## Atom Indonesia

# Effect of Starch and Chitosan Addition on Swelling Properties of Neutralized Poly(Acrylic Acid)-Based Superabsorbent Hydrogels Prepared by Using γ-Irradiation Technique

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## A R T I C L E   I N F O

## A B S T R A C T

Superabsorbent hydrogels are polymers with a 3D network that have attracted the attention of scientists and industrialists because of their fantastic ability to absorb and retain water and aqueous solutions. The most widely used and commercially available superabsorbent hydrogels are synthetic K-acrylate materials. In this novel study, superabsorbent hydrogels have been developed using natural ingredients to have more biodegradable properties. Superabsorbent hydrogels were synthesized from acrylic acid, cassava starch, and chitosan using the γ-irradiation method under different experimental conditions. The γ-irradiation technique was chosen to produce hydrogels free of residues that may remain when chemical crosslinkers are used. The effects of irradiation dose, acrylic acid composition, and the amount of cassava starch and chitosan on the characteristics of produced hydrogels were analyzed. The resulting polymers were further characterized by fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) to evaluate the structure. The thermal behavior of superabsorbent products at different neutralization doses was tested with differential scanning calorimetry (DSC). FTIR data indicated that the grafting reaction was successfully implemented in this work. SEM analysis showed that the hydrogel produced from this study was porous and there was a reduction in pore size with the addition of starch and chitosan. It can be concluded that the addition of cassava starch and chitosan affects the acrylic acid-based superabsorbent properties, which are pore size, thermal behavior, gel content, antibacterial activity, and swelling capacity in water, salt, and urea solutions. The best hydrogel was obtained by adding 0.25 g of cassava starch and 0.25 g of chitosan, using 50 % acrylic acid neutralization and 5 kGy γ-irradiation doses. The graft polymers possess the maximum swelling capacity of 670 g/g for distilled water, 520 g/g for NaCl solution, and 767 g/g for urea solution (relative to the dry weight). These products were sterile from *Escherichia coli* bacteria and had the potential to be applied as superabsorbent resins for various fields.

## INTRODUCTION*

In the last 2-3 decades, inventions in materials technology have moved very fast. Superabsorbent hydrogel polymers are three-dimensional networks that have the ability to swell and detain liquid or aqueous solutions in very large quantities within their structure. Hydrogels consist of hydrophilic polymer chains which can be produced by crosslinking, both physically or chemically, from synthetic and natural polymers [1]. Because of their great performance, hydrogels have become very popular in a number of applications, including biomedical materials [2,3], personal disposable hygiene products [4,5], wastewater treatment [6-8],

controlled-release fertilizer [9], and others. Poly(ethylene glycol), poly(acrylic acid), poly(vinyl alcohol), polyacrylamide, poly(vinyl pyrrolidone), and several polysaccharides are the most prevalent materials used to synthesize hydrogels [1].

There are advantages and disadvantages to utilization of synthetic or natural polymers as hydrogel reactants. Petrochemical-products-based materials usually have higher water-absorbing capacity but their penetration performance is relatively poorer. They are also expensive, and their effects to the environment are undesired due to their nonbiodegradability. The biodegradability of natural-polymer-based hydrogels is desirable, but they have poorer water-absorbing and retaining performance [10].

Superabsorbents presently available in the market are made from crosslinked poly-(acrylic acid) [1,8,11]. Acrylic-acid-based gels are cheaper to produce [8]. However, they are not environmentally friendly. Therefore, they are often grafted with natural polymers that can be biodegradable [12]. Research activities on natural-substance-based superabsorbents are attracting increasing interest due to their eco-friendliness and biodegradability. The natural polymers that have received much attention for study are starch [8,9,13,14] and chitosan [11,12,15,16].

Starch is a polysaccharide which in studies is often used as a backbone in developing superabsorbent hydrogel. Many reports related to cassava starch grafted with acrylic acid have been published in recent years. A study has even investigated the biodegradability of the hydrogel synthesized from the acrylic acid and cassava starch composite and proved it to be an environmentally friendly material [9].

