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Citation: **1699**, 040008 (2015); doi: 10.1063/1.4938323
View online: http://dx.doi.org/10.1063/1.4938323
View Table of Contents: http://aip.scitation.org/toc/apc/1699/1
Published by the American Institute of Physics

Swelling Properties of Cassava Starch grafted with Poly (potassium acrylate-co-acrylamide) Superabsorbent Hydrogel Prepared by Ionizing Radiation

Dhena Ria Barleany[a*], Fida Ulfiyani[a], Shafina Istiqomah[a], Heri Heriyanto[b], Rahmayetty[a], Erizal[b]

[a]Department of Chemical Engineering, University of Sultan Ageng Tirtayasa, Cilegon, Banten, Indonesia
[b]Centre for Application of Isotopes and Radiation, Jakarta, Indonesia
*email address :dbarleany@yahoo.com

Abstract. Natural and synthetic hydrophylic polymers can be phisically or chemically cross-linked in order to produce hydrogels. Starch based hydrogels grafted with copolymers from acrylic acid or acrylamide have become very popular for water absorbent application. Superabsorbent hydrogels made from Cassava starch grafted with poly (potassium acrylate-co-acrylamide) were prepared by using of ϒ-irradiation method. Various important parameters such as irradiation doses, monomer to Cassava starch ratio and acrylamide content were investigated. The addition of 7,5 % w w^{-1} acrylamide into the reaction mixture generated a starch graft copolymer with a water absorption in distilled water as high as 460 g g^{-1} of its dried weight. The effectivity of hydrogel as superabsorbent for aqueous solutions of NaCl and urea was evaluated. The obtained hydrogel showed the maximum absorptions of 317 g g^{-1} and 523 g g^{-1} for NaCl and urea solution, respectively (relative to its own dry weight). The structure of the graft copolymer was analyzed by using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

Keywords: ϒ-irradiation, cassava starch, acrylamide

INTRODUCTION

Superabsorbent polymers are materials which can absorb and retain a large amount of water or aqueous solutions. Superabsorbent materials consist of crosslinked hydrophilic polymer chains forming a 3-dimensional network structure [1]. Superabsorbents are widely used in many fields, such as burn wound dressing [2], drug delivery system [3], controlled release of fertilizer [4], and baby diapers [5].

However, most of superabsorbents are acrylic acid and acrylamide based products and cannot be biodegradaded in nature [6]. Starch is a renewable source of raw material which has been heavily studied as the back-bones for graft polymerization of vinyl monomers [1],[7],[8],[9],[10]. Both starch and vinyl monomers like acrylic acid and acrylamide are of interest as they contain a number of hydrophilic functionalities in their structure like hydroxyl and carboxyl groups [1]. Incorporation of starch into other synthetic polymers not only reduces the dependence on petrochemical-derived monomers, but also provides materials in which the starch portion can biodegrade rapidly in the environment [10].

In this study, a series of starch-g-poly(potassium acrylate-co-acrylamide) superabsorbent was prepared by ϒ-ray irradiation. The hydrogel product was analyzed to determine the efficiency of the grafting reaction. Furthermore, the swelling behaviors of the crosslinked hydrogels with respect to the irradiation dose, acrylamide amount, and starch amount on the properties of obtained polymers were investigated.

International Conference of Chemical and Material Engineering(ICCME) 2015
AIP Conf. Proc. 1699, 040008-1–040008-10; doi: 10.1063/1.4938323

Experimental

Materials

Cassava starch, acrylamide, acrylic acid, and potassium hydroxyde were as main materials, NaCl, urea, and distilled water for absorption evaluation on swelling behaviors of the products. The samples were irradiated using Irradiator Co^{60} at Centre for Application of Isotopes and Radiation, Jakarta, Indonesia. Drying process of the polymers were held in Hereaus Instrumen Vcuterm Oven (Polystar 401 HM), and the FTIR spectra were recorded on Spektrofotometer Fourier Transform Infrared Shimadzu Prestige-21.

Preparation of poly(potassium acrylate–co-acrylamide)-starch superabsorbent hydrogels.

