslinking with other moieties/monomers to increase its sensitivity to pH and temperature [18]. The group of thermoresponsive polymers includes poly(N-isopropylacrylamide) [16; 17; 19), poly(N,N-diethylacrylamide) [20], and poly (N-vinylcaprolactam) [21].

Poly(N-isopropylacrylamide)(pNIPAAm) is a thermoresponsive polymer which is applied in a wide range of promising applications because of its well-defined structure and characteristics especially its temperature sensitivity which is close to a lower critical solution temperature (LCST) [22]. Thus, the pH sensitivity of chitosan and the volume phase transition temperature of pNIPAAm have attracted the interest of various scientists to develop materials as carriers and controller the release of active substances [16; 23].

A relatively simple and inexpensive technique, that does not involve the use of toxic chemical agents and allows simultaneous sterilization of crosslinked polymers, is radiation induction [24]. A previous study used radiation as the crosslinking agent to produce graft copolymers [25], and another previous study used the irradiation method to reduce and control polysaccharides' molecular weight distribution to adjust their water solubility and gelling ability [26]. To increase the swelling ability and mechanical strength of the hydrogel, modification of the radiation method combination with other methods such as freeze-thawing has been successfully carried out by several researchers. γ-Irradiation combined with freeze-thawing was applied to synthesise pH-responsive hydrogels from poly(vinyl alcohol) (PVA) and water-soluble chitosan (ws-chitosan) [27], while PVA/carboxymethyl-chitosan (CM-chitosan)/honey hydrogels were prepared using radiation technique and a combinational method (radiation followed by freeze-thawing) [28].

In this work, novel dual responsive hydrogels from chitosan and N-isopropylacrylamide (pNIPAAm) with the addition of polyvinyl alcohol (PVA) were fabricated by introducing the combination method of freeze-thawing and γ-irradiation to induce cross-linking. Reports on swelling studies of hydrogels having a dual response to pH and temperature from a combination of 3 ingredients namely chitosan, pNIPA and PVA prepared using the freeze-thawing method followed by gamma radiation have not been found. The influence of γ-radiation dose on the gel content, the swelling properties, and the hydrogel thermal characteristics was examined in this study.

2. Materials and methods

2.1. Material

Chitosan (industrial grade, deacetylation degree of 85%, Biotech Surindo), poly(N-isopropylacrylamide) (pNIPAAm; Aldrich), polyvinyl alcohol (PVA; Merck), acetic acid (glacial, Merck), pH buffer (3, 5, 9), and distilled water were used throughout the experiment.

2.2. Preparation of pH- and Thermo-responsive Hydrogels

A total of 0.5 g of chitosan was added into 50 ml of 1 % (v/v) acetic acid solution under a stirring condition to form a chitosan solution. Meanwhile, distilled water as much as 100 ml was added into a bottle containing 5 g of PVA, then the bottle was closed and heated in an autoclave at 121°C for 30 min. PVA solution was then brought out from the autoclave and cooled at room temperature. After that, 10 ml of PVA solution was mixed with 10 ml of chitosan solution. Then, 0.5 g of pNIPAAm (0.5 g) was added to the mixed solution and then followed by a stirring process at room temperature. The final solution as much as 5 ml was taken and kept in 5-ml tubes and continued with 3 cycles of freezing and thawing procedure, where each cycle was run for 24 h (12 h for freezing and 12 h for thawing). After the freezing and thawing procedure, the samples were γ-irradiated under a constant rate of irradiation dose (2.5 kGy/min) at room temperature. The total dose of γ-irradiation for each sample was varied to 5, 10, and 15 kGy. After the irradiation process, the physical samples turned into gels. At this stage, the resulting gels are known as hydrogels. Then, the hydrogels were cut into small sizes (approximately 20 mm^2) and characterised.

2.3. Testing and Characterization

2.3.1. Transform Infra-Red (FTIR)

The samples were characterised using FTIR (Shimadzu IR – Prestige 21) to confirm the presence of functional groups of chitosan, pNIPAAm, and PVA in the hydrogels.