In this paper, novel superabsorbent polymers synthesized from neutralized acrylic acid, cassava starch, and chitosan were developed. Chitosan is a very well-known biopolymer derived from chitin. It has unique physical, chemical, and biological properties. It also has a great potential to modify or combine with other polymers [17-19]. For such special needs of superabsorbent resins as baby diapers or any other hygiene products, the antimicrobial activities and non-toxic properties of chitosan are important to obtain products that are safe for humans. In addition, superabsorbent resins grafted with chitosan are able to attain a very high liquid absorption; it can even reach hundreds of times their own dry weight [12]. However, the use of chitosan as a raw material for the manufacture of superabsorbent hydrogels has been limited. The products from chitosan usually have inferior mechanical properties compared to superabsorbents made from other polymers [15]. The grafting of acrylic acid onto cassava starch and chitosan

backbone aimed to yield a good mechanical-quality and high water-absorbency superabsorbent polymer with antimicrobial activity.

To prepare acrylic-acid-based superabsorbents, chemical crosslinkers and initiators are mainly used [11,20-22]. They are toxic components, and their trace in the products may be harmful or unfriendly for some applications, especially for personal care products and medical materials. The production of safe superabsorbents without use of initiators, catalysts, or crosslinkers was published by several researchers. The methods involved the use of microwave irradiation [23,24] and $\gamma$-irradiation [25,26].

In this study, novel superabsorbent resins were prepared through $\gamma$-irradiation technique. This technology is very safe for use in material preparation even for biomedical applications [27]. This method is also environmentally friendly because it does not use any chemical substances as crosslinking agents in the synthesis of superabsorbent hydrogels. The study aimed to find the optimum composition of cassava starch and chitosan in the hydrogel that results in the highest water swelling capacity. The influence of acrylic acid neutralizations and the total doses of $\gamma$-irradiation was also investigated.

## METHODOLOGY

### Materials

The acrylic acid used, as one of the three main materials for producing superabsorbents, was analytical grade (Merck KGaA, Darmstadt, Germany). The potassium hydroxide (KOH) used for neutralization of acrylic acid before the irradiation was industrial grade and bought from CV Cahaya Kimia, Indonesia. Cassava starch and chitosan were two of the three main materials for the grafting process. Cassava starch was available in the market and produced by PT Budi Acid Jaya Tbk, Lampung, Indonesia, and used without further purification. The chitosan sample used was pharmaceutical grade with deacetylation degree of 85 % and purchased from PT Biotech Surindo, Indonesia.

### Hydrogel synthesis with $\gamma$-irradiation

One gram of cassava starch powder was added to 20 mL of distilled water and heated while stirring at 80 °C afterward until cassava starch gelatinized completely. Meanwhile, chitosan (1 g) was dissolved in 20 mL of 2 % (w/w) acetic acid solution. Pre-weighed amounts of acrylic acid (15 mL) and potassium hydroxide (6.1 g) were

dissolved in 30 mL of distilled water and mixed well to form neutralized acrylic acid solution. The gelatinized solution of cassava starch and chitosan were then added into the neutralized acrylic acid solution and homogenized in a reactor completed with magnetic stirrer with a capacity of 250 mL, and stirred for 10 min. After homogenization, the solution was packed in a plastic container measuring 10 cm × 15 cm and thickness of 0.1 cm and then irradiated using γ-ray at various total doses (5 kGy, 10 kGy, 15 kGy, and 20 kGy). The gel products were then dried in the oven at 60 °C for 24 h and ground by using a blender (Miyako, Indonesia). The ground hydrogel in the form of powder with average particle sizes in 250-400 μm range was kept in the absence of heat, light, and moisture for further tests.

## Gel content and swelling measurements

An accurately-weighted powdered hydrogel sample (0.1 g) was put into a tea bag and then soaked for 24 h in 100 mL of distilled water at room temperature. The immersed gel product was then vacuum-dried in an oven at 60 °C for 24 h and weighed. The gel content in the hydrogel product was analyzed using a procedure reported in a previous article [28] using formula in Eq. (1).

$$Gel\ content\ (\%) = \frac{W_1}{W_0} x 100\ \% \qquad (1)$$

In (1), $W_1$ = weight of the hydrogel after soaking and drying (g) and $W_0$ = initial weight of the powder hydrogel (g). To determine the hydrogel absorption capacity value, the same method as the previous article was used [4,28]. At room temperature, 0.1 g of the powder hydrogel was soaked in distilled water (100 mL). NaCl and urea were also used in this swelling study to find the hydrogel performance in the salt solutions. In each interval of 15 s, the test sample was removed from the absorption medium and blotted on a filter paper before weighing to remove any residual liquid that is still attached to the surface of the hydrogel. Then, the swelling capacity was calculated according to the expression in Eq. (2).

$$Swelling\ ratio\ \left(\frac{g}{g}\right) = \frac{W_t - W_0}{W_0} \qquad (2)$$

In (2), $W_t$ = weight of the hydrogel (g) at a swelling state at time $t$, and $W_0$ = the initial weight of the hydrogel powder (g). The observations were carried out for 180 s.

