Effect of Crosslinking Agents, pH and Temperature on Swelling Behavior of Cross-linked Chitosan Hydrogel

Emil Budianto*, Siti Prilia Muthoharoh, Noverra Mardhatillah Nizardo

[1]Department of Chemistry, University of Indonesia
KampusUI Depok, Depok, 16424, West Java, Indonesia

Corresponding author's email: emilb [AT] ui.ac.id*

ABSTRACT— Superabsorbent hydrogels are able to absorb and keep large amounts of aqueous fluid. Superabsorbent polymer based crosslinked chitosan hydrogels were synthesized by crosslinking chitosan with various crosslinking agents, i.e. formaldehyde, acetaldehyde and glutaraldehyde. The Swelling behavior of the crosslinked chitosan hydrogels was measured by immerse the gels and the effect of crosslinking agent on water absorbency has been investigated. The crosslinked chitosan hydrogel by acetaldehyde exhibited a higher swelling ratio up to 350%. The influence of external stimuli such as pH and temperature of the swelling media has been observed. Hydrogels showed a typical pH and temperature responsive behaviour such as low pH (pH 4) and high temperature (55^{o}C) has maximum swelling while high pH (pH 10) and low temperature (35^{o}C) show minimum swelling. The film of crosslinked chitosan hydrogels were characterized by Fourier Transform Infrared Spectroscopy(FTIR).

Keywords— Superabsorbent, Chitosan, Hydrogel, Crosslinking, Swelling

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1. INTRODUCTION

Hydrogels are crosslinked three dimensional hydrophylic polymer network that can absorb water or biological fluid. The network may be chemically or physically. Superabsorbent hydrogels have the ability to absorb large quantity of aqueous fluids and keep the fluids inside their structure [1,2]. Due to their unique properties, the research of superabsorbent hydrogels increases significantly in recent year to be applied in several fields, namely medical, pharmacy, chemistry, food packaging, paper industry, holticulture, and oil drilling [1].

Chitosan is a compound which can be prepare as superabsorbent hydrogels. Chitosan is a natural polymer which composed from copolymer of 2-glucosamine and N-acetyl-2-glucosamine and a derivation of chitin by deacetylation. Besides its absorbsion capability, the biocompatibility and biodegradability of chitosan make chitosan to become a popular material in the research of hydrogels, especially in pharmaceutical and medical application [3, 4, 5, 6].

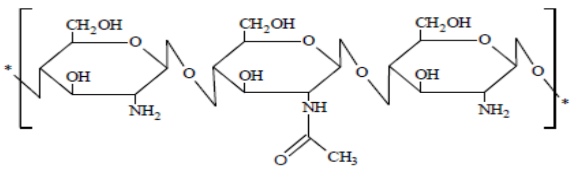


Figure 1. Structure of chitosan

However, the hydrogels may have poor mechanical stability. In order to increase their mechanical stability, chitosan hydrogels is crosslinked with crosslinker, such as glutaraldehyde [7].

In this paper, the effect of crosslinking agents (formaldehyde, acetaldehyde, glutaraldehyde) and concentration of crosslinking agents on swelling and degree of crosslinking in chitosan hydrogels will be reported. The paper reports also effect of external stimuli such as pH and temperature on swelling behavior of cross-linked chitosan hydrogel. The hydrogels were characterized by dertermining their swelling behaviour, degree of crosslink, and infrared spectroscopy.

2. MATERIALS AND METHODS

Materials
Chitosan powder (MW 200,000g/mol; degree of deacetylation 85%; PT. Biotech Surindo). Formaldehyde 37% (Merck-Darmstadt, F. R. Germany), acetaldehyde 99% (Merck-Schuchardt, Germany), glutaraldehyde 70% (Sigma-Aldrich Chemie). All materials were used as received.

Chitosan solution 2% (w/v)
Chitosan powder of 2 grams were weighed and then dissolved in 1% acetic acid (v/v) and stirred mechanically in room temperature.