15 ml of acrylic acid were measured, and 23 ml of distilled water was then added to form an acid solution. Potassium hydroxyde was then used to neutralize the solution and formed a solution of potassium acrylate. Acrylamide was added to the reactor mixture (5-12,5 gr) and the mixture was continouesly stirred, resulted a solution of potassium acrylate-acrylamide. Various quantities of Cassava starch (0,25 gr; 0,5gr; 0,75gr; and 1gr) were prepared and then dissolved gradually in 50 ml of distilled water that has been heated at a constant temperature of 60°C while mixing until uniform starch solution was obtained. Addition of the starch solution to the reactor containing a solution of acrylamide and potassium acrylate mixture was done and mixed to get a homogenous solution. The solution mixture was packed in a plastic container 10 cm x 15 cm with a thickness of 0.1 cm, and then irradiated using ϒ-rays (5 kGy, 10 kGy, 15 kGy and 20 kGy). Product resulted from irradiation equipment in the form of gel was then removed from the plastic container and sliced into small pieces to facilitate the process of drying and grinding. Drying process was done using an oven at 60 ° C for 24 hours. Dried and granulated superabsorbent obtained was kept in a dry place for further analysis.

Infrared Analysis

The superabsorbent hydrogels resulted from the experiment were placed on the flat plate crystal samplestage and a tip ATR (Attenuated Total Reflectance) tool was pressed on the samples. Starch powder was mixed with potassium bromyde solid and recorded with DRS (Diffuse Reflectance Spectroscopy) system. A spectrum for each sample was obtained using Shimadzu IR Prestige-21 spectrometer model 800 series from 4000 to 500 cm^{-1}

Scanning Electron Microscopy (SEM) Analysis

For SEM studies, samples were coated with 100 A thick layer of gold by means of a Denton II vacuum sputter coater to minimize the charging of the samples, and then mounted onto aluminium stubs using conductive carbon tape and conductive paint to ensure efficient charge dissipation. Scanning Electron Microscopy images were analyzed with a SEM 515/RDAX PV 9900.

Gel Fraction studies

The hydrogel samples (0,1 gram) were inserted in a tea bags and immersed in 100 cc of water for 24 hours. The gels were then dried at 60°C to investigate the soluble fraction in the samples gravimetrically.

$$Gel\ fraction\ (\%) = Wg/Wo \times 100 \qquad (1)$$

Where *Wg* is the weight of dried hydrogel after extraction and *Wo* is the initial weight of the hydrogel.

Swelling studies

The degree of swelling was determined by using gravimetric method. Dried hydrogel (0,1 gr) were immersed in 100 cc of distilled water at room temperature. NaCl and urea were also used in this swelling study to find the hydrogels performance in the salt solutions. At 15 seconds time intervals, the samples were removed from the swelling medium and blotted on a filter prior to weighing to remove excess surface moisture. The swelling ratio was calculated according to the following expression :

$$Swelling\ ratio = Wt/Wo \quad (2)$$

where Wt is the weight of the swollen hydrogel at time t and Wo is the initial weight of the dried hydrogel. The studies were carried out for 180 seconds.

EDS studies

The Equilibrium Degree of Swelling (EDS) was calculated using equation (2) by changing Wt to We which means the equilibrium weight of the swollen hydrogel.

Thermal Analysis

Differential Scanning Calorimetry (DSC) profiles of the samples were recorded by means of Shimadzu DSC 60. Approximately, 5 mg of the hydrogel samples were sealed in an allumunium pan, and then heated from room temperature to 600^{o}C at a heating rate 10^{o}C/minute.

RESULT AND DISCUSSION

Study of the influence of irradiation dose on the gel content

Various irradiation doses were applied in this experiments (5 kGy, 10 kGy, 15 kGy and 20 kGy). The effect of irradiation doses on gel content for poly (potassium acrylate-co-acrylamide) without starch is shown in Figure 1. As can be seen, the gel content decreases with increasing irradiation doses from 50kGy to 20 kGy. This study resulted the optimum gel content of 96,18% which was reached when the ϒ-irradiation dose was adjusted at 5 kGy.