## Instrumental analysis

FTIR characterization was conducted using a Shimadzu IRPrestige-21 spectrometer Model 800 series from 4000 to 500 cm$^{-1}$ to measure the absorption spectra of samples, while the surface morphology structure of the hydrogel product was analyzed by using a SEM 515/RDAX PV 9900. The antibacterial activity of the gel was tested through the most probable number (MPN) method. To record the differential scanning calorimetry (DSC) profiles of samples, a Shimadzu DSC 60 was used.

## RESULTS AND DISCUSSION

### The mechanism of reaction

The mechanism of crosslinking in solution for hydrogel formation using gamma-ray irradiation has been reported [29,30]. The radical polymerization reaction will occur in solution by a mechanism that follows steps such as initiation, propagation, and termination. During irradiation in aqueous media, three reactive species are formed, namely hydrated electrons, hydroxyl radicals, and hydrogen radicals. In this case, electrons have low reactivity, and hydrogen radicals have a meager contribution to the formation of macroradicals, and therefore hydroxyl radicals are predicted to have a major role in the reaction of producing hydrogels from polymeric materials. On the other hand, bond breaking can also occur in acrylate and chitosan polymer chains when exposed to radiation using gamma rays to form free radicals [31,32]. As a result, many possible bonding schemes occur between the formed radicals. The possible reaction mechanism for the synthesis of hydrogels from neutralized acrylic acid, cassava starch, and chitosan is illustrated in Fig. 1.
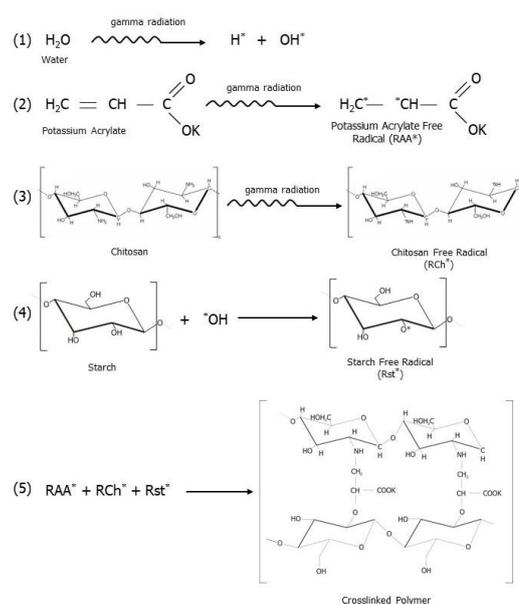


**Fig. 1.** Plausible mechanisms of crosslinking reaction in the formation of hydrogels from potassium acrylate, starch, and chitosan.

The hydrogel formation reaction scheme in this study can be assumed as follows: when the water mixture of neutralized acrylic acid, starch, and chitosan was irradiated by gamma radiation, hydroxyl radicals were produced from water. Hydroxyl radicals abstract hydrogen atoms of macromolecules and thus macroradicals are then formed. The macroradicals then crosslink with each other to form a complex three-dimensional network called a hydrogel.

**Characterization of the products**

FTIR spectrum of potassium acrylate, chitosan, starch, and the hydrogel prepared with irradiation is shown in Fig. 2.
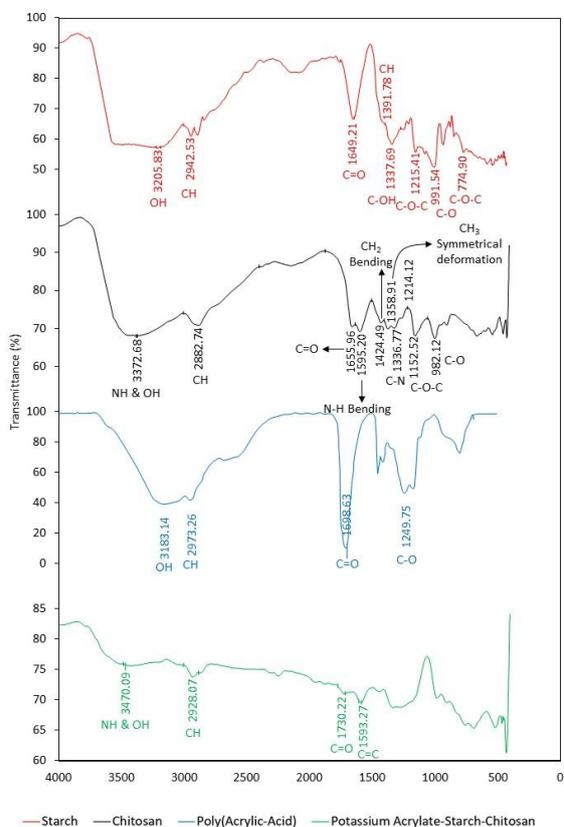