Preparation of crosslinked chitosan hydrogels Various crosslinker compositions (1, 1.5, 2mL) were added into chitosan solution 2% (w/v). The crosslinker types being used were 0.1M formaldehyde, 0.1M acetaldehyde, and 0.1M glutaraldehyde. The crosslinking reaction were performed in room temperature and various reaction time (30, 60, 120 minutes). Variation of cross-linked concentrations is shown in Table 1.

Chitosan hydrogel film synthesis
Resulting crosslinked chitosan hydrogel was poured into container and dried overnight at room temperature. After that, these samples were dried in the oven at 60ºC so that they dried completely.

Swelling determination of chitosan hydrogels
The swelling behaviour of the chitosan hydrogels were determined. Dry film chitosan hydrogels were weighed and then immersed in distilled water for 30 minutes. In this part, temperature (35, 45, 55ºC) and pH (4, 7, 10) were varied. After that, the samples were blotted to remove excessive surface water with filter paper. Finally, the swollen hydrogels samples were weighed and the swelling ratio was determined by equation 1.

$$\%\,Swelling = \frac{Ws - Wd}{Wd} x100 \qquad (1)$$

Where Ws is the weight of swollen hydrogels and Wd is the weight of dry film [4].

Degree of crosslinking determination
A weighed amount of chitosan hydrogel film were extracted by immersing them in acetic acid for 24 hours. Then, they were dried to a constant weight in oven at 60ºC. After that, the degree of crosslinking was calculated gravimetically as equation 2 below:

$$\%DC = \frac{Wg}{W0} x100 \qquad (2)$$

Where Wg is the weight sample after extraction and W_0 is before extraction [6].

Structure chitosan hydrogels determination
Crosslinked chitosan hydrogel films were characterized by FTIR (IRPrestige-21, Shimadzu).

Table 1. Variation used in this experiment

Crosslinking agents	Volume (mL) of crosslinking agents	Reaction time (minutes)
Formaldehyde 0.1M	1 mL, 1.5mL, 2mL	30min, 60min, 120min
Acetaldehyde 0.1M		
Glutaraldehyde 0.1M		

3. RESULTS AND DISCUSSION

Effect of reaction time on chitosan hydrogels

The yellowish chitosan hydrogels were formed after the reaction time of 1 hour as shown in Figure 2. This result is the same as previous result [4,6]. The film of chitosan hydrogels was made to simplify the characterization because it has good mechanical and barrier properties [8].

Figure 2. Crosslinked chitosan hydrogel film

In order to know, whether the hydrogels were completely cross-linked, the swelling ratio was determined. Figure 3 showed that the percentage of swelling ratio decreased with increasing reaction time. Crosslinking reaction is often undertaken to reinforce the hydrogels structure. Also, it improves the physical and mechanical properties of the hydrogels [9]. The crosslink between amine group in chitosan with carbonyl group in crosslinker might be increased by increasing reaction time. Hence, not only the mechanical properties of this hydrogels is better, but also the structure become stronger and denser. This caused the decreasing of swelling capability of this hydrogels [6].