2.3.2. Thermo Gravimetric Analysis (TGA)

In this study, the TGA was examined to find the thermal properties of synthesized hydrogels. During the heating process, there was decreasing in the hydrogel weight due to thermal degradation. The thermal characteristics of the hydrogels were measured using DTG-60 TA WS-60 Shimadzu at a temperature in the range of 20 – 600°C.

2.3.3. Swelling study

The swelling behaviour of the non-crosslinked and crosslinked gels was examined by swelling the gels in media at different pHs and temperatures. Pre-weighed dry hydrogels were immersed in pH-5 buffer solutions at a temperature of 30°C for 24 h. The gels were withdrawn from the solutions at different time intervals and their wet weights were determined after the withdrawn gels were absorbed for the first time with filter papers and immediately weighed. The swelling ratio was determined using the equation (1) based on the study reported by Erizal [29].

$$Swelling\ ratio\ (\%) = \frac{w_s}{w_d} \times 100\% \qquad (1)$$

Where swelling ratio also can be named as the water absorption (% wt) of the gels, Wd and Ws are the sample weights in the dry and swollen states, respectively.

2.3.4. Gel Content Measurement

Hydrogel powder as much as 0.01 g (W_0) was packed in the tea bag. Then, the tea bag containing the hydrogel powder was immersed in distilled water for 24 h at room temperature. After that, the tea bag was dried in an oven for 24 h at 60°C and weighed (W_1). Gel content was determined using the equation (2).

$$Gel\ content\ (\%) = \frac{w_1}{w_0} \times 100\% \qquad (2)$$

where w_1 is the dried gel weight (g) and w_o is the initial gel weight (g).

2.3.5. SEM Study

The superabsorbent hydrogel samples were soaked for 24 h until a swelling equilibrium was reached and then frozen for 24 h. The samples were dried using a freeze dryer at -105°C and then coated with a thin layer of gold and analyzed by using a Scanning Electron Microscope (SEM) EDX Carl Zeiss EVO MA10.

3. Results and discussion

3.1. Structure Analysis

Chemical modifications induced by the irradiation process are analyzed using FTIR. The spectra of nonirradiated and irradiated hydrogels are showed in Fig. 1 and marked with arrows. The FTIR shows peak shifts caused by interactions between two or more polymer mixtures used through hydrogen bonding, formation of coordinate bonds, or any other complex. The spectra that emerge from an FTIR image can produce the same characteristic features as individual polymers or sometimes several of the band shifts from their original position [30].