**Fig. 2.** FTIR spectra of hydrogel from acrylic acid, cassava starch, and chitosan.

The band at 3470.09 $cm^{-1}$ correlates to N–H stretching in functional groups of chitosan. The presence of residual N-acetyl groups from chitin was confirmed by the bands at 1655.76 $cm^{-1}$ (C=O stretching of amide I) and 1595.20 $cm^{-1}$ (N–H bending of amide II). An absorbance peak at around 1649.21 $cm^{-1}$ in functional groups of starch is attributed to the C–O bending associated with the OH group. The IR spectrum of the hydrogel shows an absorption peak of about 2928.07 $cm^{-1}$ arising from stretching C–H, and the intensity of this band

is higher than that of acrylic acid, starch, and chitosan as raw materials, and C=O groups of poly-(acrylic acid) are shown by the band at the local wave number 1730.22 $cm^{-1}$. The band at 1500-1700 $cm^{-1}$ (1593.27 $cm^{-1}$) in the spectrum of resulting hydrogel from acrylic acid, cassava starch, and chitosan is attributed to $H_2C=CH_2$ groups stretching. The appearance of $H_2C=CH_2$ functional groups is the fact that there is still acrylic acid in the form of homopolymer in the polymer product of hydrogel resulted in this study. This is based on the mechanism of the neutralization reaction of acrylic acid with KOH which predicts that potassium acrylate will lose the bond of the C=C chain after irradiation due to the energy effect that breaks the bond and the presence of interference from free radicals H*, causing the double bond to become a C–C single bond [29].

**Morphological analysis**

The SEM micrograph of the surface structure of the superabsorbent hydrogel produced by grafting polymerization from acrylic acid, cassava starch, and chitosan is shown in Fig. 3.
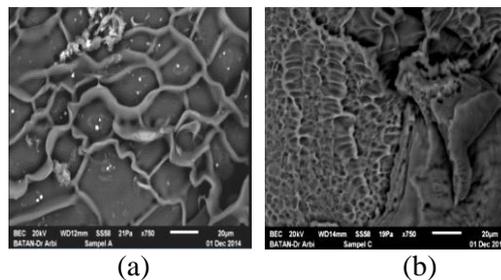


**Fig. 3.** SEM image of the hydrogel, (a). Poly-(acrylic acid) hydrogel without cassava starch and chitosan, (b). Hydrogel with cassava starch and chitosan.

Hydrogel produced from this study has a porous structure. These pores are considered areas of water permeation and where interactions occur between external stimuli and hydrophilic groups of graft polymers [22]. The micrograph of a poly-(acrylic acid) superabsorbent hydrogel at 750× magnification, in Fig. 3(a), shows a porous structure with an average pore size of 38.15 μm. The pores are homogenously distributed into the hydrogel matrix. The superabsorbent poly-(acrylic acid) hydrogel with cassava starch and chitosan, shown in Fig. 3(b), has a smaller pore structure with an average pore size of 9.85 μm but seems to be more irregular. The changes in morphology and pore size of poly-(acrylic acid) hydrogel are promoted by adding starch and chitosan in the grafting reaction. The presence of starch and chitosan in the hydrogel structure increases the number of the hydrophilic groups. Some papers reported that acrylic acid could

be successfully grafted onto cassava starch [8] or chitosan [11,16]. As can be seen in the SEM photograph, hydrogel synthesized in the presence of starch and chitosan, as shown in Fig. 3(b), shows more interconnected networks compared to Fig. 3(a) (without starch and chitosan), which causes the increase of the pore numbers and the decrease of the average pore size.

