

Copolymerization of Onggok-Chitosan-Acrylamide with Irradiation Technique of Gamma Ray as Slow Release Material in Phosphate Fertilizer

Ladiya Puspita Ningrum¹, Asep Saefumillah², Gatot Trimulyadi Rekso³

^{1,2}Chemistry Department, University of Indonesia

Jalan Lingkar Kampus Raya, Pd. Cina, Beji, Kota Depok, Jawa Barat 16424, Indonesia, *email:
ladiyapuspitaningrum@gmail.com

³Proses Radiasi, BATAN, Lebak Bulus, Jakarta

Abstract

In a country with majority of agricultural land, is like Indonesia, fertilizers play an important role in improving the quality of crop production. For fertilizer efficiency, copolymer was developed to modify the fertilizer to have a slow release property. In this study, the synthesis of copolymers of chitosan-acrylamide (AAm) by gamma ray irradiation techniques was done to utilize waste, reduce production costs, and create biodegradable copolymer. The copolymer was prepared with composition of onggok:chitosan 2:2% (w/v) and varied acrylamide. In addition, there were performed the dose variation in gamma-ray irradiation (5, 10, 15, and 20 kGy). The results showed that the optimum copolymer with AAm 7% irradiation dose 15 kGy as modified phosphate fertilizer material. Furthermore, the result of gel fraction, solution development of fertilizer, and slow release of phosphate fertilizer 79,13%; 619.59%; and 11.51%, respectively. The optimum copolymer was characterized by FTIR, DSC, and SEM. Measurement of slow release properties was performed by the desorption-absorption method. Kinetic reaction of the fertilizer release from the copolymer was obtained following the first order. Activation energy could be obtained by connecting the rate constant and temperature, i.e. 38024.08 J/mol. The quality of copolymer was influenced by chitosan and acrylamide compositions and irradiated doses, whereas fertilizer absorptions were affected by immersion time, pH, and temperature.

Keywords: Onggok, chitosan, gamma irradiation, copolymer, slow release.

Introduction

The development of agriculture in agrarian countries such as Indonesia is increased because of the rapidly increasing population, hence the need for food also increases. However, this increase in agriculture causes environmental problems such as water pollution due to eutrophication. In 2015, millions of dead fish were stranded on the edge of Ancol Beach due to the destruction of aquatic ecosystems (Gurit Adi Suryo, 2015). Eutrophication is a process of enriching nutrients in waters sourced from agricultural waste and waste discharges that stimulate the growth of aquatic plants and adversely affect the aquatic system (M.

H Tusseau-Vuilleman, 2001). Therefore, for agrarian countries in order to reduce it by paying attention to the administration of fertilizer in plants, which is known with controlled-release method fertilizer (CRF) (Shavit, et al, 2002: 1). CRF is a useful method of reducing the rate of loss of fertilizer from soil due to washing by rainwater or irrigation water (Wang, et al., 2010: 181). This CRF method can be obtained by using copolymers that inhibit the release of water and nutrients so that there were materials that were wasted (Jamnongkan, et al., 2010: 43-44).

The majority of copolymers were synthesized used acrylic acid (AA) and acrylamide (AAM), but they were less environmentally friendly and expensive (Wang & Wang, 2010). So that, it were looked for alternatives to produce copolymers that were biodegradable and cheap. Wu and Liu (2008) coated NPK fertilizers with chitosan-polyacrylic acid-co-acrylamide which gave good dispersion and compatibility in inorganic and organic phases. In 2011, Shenghua Lv conducted the preparation of metacrylic-acrylamide-acid degradable chitosan copolymer for the leather industry as an amphoteric retaining agent which produced excellent antimicrobial and dyeing capabilities. In 2015, Gatot Trimulyadi made a fertilizer coating material from the synthesis of CMC-starch-chitosan-acrylamide copolymers which resulted in increased of developmental value and increased acrylamide concentrations which indicating increased crosslinking. Thus chitosan and acrylamide could be used as materials to produce eco-friendly copolymers.

Scientists develop environmentally-friendly research, i.e. copolymer synthesis with the addition biomass which were biodegradable and biocompatible. Some of the mass that were abundant and easy to obtain were carbohydrates or polysaccharides. Agricultural waste such as bagasse, rice straw, tapioca dregs could be used as an alternative material containing polysaccharides, i.e. onggok. Onggok is a solid waste of tapioca flour industry that can be obtained up to 75% from raw material with the remaining carbohydrate content was 65.9% (Retnowati and Susanti, 2009).

In this research, synthesis of copolymer-chitosan-acrylamide copolymer as materials for modification of phosphate fertilizer based on its developmental

property, slow release, and biodegradability have been performed. This development property will make the fertilizer absorb water and remain on the soil, while the slow release makes fertilizer release nutrients according to the needs of the plant. Thus, the copolymer can reduce phosphate waste from fertilizers because the application of phosphate fertilizer in plants becomes more effective and efficient when modified with these synthesized copolymers.

Materials and Method

Materials and Instrumentations

The materials used in this research were onggok, chitosan, acrylamide, phosphate fertilizer, acetic acid, KH_2PO_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 24\text{H}_2\text{O}$, NH_4VO_3 , concentrated HNO_3 , HCl , NaOH , and KBr powder. The required equipment and instrumentations were flat plastic container measuring $20 \times 20 \text{ cm}^2$, Co-60 irradiator, Brookfield visionary needle LV2 and LV4, tea bag, oven, waterbath, Fourier Transform InfraRed (FTIR), Differential Scanning Calorimetri (DSC), Scanning Electrone Microscope (SEM), mortar, 200 mesh strainer, beaker, UV-Vis spectrophotometer.