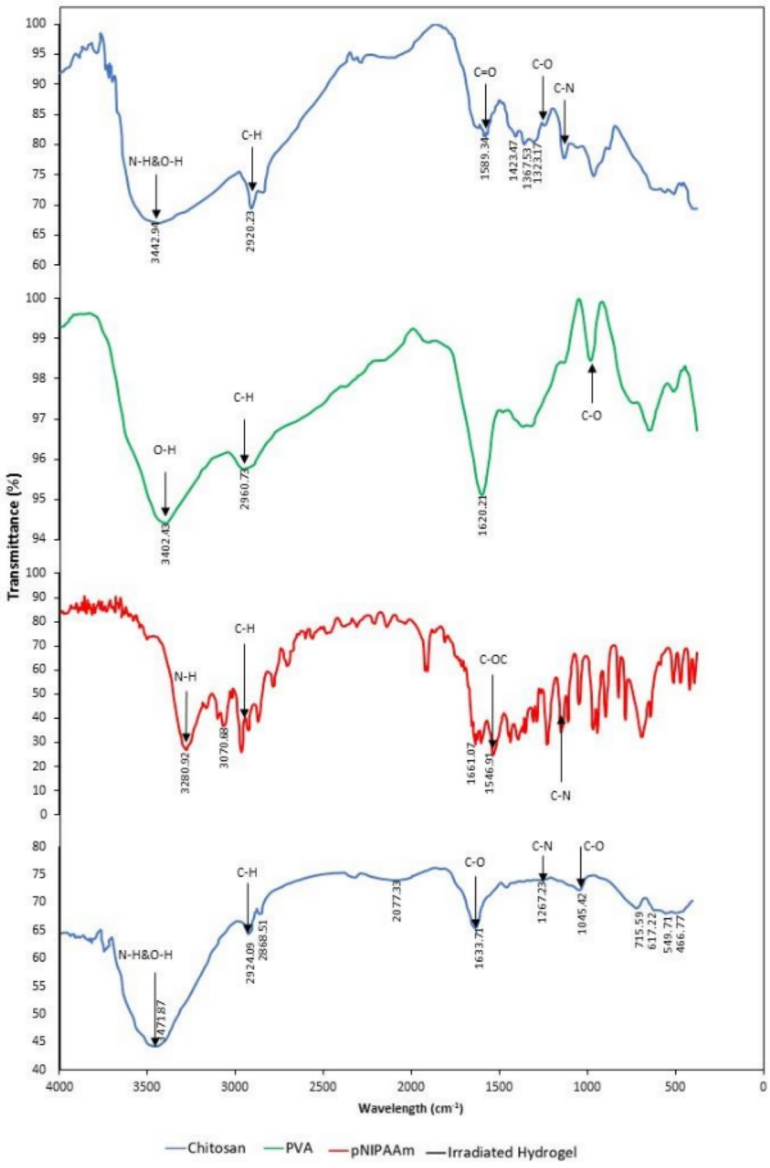

Fig. 1. FTIR spectra

In the spectrum of PVA, the peaks are observed at 3402.4 cm^{-1}, corresponding to the O-H groups. The absorbance at 2960.73 cm^{-1} can be attributed to the CH stretching, and the absorbance at 1004.96 cm^{-1} corresponds to the C=O stretching. In the spectrum of pNIPAAm, the absorption bands at 3280.92 cm^{-1}, 3070.35 cm^{-1}, 1546.91 cm^{-1}, and 1170.24 cm^{-1} are attributed to stretching vibration absorption peaks of –NH, C-H, C=O, and C-N, respectively. The spectrum of chitosan shows the peak at 3442.94 cm^{-1} which is attributed to O-H and N-H, the peak at 2920.23 cm^{-1} which corresponds to C-H, and the absorbances at 1589.34 cm^{-1}, 1255.45 cm^{-1}, and 1154.25 cm^{-1} which are attributed to C=O, C-O, and C-N, respectively. When the mixture of chitosan-pNIPAAm-PVA is irradiated, the grafted hydrogel is produced, and its FTIR spectrum is presented in a curved shape. The irradiated hydrogel spectrum confirms the N-

H & O-H groups at a wavelength of 3471.87 cm^{-1}, C-H groups at a wavelength of 2924.09 cm^{-1}, C=O groups at a wavelength 1633.71 cm^{-1}, the C-N group at a wavelength of 1267.23 cm^{-1} and the C-O group at a wavelength of 1045.42 cm^{-1}.

It is found that the spectrum of the hydrogel has the same peaks as the peaks of the spectra of chitosan, pNIPAAm, and PVA, but the intensity of the peak at 3471.87 cm^{-1} is lower compared to that of the same peak in the spectra of chitosan and pNIPAAm. The O-H and N-H groups in the hydrogel have a long, tapered and broad spectrum shape with relatively low intensity, different from the O-H groups in PVA and chitosan, and the N-H groups in pNIPAAm and chitosan which tend to be a short shape with higher intensity. It confirms that chitosan, pNIPAAm, and PVA are crosslinked to form an interpenetrating network which causes the accumulation of O-H and N-H groups so that the spectral form is longer and wider with lower intensity [17, 31, 32].