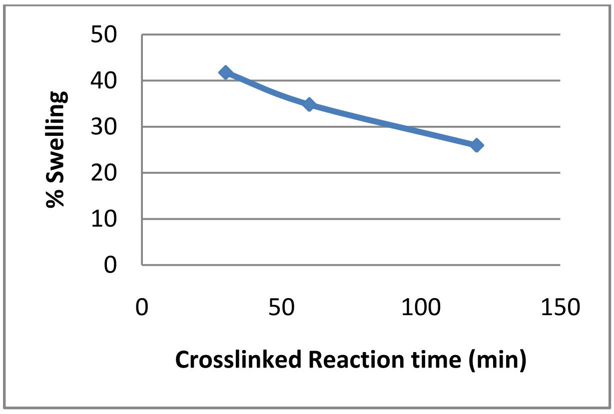
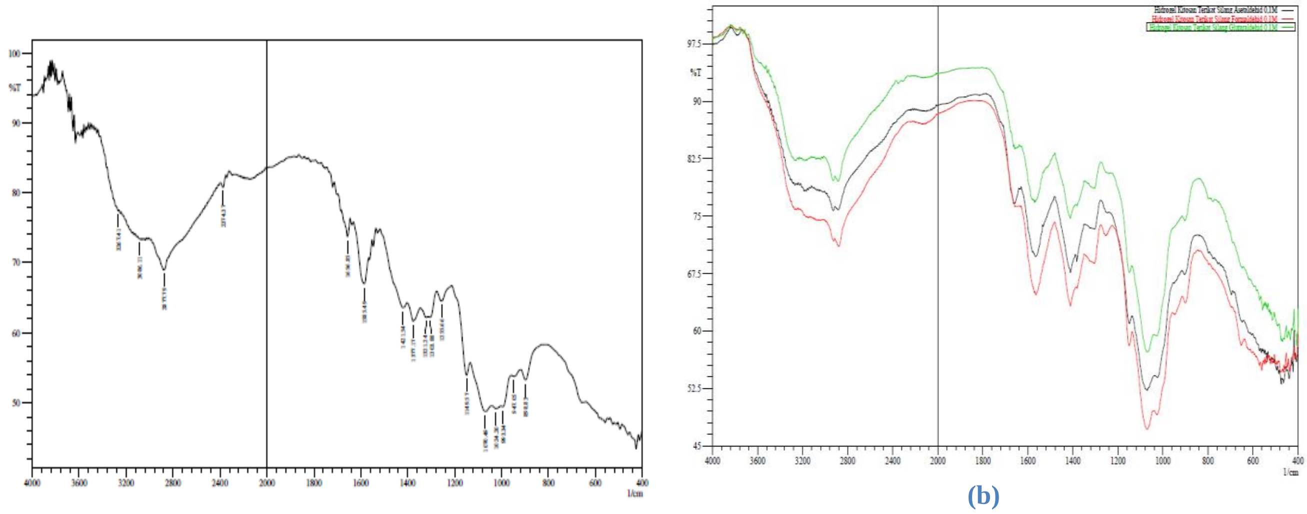


Figure 3. Effect of reaction time on swelling ratio

Thus, one may conclude that the chitosan hydrogels were crosslinked with the reaction time of 120 minutes.

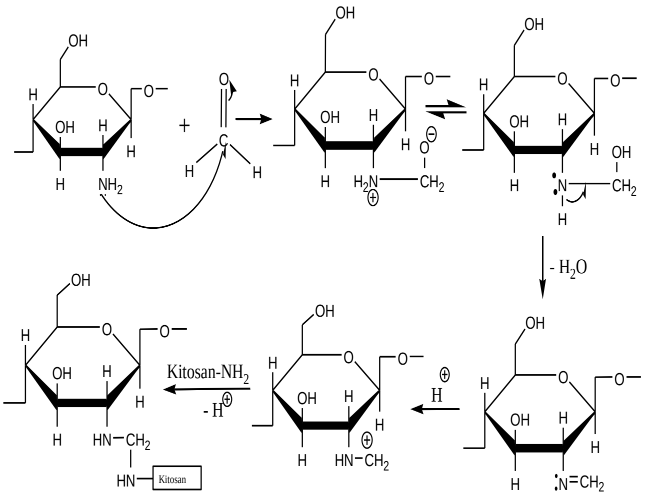
Effect of crosslinking agent types and amount of crosslinking agents on swelling of chitosan hydrogels

It is shown at IR spectra on Figure 4 (a) that the specific peak of chitosan is broad in the range of 3500-3000 cm^{-1}1592-1550 cm^{-1}, which represent the hydroxyl and amine group respectively. It is shown also that the carbonyl stretching vibration occured at 1656 cm^{-1}which lead to carbonyl residue of acetamide group in chitin.
On the other hand, Figure 4 (b) shows that the intensity of amine groups(1560-1580 cm^{-1}) decreases as the changing of crosslinker type (formaldehyde, acetaldehyde, and glutaraldehyde). This peak proves that the base schiff after crosslinking reaction has been formed as the mechanism shown in Scheme 1 [10].