## Thermal examination

Acrylic acid used in this study was neutralized using potassium hydroxide. Measurement with a differential scanning calorimeter (DSC) in this research was performed to characterize the thermal behavior of the superabsorbent product at different doses of neutralization. Figure 4 shows the DSC thermograms of neutralized acrylic acid-based superabsorbent hydrogels at total irradiation dose of 10 kGy. The 25 % neutralization of acrylic acid-based superabsorbent results in a first exothermic peak at the 340.40 °C melting temperature and a second peak at 385.87 °C. The neutralization of 50 % results in a first peak at the 349.55 °C melting temperature and a second peak at 433.13 °C. The 75 % neutralization results in a first peak at the 358.74 °C melting temperature and a second peak at 450.48 °C. The two peaks represent the cross-linked hydrogel in the form of homopolymer (acrylic acid) and copolymer (acrylic acid-co-potassium acrylate) that are interconnected or crosslinked. This fact can be explained by the partial neutralization of acrylic acid [4]. The reaction product consists of a mixture of potassium acrylate and unneutralized acrylic acid. When the mixture is irradiated, it will produce both types of polymers. The figure also shows that the hydrogel resulting from 100 % neutralization of acrylic acid is predominantly potassium acrylate, represented by a broad peak at the melting temperature of 390.44 °C and 429.88 °C. These results align with the results obtained in previous study that higher degrees of neutralization produce hydrogels with higher melting points [4].
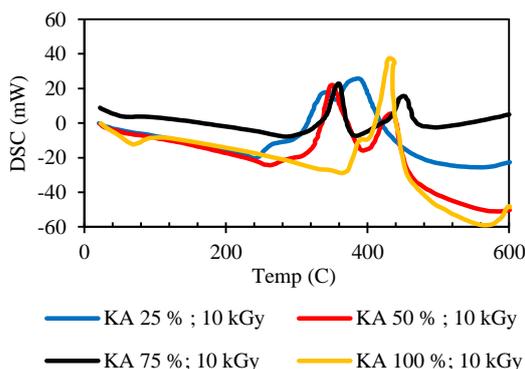


**Fig. 4.** DSC thermograms of the neutralized acrylic acid polymers.

## Water swelling behavior of hydrogel with different treatments of acrylic acid neutralization and doses of irradiation

The previous study [4] found that degree of neutralization was related to the swelling behavior of a superabsorbent. It was also reported that the longer the superabsorbent was soaked in the water, the more water was absorbed into the hydrogel matrix, causing the hydrogel to swell more. The study results related to the effect of neutralization and radiation dose on the ability of hydrogels to absorb and store water are shown in Fig. 5.
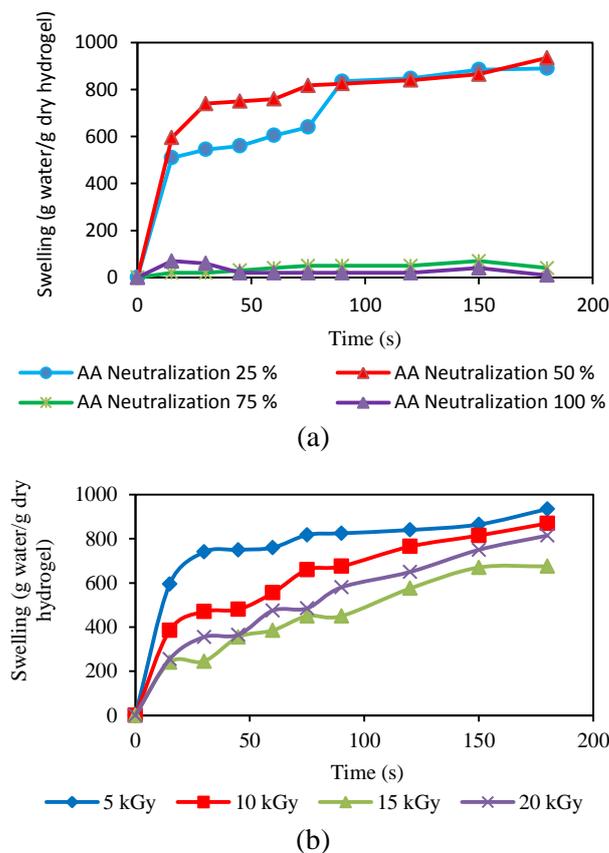


(a)



(b)

**Fig. 5.** Water swelling capacity of the hydrogels, (a). effect of acrylic acid neutralization, (b). effect of total irradiation dose.