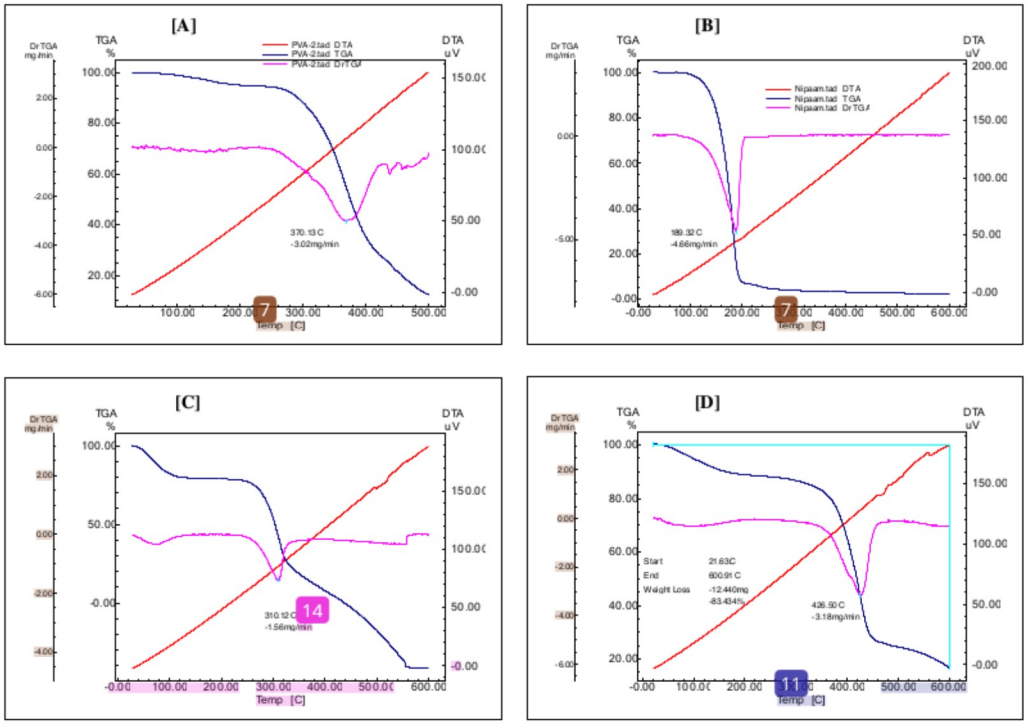

Fig. 2. Thermograms of the reactants and the irradiated hydrogel: A) PVA, B) pNIPAAm, C) chitosan,) irradiated hydrogel

The thermograms (Fig. 2) show changes in the weight of a compound as a function of temperature and time. The Fig. 2 (A) shows the thermogram of PVA. The PVA as much as 10 mg is heated at the temperature range of 20°C to 500°C for 2 h. In the beginning, the PVA sample shows small weight loss due to water evaporation at ±100-200°C, and then the sample weight is continuously degraded. Significant weight loss of PVA is performed at a temperature of 260°C until 500°C. The melting point of PVA is 200°C. Based on TGA (DTG-60) analysis, the biggest value of PVA weight loss is -3.02 mg min^{-1} which is obtained at a temperature of 370.13°C. Furthermore, the Fig. 2(B) shows the thermogram of pNIPAAm. The pNIPAAm as much as 10 mg is heated from 25°C to 600°C for 115 min. At the heating temperature range of ±100-200°C, the weight of pNIPAAm decreases. Based on TGA (DTG-60) analysis, the biggest pNIPAAm weight degradation occurs at a temperature of 189.32°C with a degradation rate of -4.66 mg min^{-1}. The Fig. 2(C) shows the thermogram of chitosan. The chitosan as much as 10 mg is heated from 25°C to 600 °C for 115 min. Water evaporation occurs in the chitosan sample at a heating temperature of ±30-100°C. The significant decrease in chitosan weight is performed at 260°C and the weight starts to be constant at 560°C. Based on TGA (DTG-60) analysis, the biggest value of chitosan weight loss is -1.56 mg min^{-1} which is obtained at

310.12°C. Moreover, after the thermal process, the weight of hydrogel resulting from γ-irradiation dose of 5 kGy decreases by -83.434 %, as shown in Fig. 2 (D). That value represents the number of hydrogels that are degraded as a result of heat treatment.

The thermal decomposition characteristics of pNIPAAm and chitosan shown in Fig. 2 (B) and Fig. 2 (C) are similar to the results published in a previous study on pH and thermosensitive hydrogels, where the weight of pNIPAAm was reduced more than that of chitosan at high temperature treatment[33]. Another previous study also proved that the introduction of PVA made the thermal decomposition of chitosan hydrogel change to a higher temperature [34]. The weight loss of the hydrogel due to heat treatment is smaller than the weight loss of its raw materials such as PVA, pNIPAAm, and chitosan. The high value of the hydrogel weight loss is correlated to the impurities contained in the samples and the crosslinking homogeneity of the polymer. These results reveal that the radiation causes a rapid cross-linking and affects the increase in the polymer's thermal stability indicating difficult decomposition and a high flame-retardant effect [35].