(a) (b)

Figure 4. Infrared spectrum of chitosan (a) and chitosan hydrogel film with various crosslinker: glutaraldehyde (green), acetaldehyde (black) and formaldehyde (red) (b)



Scheme 1. Cross-linked reaction between chitosan with formaldehyde

It was explained in previous research that the molecular interaction between chitosan and glutaraldehyde was in the crosslinking site of amine group [11]. Therefore, the more amine group in chitosan hydrogels crosslinked, the less amine will be transmitted.

In order to know further, how strong the crosslinking of these chitosan hydrogels is, degree of crosslinking was determined. Figure 5 tells us that the physical appearance of chitosan hydrogel crosslinked with glutaraldehyde were quite able to maintain its form. The results of degree of crosslinking measurement in Figure 7 is also confirmed the stability of chitosan hydrogel crosslinked with glutaraldehyde, while it had the highest degree of crosslinking of 91%. Meanwhile, chitosan hydrogels crosslinked with formaldehyde and acetaldehyde got degree of crosslinking of 72.5 and 38% respectively. Figure 7 also shows that the more volume of crosslinking agent is, the higher degree of crosslinking is. This occured because of the structure difference of these three crosslinking agents (Figure 6), where glutaraldehyde has two carbonyl groups (C=O), which more likely react with amine groups in chitosan backbone to form crosslinking site. Thus, the crosslinking reaction between chitosan and glutaraldehyde happened faster and the structure is more rigid than with formaldehyde and acetaldehyde.

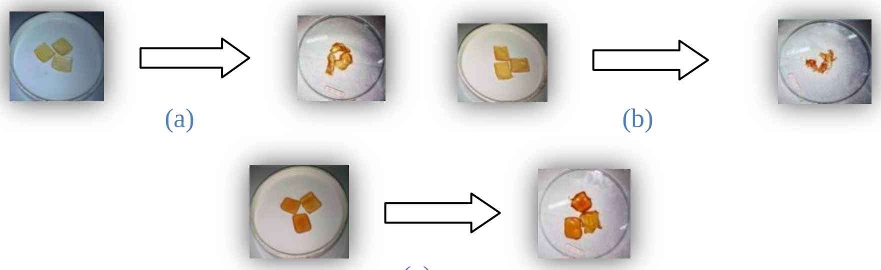


Figure 5. Physical appearance of crosslinking degree determination of cross-linked chitosan hydrogel film with (a) formaldehyde, (b) acetaldehydeand (c) glutaraldehyde

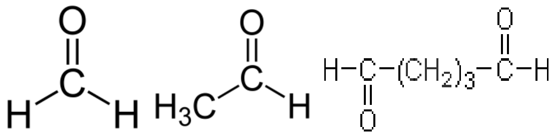


Figure 6. Structure of (a) formaldehyde, (b) acetaldehydeand (c) glutaraldehyde

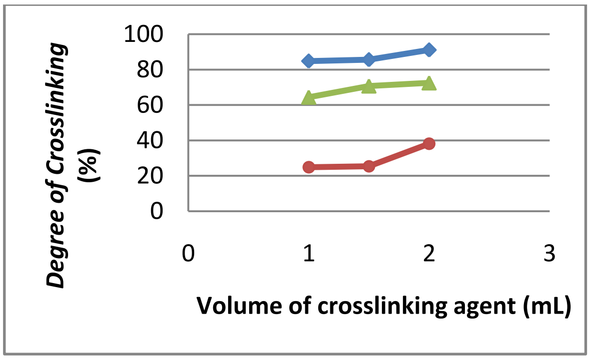


Figure7.Degree of crosslinking of chitosan hydrogel film with glutaraldehyde (blue), formaldehyde (green)and acetaldehyde (red) at various volume