As shown in Fig. 5(a), there is an increase in the water swelling value of the hydrogel for the 180 seconds of observation time. At 25 % and 50 % acrylic acid neutralization, the swelling value increased since the beginning of immersion, then it became constant. This is due to the longer immersion time that allows more water to be absorbed into the pores of the superabsorbent hydrogel. The water absorption ability of superabsorbent will be constant or reach a state of equilibrium when the network is completely filled with water molecules. The 50 % neutralization of acrylic acid gives the highest water swelling capacity of the superabsorbent polymer

(900 g water/g dry hydrogel) after 180 seconds of measurement. Lower values of swelling capacity are obtained at higher neutralization ratios (75 % and 100 %). In fact, higher neutralization ratio promotes higher salt production and, consequently, the hydrogel component can be dissolved into the water [29], and attributes to the decreasing of swelling capability. Previously [11], the superabsorbent water absorption capacity decreased due to the increase in soluble ingredients.

Increasing of total irradiation dose causes the decrease in water swelling capacity. Superabsorbent hydrogel with total irradiation dose of 5 kGy shows the highest absorbency (935 g water/g dry hydrogel). Higher dose of $\gamma$-irradiation enhances more chains during the grafting reaction and reduces the free section among the polymer chains. This fact promotes the smaller pore size of the superabsorbent, and as a result, the structure with a very high number of crosslinks cannot expand to hold large amounts of water [22]. Figure 5(b) shows the water absorption of the grafted hydrogel with various total doses of irradiation from 5 to 20 kGy.

The higher swelling values obtained in this study were higher than the highest swelling value of hydrogels from previous studies using acrylic acid [4,31]. A study with 50 % acrylic acid neutralization using potassium resulted in a swelling value of 240 g water/g dry hydrogel [4]. Another study examined the effect of radiation dose on the swelling ratio of chitosan and sodium acrylate hydrogels, showing the highest equilibrium swelling result of 380 at 10 kGy [31].

## Effect of starch and chitosan addition to the water swelling of hydrogel

The addition of cassava starch significantly affects the swelling capacity of superabsorbent hydrogel synthesized through $\gamma$-irradiation. The superabsorbents swelling behavior as a function of cassava starch and chitosan quantity are illustrated in Fig. 6.

Figure 6(a) shows that the increase of starch weight in the reactant mixture is accompanied by the decreased value of swelling capacity of the hydrogel. In this research, the highest swelling value (847.5 g water/g dry hydrogel) was obtained through the use of 0.25 g starch. Starch can absorb water because it has an OH-cluster which is known to be hydrophilic. However, a decline in the swelling ratio of grafted hydrogel at higher amounts of starch may occur due to the excess starch filling the polymer network when the physical crosslinking occured [3].

The polymer density becomes higher and causes some difficulty for water to diffuse into the hydrogel matrix [28].

Effects of chitosan quantity in the superabsorbent grafted polymer with total irradiation dose of 5 kGy are presented in Fig. 6(b). The highest value of swelling capacity reaches 670 g water/g dry hydrogel, and decreases at higher addition quantity of chitosan. This case indicates that the optimum composition of chitosan in the superabsorbent grafted polymer is 0.25 g. The lower swelling capacity attained with more chitosan may be due to the polymer network getting filled by excess chitosan instead.
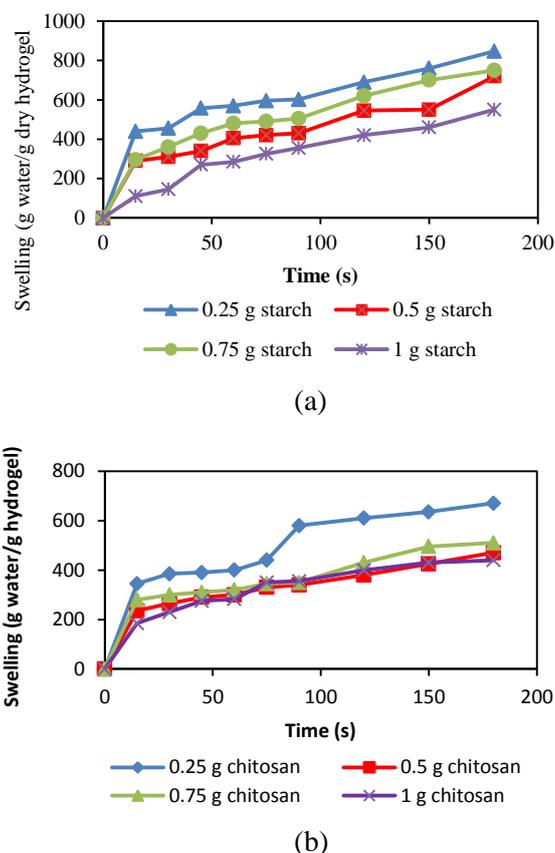


(a)



(b)

**Fig. 6**. Water Swelling Behavior of Hydrogel, (a). effect of cassava starch addition, (b). effect of chitosan addition.