3.2. Effect of irradiation dose on the gel contents and swelling properties

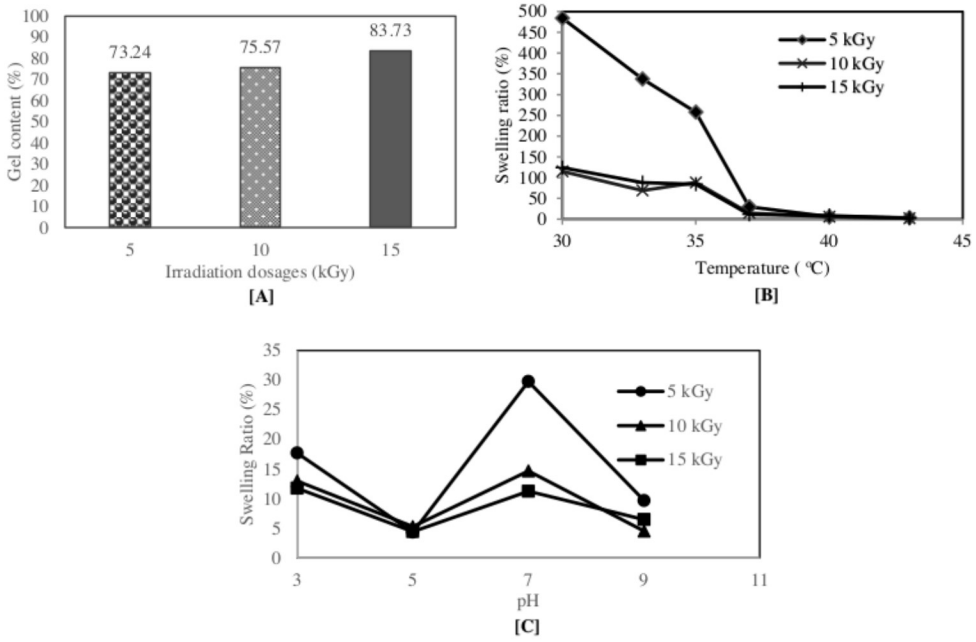

Fig. 3. Physical characteristics of the irradiated hydrogels: [A] gel content, [B] swelling study at different temperatures (pH 7), [C] swelling study at different pHs (temperature 30°C)

Fig. 3(A) shows the gel contents of the resulting hydrogels at various total irradiation doses. The gel content data shows that there are enhancements in gel content with the addition of total irradiation doses. A higher dose produces a higher conversion, and as a result, a higher gel content in the hydrogel can be reached. The gel content increases with the increase in the total irradiation dose [36]. It is well-known that gel content and swelling ratio can also be correlated with crosslinking density. It means that the greater the gel content, the higher the crosslinking density. Similar results with this study were obtained in hydrogel synthesis using the γ-radiation method from poly(acrylic acid) and poly(ethylene glycol)diacrylate loaded with Ca^{2+} [37] and gelatin-poly (γ-glutamic acid) [38]. Furthermore, a previous study found that chitosan crosslinked pNIPAAm hydrogels exhibited an increase in grafting percentage and grafting efficiency with the increase in the dose due to the increasing concentration of free radicals formed in the polymer substrate [39].

At pH 7, the swelling ratio decreases significantly with an increase in temperature from 30 °C to 37 °C, and then the swelling ratio is constant from a temperature of 37°C to 43 °C (Fig. 3(B)). It means that the hydrogels resulting from this research have the LCST (Lower Critical Solution Temperature) value of 37°C. The pNIPAAm has hydrophilic and hydrophobic groups affecting unique swelling and deswelling behaviour. The hydrogel swells at a temperature below the LCST and de-swells at a temperature above the LCST. The amount of hydrophilic groups (-NH) and hydrophobic groups (alkyl) in pNIPAAm influences the value of LCST. Hydrophilic groups are commonly weak, so the bonds are easily broken and crosslinked with suitable groups from other materials. The increase in irradiation dose causes a decrease in swelling capacity at various pH conditions. More crosslinked bonds formed due to the irradiation process result in some difficulties for water or aqueous solution to be absorbed into the hydrogel matrix. The swelling behaviour of the hydrogel at different pHs is shown in Fig. 3(C). The highest swelling ratio is reached at pH 7, while de-swelling occurs at pH 9. Unique swelling properties at different pHs are affected by the hydroxyl group (-OH) and amine group ($-NH_2$) in chitosan [40].