Figure 7 and 8 show the trends of degree of crosslinking and swelling ratio of chitosan hydrogel film respectively. It can be informed from these graph that swelling ratio is inversly proportional to degree of crosslinking for each crosslinker. This result is the same as Wu and Jin's [12, 13] and can be concluded that the more crosslinking agent being used, the higher degree of crosslinking can be achieved. As consequence of that, the amount of water being trapped inside polymer network was low and caused the low swelling ratio. Hence, the absorbtion and swelling ability of chitosan hydrogels depend on hydrophylic groups and degree of crosslinking [4]. By looking at Figure 8, it is concluded that chitosan hydrogelswith 1mL acetaldehyde gave the highest swelling ratio of 350%, while formaldehyde and glutaraldehyde crosslinker gave lower swelling ratio of 150% and 50% respectivrly.

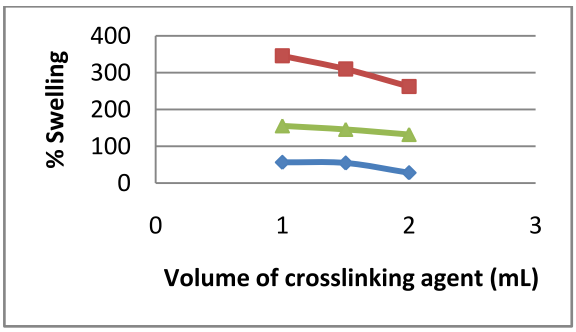


Figure 8.Swelling Ratio of cross-linked chitosan hydrogel film with acetaldehyde (red), formaldehyde (green), and glutaraldehyde (blue)

In addition, the strengthness of polymer hydrogel was affected by the amount of added crosslinking agent. It is shown in Figure 9, that crosslinked chitosan hydrogels with volume of crosslinker of 1mL had the highest swelling ratio and it decreased along with increasing crosslinker volume. The lower amount of crosslinking agents is, the lower the strengthness is, so that the structure can expand flexibly while absorbed its medium. However, since the degree of crosslinking was low, the hydrogels could probably be break and dissolved in its medium [14]. This condition was very suitable to make chitosan hydrogels as biodegradable superabsorbent.

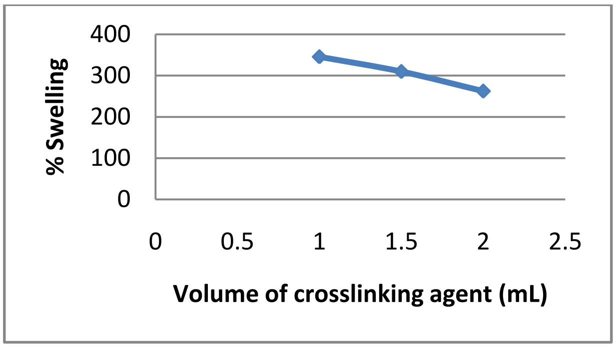


Figure 9.Swelling Ratio of cross-linked chitosan hydrogel film with acetaldehydeat various volume

Effect of pH on swelling chitosan hydrogels

Swellingis a phenomenonin which water or biological fluid trapped in polymer network. The ability of hydrogels to swell depends on their chemical structure and characteristic of its media [10]. Figure 10 shows that the maximum swelling of chitosan hydrogels was reached in the acid condition and it decreases along with increasing pH value of its medium. This is due to the fact that the concentration of H^+ was high in low pH and this increased the protonation of amine group to chitosan to form $–NH_3^+$. Thus, the polymer chains within hydrogels are repealed each other. However, by increasing pH, the amine groups were deprotonated, hence the repulsion between polymer chains in hydrogels decreased. This leads to rigid structure of hydrogels and reduced their absorption ability [4,9, 15,16] and the process is already described by Hyunmin [17].