The effect of using natural polymers in the manufacture of hydrogels on their water absorption capacity has also been tested [31,33]. In the studies that have been carried out, it is also stated that the absorption capacity of the hydrogel decreases with the increasing proportion of natural polymer used in the composition.

## Effect of chitosan addition to the nacl swelling and urea swelling of hydrogel

The influence of chitosan addition variation from 0.25 to 1 g is illustrated in Table 1.

**Table 1**. Effect of chitosan addition to the gel content and swelling behavior of hydrogel.

| Chit. (g) | Gel Cont. (%) | NaCl Swelling (g/g hyd.) | Urea Swelling (g/g hyd.) | EDS (g/g hyd.) |
|---|---|---|---|---|
| 0.25 | 93.49 | 520 | 767.50 | 810.00 |
| 0.50 | 90.00 | 320 | 660.00 | 761.67 |
| 0.75 | 90.00 | 295 | 490.00 | 680.00 |
| 1.00 | 89.00 | 290 | 310.00 | 661.67 |

Table 1 shows that the best gel content (93.5 %) of the hydrogel product from this experiment is obtained by using 0.25 g chitosan at a total irradiation dose of 5 kGy. The gel content decreases at higher quantities of chitosan. Increasing the weight ratio of acrylic acid to chitosan causes more acrylic acid molecules to be grafted onto the backbones of chitosan [11]. In contrast, excess chitosan causes a decrease in polymer density and consequently decreases gel concentration of the product.

The swelling capacity of NaCl and urea decreases because of the addition of chitosan composition. The highest NaCl solution swelling is obtained by using 0.25 g of chitosan, *i.e.*, 520 g water/g dry hydrogel. Absorption of urea solution was carried out at a concentration of 90 mg/100 mL for 1 h, where the highest swelling for urea solution is also obtained with the addition of 0.25 g chitosan (767.50 g urea solution/g dry hydrogel).

Influence of chitosan amount on equilibrium degree of swelling (EDS) of hydrogel from acrylic acid, cassava starch, and chitosan are studied up to saturation condition. Decreasing EDS with the increasing chitosan composition is due to excess chitosan after the irradiation procedure filling the hydrogel network. The more chitosan is added, the more matrix are filled by the excess chitosan; thus, water cannot diffuse in a large quantity into the polymer network, and as a result, the swelling capacity of hydrogel is reduced.

## Antibacterial analysis

The most probable number (MPN) value estimates the number of units or colony-forming units in the sample. MPN value of the grafted hydrogel resulted in this study is 0 (zero) for *Escherichia coli*. In other words, it can be explained that the hydrogel product from this study is sterile from *Escherichia coli* bacteria. This may be caused by the γ-irradiation method which can kill several species of microorganisms. The γ-irradiation process and thermal crosslinking to produce hydrogel are safe technologies that result in safe products, and do not require processes of purification and sterilization [26].

## CONCLUSION

The addition of cassava starch and chitosan affects the properties of acrylic acid-based superabsorbent. The effects included pore size, thermal behavior, gel content, antibacterial activity, and swelling capacity in the water, salt, and urea solution. The best superabsorbent hydrogel product synthesized from acrylic acid, cassava starch, and chitosan is obtained to the composition of 50 % acrylic acid neutralization, with the addition of 0.25 g cassava starch and 0.25 g chitosan by using a total γ-irradiation dose of 5 kGy. The highest gel content is 93.5 %, and the swelling capacities are 670 g/g dry hydrogel for water absorption, 520 g/g dry hydrogel for the absorption of NaCl solution, and 767.5 g/g dry hydrogel for the absorption of urea. This study confirms that all the products are sterile from *E. coli* bacteria.

## AUTHOR CONTRIBUTION

D. R. Barleany and Erizal equally contributed as the main contributors of this paper. All authors read and approved the final version of the paper.

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