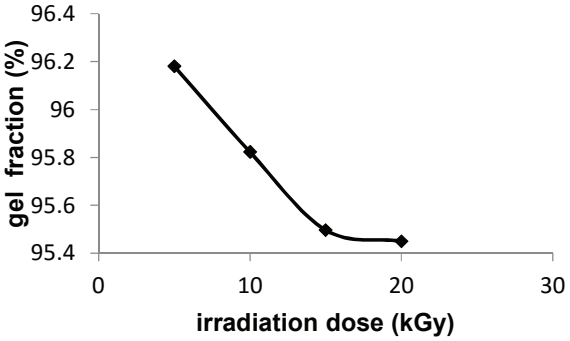


Figure 1. Effect of irradiation doses on gel fraction

ϒ-irradiation dose directly affects the reaction process and its results. This experiment was running at a constant dose rate of 10 kGy/h. An increase in the total dose enhances the formation of the radicals in the reaction mixture and induces a higher conversion for both the homopolymer and the graft copolymer. The gel content is related to the cross-linking density [10]. The decrease in the gel content could be the chain scission effect of the polymer at a longer reaction time.

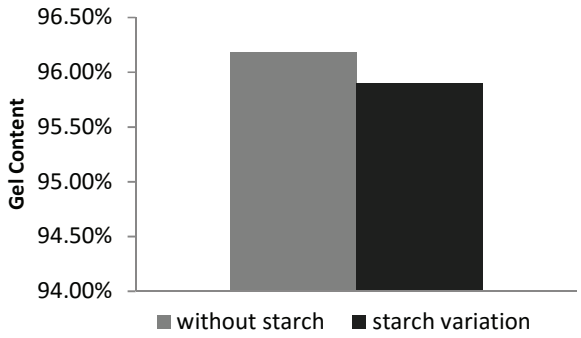


Figure 2. Comparison of gel content between poly(potassium acrylate-co-acrylamide) and Cassava starch grafted with poly(potassium acrylate-co-acrylamide)

Addition of 0,5 gr of starch forms poly(potassium acrylate-co-acrylamide)-g-starch, gel content was becoming 95,9 % (Figure 2), lower than the gel content of the poly(potassium acrylate-co-acrylamide). Starch is a natural polysacharide which could be degraded by a high dose radiation. Polysaccharides dissolve easily in water, cannot form the stable hydrogel [7]. The same case was occured when hydrogel was prepared from honey by using ϒ-ray. It was observed that the decrease in gelation of hydrogel by the addition of polysacharide can be atributable to work as plastisizer in the hydrogel [11]. In addition, starch also act as Interpenetrating Polymer Networks (IPN) which will be trapped in the polymer network when physical cross-linking occurs [8],[10].

Effect of irradiation dose on the water swelling of copolymer

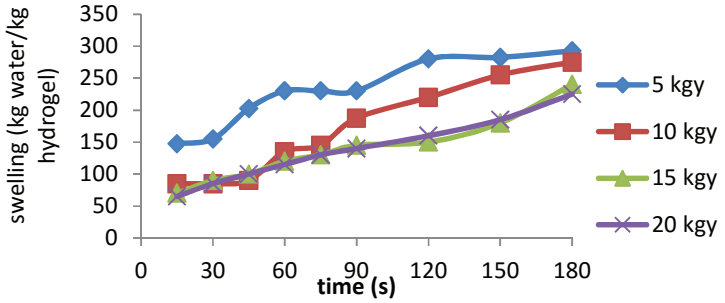


Figure 3. Effect of the irradiation doses (kGy) on the absorption properties of copolymer

Swelling ratio is one of main parameters from hydrogel especially for testing the quality of a material as an absorben. Figure 3 shows the relation between swelling ratio of poly(potassium acrylate-co-acrylamide) hydrogel using quantities of acrylamide 7,5 gr. During the increasing of time immersing in water, swelling ratio of poly(potassium acrylate-co-acrylamide) superabsorbent continually increases.

Swelling ratio of hydrogel superabsorbent is also affected by ϒ-irradiation doses. The increasing of dose of radiation from 5 kGy to 20 kGy caused the decreasing of swelling ratio. Swelling ratio represents the ability of hydrogel to absorb water or aqueous solution. The polymer chains restricted in swelling by elastic retraction forces of the network. The more the chains separate from each other, the more stiffness of the polymer chains become [10]. The highest water absorption is detected in the superabsorbent copolymer prepared with 7,5 gr of acrylamide using total dose of 5 kGy. However, the higher dose of radiation resulted the chains scission of the polymer. The chains scission causes the decreasing of cross-linking network, and as a result the capacity of water swollen also decreases.