pH acidpH base

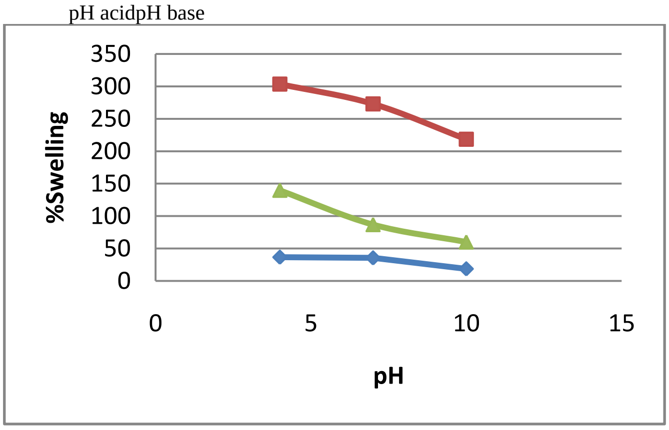


Figure 10.Effect pH on swelling ration of cross-linked chitosan hydrogel film with acetaldehyde (red), formaldehyde (green) and glutaraldehyde (blue)

The explanation from swelling behavior in Figure 10 is as follow: chitosan hydrogels with cross-linker of acetaldehyde had low degree of crosslinking, so that the percentage of swelling ratio got higher [10]. The opposite way was happened with chitosan hydogels using glutaraldehyde as cosslinker, which had the highest degree of crosslinking among all, got the lowest swelling ratio. Thus, degree of crosslinking is indeed affects the swelling ratio of hydrogels in various pH.

Effect of temperature on swelling ratio of chitosan hydrogels

Figure 11 describes the swelling behavior of chitosan hydrogels in various temperature. From the chart, one can see that increasing temperature leads to increasing swelling ratio. The reason for that is because the dissociation of hydrogen bonding of amine groups in chitosan with water molecules inside hydrogels network was likely to occur. Hence, the polymer chains in hydrogel relaxed but this relaxation was still limited by the crosslinker amount and types [10]. Therefore, as it is shown in Figure 11, swelling ratio of chitosan hydrogels with crosslinker of glutaraldehyde were relatively constant. In contrast,when acetaldehyde was used as crosslinker, the swelling ratio of chitosan hydrogels rose significantly.

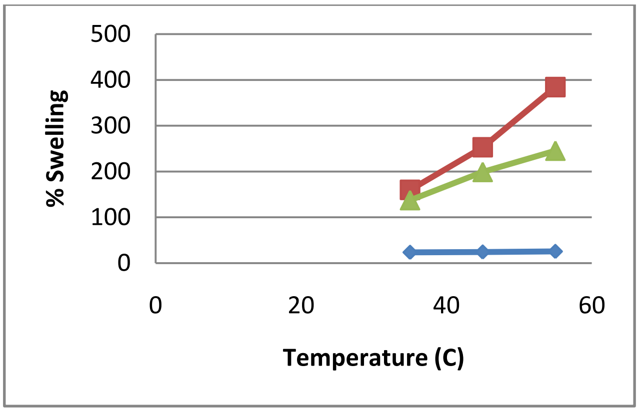


Figure 11.Effect Temperature on swelling of cross-linked chitosan hydrogel film withacetaldehyde (ed), formaldehyde (green) and glutaraldehyde (blue)

4. CONCLUSION

Superabsorbent polymer of chitosan hydrogel were successfully synthesized by varying crosslinking agents i.e. formaldehyde, acetaldehyde and glutaraldehyde. Optimum crosslinking time to prepare chitosan hydrogels is 120 minutes at room temperature. Chitosan hydrogel which is cross-linked by acetaldehyde has high swelling ratio i.e. 350% and good sensitivity to pH and temperature.

5. REFERENCES

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