3.3. SEM Analysis

In this study, SEM analysis is carried out on hydrogels which have the highest swelling ratio values at various temperatures and pH, namely temperature 30°C and pH 7. SEM test results for the hydrogels prepared by freeze-thawing followed by irradiation at various magnifications are shown in fig. 4.

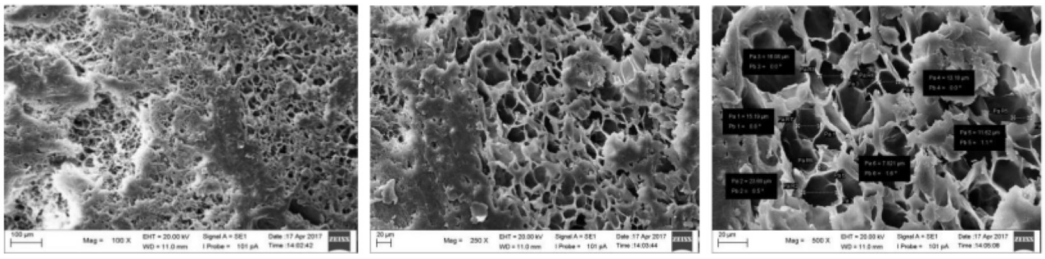

Fig. 4. Irradiated hydrogel SEM image after swelling condition at a temperature of 30°C and pH 7

Fig. 4 shows the hydrogel morphology and pore size during the swelling test at 30°C and pH 7. It can be seen from the Fig. 4 that the hydrogel has relatively uniform pores with an average diameter of 14.6 μm. The results of the SEM analysis show the large hydrogel pore size because at 30°C and pH 7 the hydrogel experiences swelling with the greatest ratio compared to other temperatures and pHs, and as a consequence, there is a change in the network structure. Changes in the structure of the hydrogel network will result in changes in the diameter size after swelling conditions.

A previous study [27] stated that the method of hydrogel synthesis by freeze-thawing and freeze-thawing followed by irradiation produced larger pores compared to irradiation and irradiation followed by freeze-thawing, but resulted in a smaller swelling value. The pore size is influenced by the hydrogel preparation method in the initial step, but the large pore size does not guarantee the large swelling ability of the hydrogel. The fact is that this current research is carried out using the freeze-thawing stage followed by irradiation and produces the greatest swelling at a temperature of 30°C and a pH of 7 compared to other temperatures and pHs (Fig. 3). The obtained results need to be compared with previous studies to find a correlation between pore size and the swelling ability of the hydrogel. Based on the results of the swelling test, it indicates that the hydrogel has an LCST of 37°C at pH 7. At 30°C, the pore size of the hydrogel will be larger than at 37°C and 43°C. This is because at 30°C and pH 7 the hydrogel has not yet been at LCST temperature so the pores and diameter size of the hydrogel have not undergone a contraction or shrinking process. This is confirmed by a statement that pNIPAAm-based polymer excretes its fluids at a temperature close to that of the human body ~ 37°C [41].

4. Conclusion

In this work, pH and thermoresponsive hydrogels are successfully synthesized from chitosan, pNIPAAm, and PVA using freezing and thawing methods followed by the γ-irradiation method. The hydrogel with the highest value of gel content (83.73 %) is obtained by the use of 0.5 g of pNIPAAm with a total radiation dose of 15 kGy. The hydrogel

with the highest swelling ratio (484.146 %) is obtained by the use of 0.5 g of pNIPAAm with a total radiation dose of 5 kGy at a temperature of 30°C and a pH of 7. The increase in total radiation dose increases the gel content, and decreases the swelling ratio, but does not give a significant effect on the LCST value. This work confirms that the LCST of the hydrogel is correlated to the pH condition.

Acknowledgements

The financial support from the Ministry of Education, Culture, Research, and Technology of the Republic of Indonesia through the National Competitive Basic Research Grant (No. B/439/43.9/PT.00.03/2022) is greatly appreciated.

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