Effect of amount of acrylamide on water swelling of copolymer

Various quantities of acrylamide are used in this research (5 gr; 7,5 gr; 10 gr; and 12,5 gr). Swelling ratio from variaous quantities of acrylamide using radiation dose of 5 kGy are investigated and shown in Figure 4. The increasing of water swelling ratio of superabsorbent hydrogel was occured in the weight of acrylamide range from 5 gr to 7,5 gr. The highest water swelling ratio is 460 gr/gr and decreases when mass of acrylamide are above 7,5 gr (10 gr and 12,5 gr).

Acrylamide is a hydrophilic monomer which have the ability to absorb water in large quantities. At higher mass of acrylamide, viscosity of the reactant mixture also increases. There are some free radicals movement which are not crosslinked and as a result, the capacity of water absorption decreases.

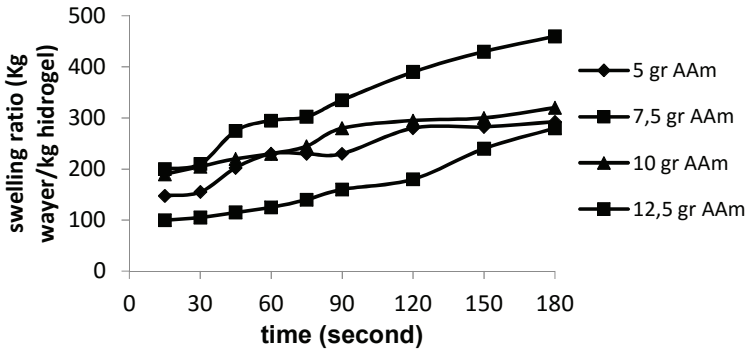


Figure 4. Effect of acrylamide (AAm) quantities on the absorption properties of poly(potassium acrylate-co-acrylamide) at irradiation dose 5 kGy

Effect of starch quantities on the water swelling

Figure 5 shows the water absorption capacity of grafted hydrogel with various compositions of starch from 0,25 gr to 1 gr. Increasing of hydrogel's swelling ratio are occured on the starch addition from 0,25 gr to 0,5 gr. The highest value of swelling capacity is 470 gr/gr and decreases at higher addition mass of starch. This case indicate that the optimum composition of starch in the superabsorbent grafted polymer is 0,5 gr and the pore size study from micrograph test result is shown in Figure 11.

Starch is able to absorb the water because it has a cluster of OH^- which are hydrophilic. However, the declining in the swelling capacity of grafted hydrogel at higher amount of starch may occur due to the excess of starch which will fill in the polymer network when the physical cross-linking occurs [8], [10]. The polymer density will be higher and cause some difficulties for water to diffuse into the matrix of hydrogel [8].

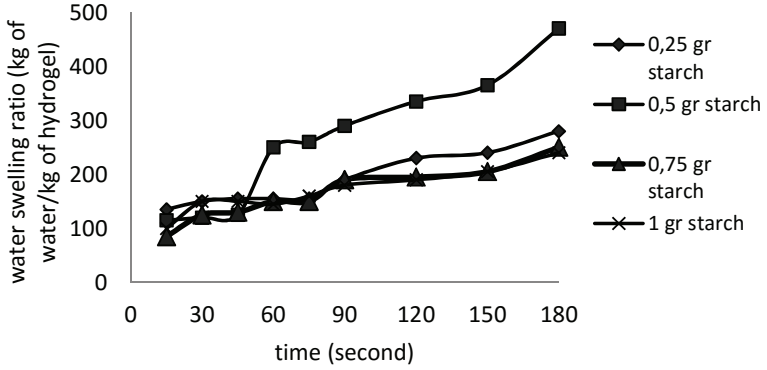


Figure 5. The relationship between the amount of starch and the water absorption properties of polymer starch-g-poly(potassium acrylate-co-acrylamide)

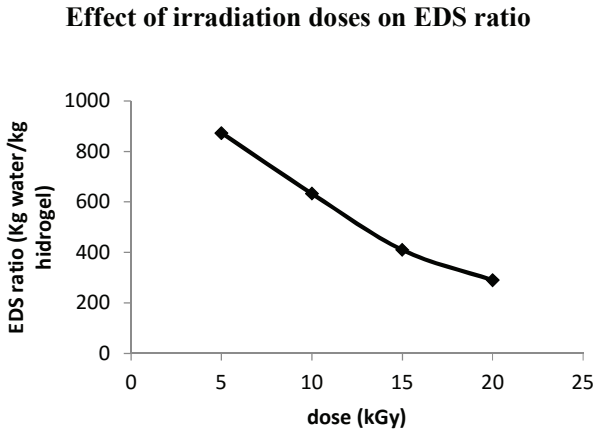


Figure 6. The relationship between irradiation doses (kGy) and the Equilibrium Degree of Swelling (EDS) ratio

During the mass transfer process, water are swelling into hydrogel network to fulfill the spaces in the matrix. This process are continued until the state of equilibrium (EDS) are achieved [12]. Influence of radiation doses against EDS of hydrogel starch-g-poly(potassium acrylate-co-acrylamide) are studied up to saturation condition for 24 hours and the values are shown in Figure 6. The 5 kGy dose of gamma radiation results a ratio of EDS 873,33 gr/gr. Increasing of radiation dose that are used in this research results decreasing of EDS ratio. On the other word, it can be said that the polymerization process of hydrogel superabsorbent starch grafted with poly(potassium acrylate-co-acrylamide) reached the optimum dose of 5 kGy gamma radiation. Due to the possibility of chain scission at higher dose of radiation [7], the hydrogel reach chemical equilibrium at shorter time [9].

The influence of starch quantities to the NaCl and urea swelling properties

The resulted hydrogels were tested to measure the absorption capabilities to the salt components contained in the urine, that are NaCl and urea. The test of salt swelling is similar with the water swelling test. Hydrogel samples were immersed in solutions of NaCl and urea for 1 hour, then filtered to determine their absorption ability.

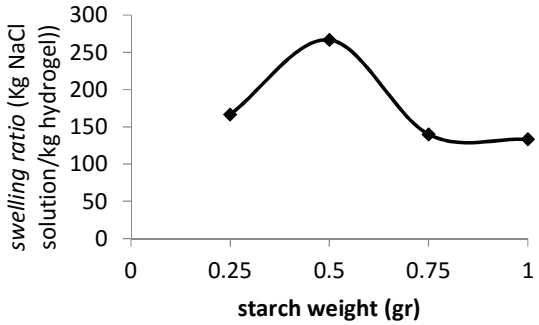


Figure 7. The relationship between starch content and NaCl solution absorption of hydrogel

Figure 7 shows the effect of starch composition to the swelling ratio of NaCl solution at 5 kGy total dose of radiation. The concentration of NaCl solution used in this absorption experiment was 0.009% (w/v). It is showed in Fig. 7 that the hydrogel superabsorbent of grafted polymer with gamma radiation dose of 5 kGy and 0.5

gr amount of starch results swelling ratio of 266.67 gr/ gr. The swelling ratios are then decrease in the using of 0,75 gr and 1 gr of starch.

Swelling ratio in NaCl solution could be smaller than its swelling in the water because of the very low osmotic pressure due to the ions of Na^+ and Cl^-. There are a large difference between the concentration of those ions in salt solution and in the hydrogel network. When the hydrogel is immersed in water, there will be a maximum osmotic pressure which enhance rapid swelling of gel [12].

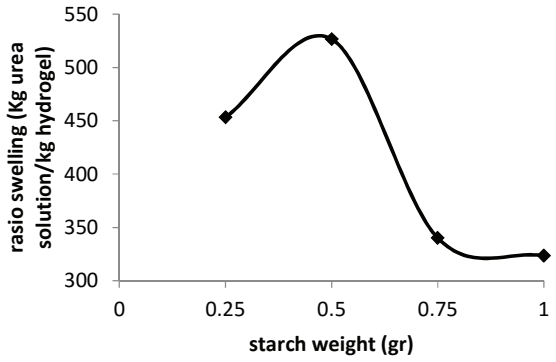


Figure 8. The relationship between the starch content and urea solution absorption of hydrogel

Effet of starch quantities in the hydrogel to the urea swelling behavior can be seen in Figure 8. The urea concentration used in the absorption test was 0.09% (w/v). It can be seen that the increasing of starch quantity from 0,25 gr to 0,5 gr causes the rising of urea swelling ratio of the polymer and reach the largest number of 526.67 gr / gr. The absorption capacity then decreases at the using of 0.75 gr and 1 gr of starch. It means that 0,5 gr is the optimum formula for starch composition which result the largest amount of salt solutions absorption (NaCl and urea).

Effect of gamma radiation dose to DSC

Differential Scanning Calorimetry (DSC) analysis is used to determine the melting point of the polymer. The DSC peak on the graph gives the information about the melting condition of certain compound at any temperature and molecular weight. The DSC analysis result of this study is shown in Figure 9. The melting point of acrylamide (red) was detected less than 100°C, while the melting point of the hydrogel of poly (potassium acrylate-co-acrylamide) exceeds the boiling point of acrylamide. The melting point of poly(potassium acrylate-co-acrylamide) at radiation doses of 5 kGy, 10 kGy, 15 kGy, and 20 kGy are 121.98 ^oC, 133.36 ^oC, 136,51 ^oC, and 134.20 ^oC with the heating rate was 10 °C/min. This high melting point is due to crosslinking phenomena which has been occurred between the monomers of acrylamide and potassium acrylate [8].

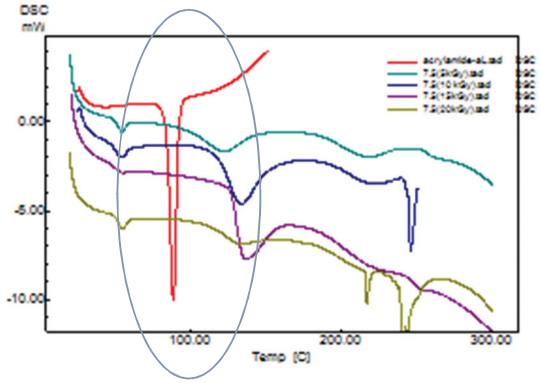


Figure 9. The result of DSC thermal poly (Potassium Acrylate-co-Acrylamide)

FT-IR study for hydrogel starch-g-poly(potassium acrylate-co-acrylamide)

FT-IR spectrum measurement is intended to represent the functional groups that exist in superabsorbent polymers. Superabsorbent hydrogel product with a composition of 7.5 gr of acrylamide and starch of 0.5 gr with 5 kGy total dose of radiation was analyzed by means of FT-IR to ensure the polymerization reaction. As expected, from Figure 10 can be seen that some functional groups exist in this hydrogel are poly (potassium acrylate), acrylamide, and starch. Results identification spectrophotometric measurement wave hydrogel poly (AAM-co-KA) -starch can be seen in Figure 10

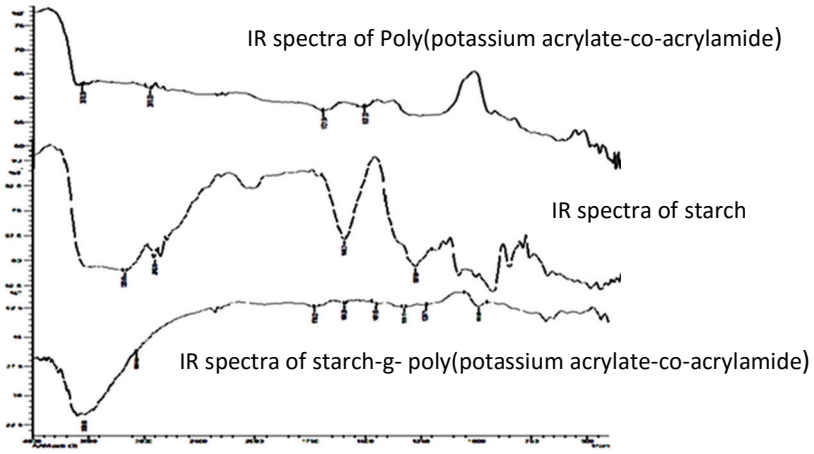
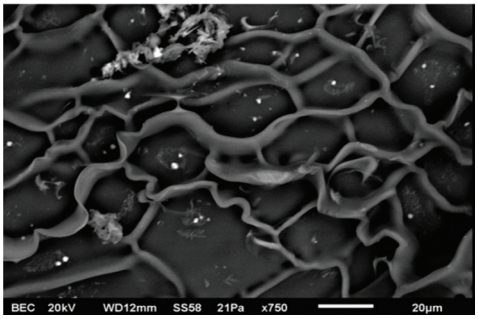


Figure 10. The results of FT-IR

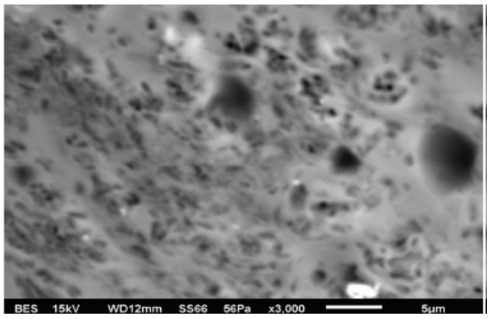
Figure 10 shows that IR spectra of starch-g-poly (potassium acrylate-co-acrylamide) consist of C = O (potassium acrylate) in wavelength 1730.22 cm^{-1}, CO group (from starch) on wavelength 1326.12 cm^{-1}, C=C group (from potassium acrylate) in wavelength 1595.2 cm^{-1}, OH group (from starch) in wavelength 3069.24 cm^{-1}, and the NH_2 group (of acrylamide) in wavelength 3538.56 cm^{-1}. These data indicates the occurrence of cross-linking reaction between acrylamide, potassium acrylate and starch during the irradiation process [13].

Morphology Evaluation

SEM (Scanning Electron Microscopy) evaluation is performed to examine the morphology, shape, size and porosity of the hydrogel. The changes on morphology and pore size of poly (potassium acrylate) hydrogel promoted by addition of starch and acrylamide in the grafting reaction were investigated through SEM images (Figure 11). As can be seen, poly (potassium acrylate-co-acrylamide) hydrogel (Figure 11a) shows interlaced network and highly porous morphology. The pores show small average size and are homogenously distributed into the hydrogel matrix. Using a magnification of 750 times, the average diameter of pores is 24,44 μm. The pores structure looks like a sponge and there are interconnected networks due to the cross-linking of potassium acrylate.



A



B

Figure 11. SEM images of (A) poly (potassium acrylate), (B) starch grafted with poly(potassium acrylate-co-acrylamide)

The starch grafted with poly (potassium acrylate-co-acrylamide) (Figure 11b) seems to be more irreguler with small pores and foliaceous aspect. The presence of starch into the hydrogel matrix should increase the amount of hydrophilic group, which make diffusion of liquids inward the matrix easier and faster [14]. The average pore size is 1.31 μm, smaller than the average pore size of poly (potassium acrylate). This fact is due to the matrix which are soo tight between acrylamide, potassium acrylate and starch. However, the hydrogel made from starch grafted with poly (potassium acrylate-co-acrylamide) still has a good performance on absorbing of water and salt solutions.

CONCLUSION

Cassava starch-g-poly(potassium acrylate-co-acrylamide) was synthesized through simultanous crosslinking and graft polymerization acrylic acid/acrylamide onto starch. Swelling capacity of the hydrogels is affected by the dose of radiation, acrylamide content, and starch content. The optimum composition which result

the highest swelling capacity of starch-g- poly(potassium acrylate-co-acrylamide) from this study is 7.5 gr of acrylamide and 0.5 gr of starch with 5 kGy total dose of gamma radiation. The best hydrogel product obtained from this research has a gel fraction of 95.9%, with the average pore size 1.31 µm which is able to absorb large amount of water, NaCl and urea solution (swelling ratio) sequentially, are 470 (g / g), 316.67 (g / g), and 526.67 (g / g), and the melting point temperature is reached 121,98 ^{o}C.

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