Procedures

Synthesis of Copolymers (Wiwien, et al, 2012)

It was prepared the copolymer ingredients such as onggok, chitosan, and acrylamide with the concentration variations shown in Table 3.1. The ingredients were mixed and added up to 200 mL of distilled water, stirred for one hour at 90°C to form a thickened solution. The solution was allowed to stand at room temperature for 60 minutes. The solution was packed in a flat plastic container measuring $20 \times 20 \text{ cm}^2$. Then, the solution was irradiated using a Co-60 irradiator with variations of 5, 10, 15, and 20 kGy.

Table 3.1. Concentrations of Copolymer Material

Samples	Chitosan (w/v)	Onggok (w/v)	AAM (w/v)
I	2%	2%	1%
II			3%
III			5%
IV			7%

1) Measurement of Copolymer Viscosity (Akhmad Rashid, 2016)

The copolymer that have been prepared, was immobilized in room temperature then measured the viscosity using a Brookfield viscometer. In the copolymer before irradiation was used the needle type LV2 speed 6 rpm, Finder Factor (FF) 50. While the copolymer after irradiation was used the needle type LV4 velocity 0.6 rpm, FF 104. The viscosity value of copolymer before and after irradiation compared to it can be seen that the copolymerization process occurred in the sample.

2) Determination of Development Capacity (Gatot and Anik, 2007)

A number of 0.1 g copolymer was taken and inserted into the wire gauze with known weights. Then each was soaked in aquades with intervals of 5-30 minutes. The copolymer was separated at 5, 10, 20, 25, 30 minutes by hanging it, to separate from the unadsorbed distilled water. Then the copolymer was weighed. Development capacity was also carried out in 20% phosphate fertilizer and KH_2PO_4 .

Capacity of development (Se) can be calculated by the following formula.

$$\text{Se} \times 100\%$$

M1 : dry gel mass

M2 : gel mass after development test at t minute.

Determination of Gel Fraction (Vienna, 2013). Copolymers of 0.2 g of the irradiated product are packed in a wire gauze that known the weight. Then, it was soaked in hot water (± 90 °C) for 5 hours. Then dried in an oven at 60 °C to a constant weight. The gel fraction is calculated by the following equation.

% Gel Fraction=

3) Test of Slow Release of Phosphate Fertilizer (Nasih, 2008)

The copolymer that was weighed as much as 0.1 g and contacted with a 20% fertilizer solution or KH_2PO_4 was measured its slow release properties in water. Every time period, the water of the bath was piped 10 mL and then added 10 mL of aquades again into the bath. For knowing the slow release properties of the copolymer, the immersion was carried out with a period of 10, 20, 30, 40, 50, 60, 120, 180, 240, 300, 360 min. The water of the immersion was measured in phosphate content by molybdat-vanadate method on UV-VIS spectrophotometer. Then the results of measurement of phosphate content in water compared with soaking time. The same procedure was done for the release of pH variation (pH 3.45 and 10) and temperature variation (28, 50, 60 °C). If it is successful, it would show the slow release of phosphate from the copolymer.

4) Measurement of Phosphate Levels Released with UV-Vis Spectrophotometer Method Fardiaz (Nasih, 2008)

The sample was determined by piped of 1 mL of the sample solution into the flask and added with 3.1 mL of molybdate-vanadate reactant and subjected to aquades until 25 mL. The solution was measured by a visible spectrophotometer at 400 nm. The sample would react with these reagents and form yellowish-orange vanadimolibdiphosphate acid complex. The equation of the reaction can be seen in the following equation.



5) Characterization of Copolymers (Gatot Trimulyadi, 2014)

The optimum copolymer was analyzed its functional group with Fourier Transform InfraRed (FTIR) at 4000 to 400 cm^{-1} using KBr powder. In addition, it was analyzed its thermal stability using the Differential Scanning Calorimetry (DSC) instrument and to ensure the surface morphology of the copolymers formed, the copolymer was analyzed using Scanning Electron Microscope (SEM).

Results and Discussion

1. Synthesis of Onggok-Chitosan-Acrylamide Copolymer

The irradiated copolymers have different physical forms depending on the dosage of gamma rays and the concentrations of acrylamide. To know the reaction of copolymer that happened, it can be seen in Figure 4.1. The first stage of copolymerization reaction with irradiation technique was the initiation stage. The initiation stage was the stage of free radical formation by gamma ray radiation. The first molecule that was exposed was H₂O because of the most amount in the mixture. The covalent bonds of H₂O broke off to form free radicals HO• and H•. The H• attacked amylose to form amylose-O•. Furthermore, on the propagation process, amylose-O• attacked monomer (acrylamide) and HO• attacked the polymer (chitosan). The propagation process continued until the monomer becomes a polymer. The last stage was termination, the growth activity of free radical polymer was stopped by the reaction of other monomer radicals to form the copolymer (Erizal, 2014).

In the following mechanisms the content of the onggok that played a role in the copolymerization reaction was only amylose. This was due to the highest content of onggok was starch, but the starch was actually divided into amylose and amylopectin. However, in this study, the onggok used was predicted have low amylopectin content because it was seen from its non-sticky physical form (Damardjanti, 1995).

Based on the mechanism above, the copolymers that were formed in this study were classified as random copolymers. Generally, random copolymers could be formed when a monomer having a double bond undergoes a copolymerization reaction through a radical polymerization process (Dieter A. S., et al, 2012). Although the synthesized copolymers in this study did not perform a special synthesis technique, it can be concluded that copolymerization reactions have occurred. It can be proven on the copolymer characterization results through FTIR and DSC data.

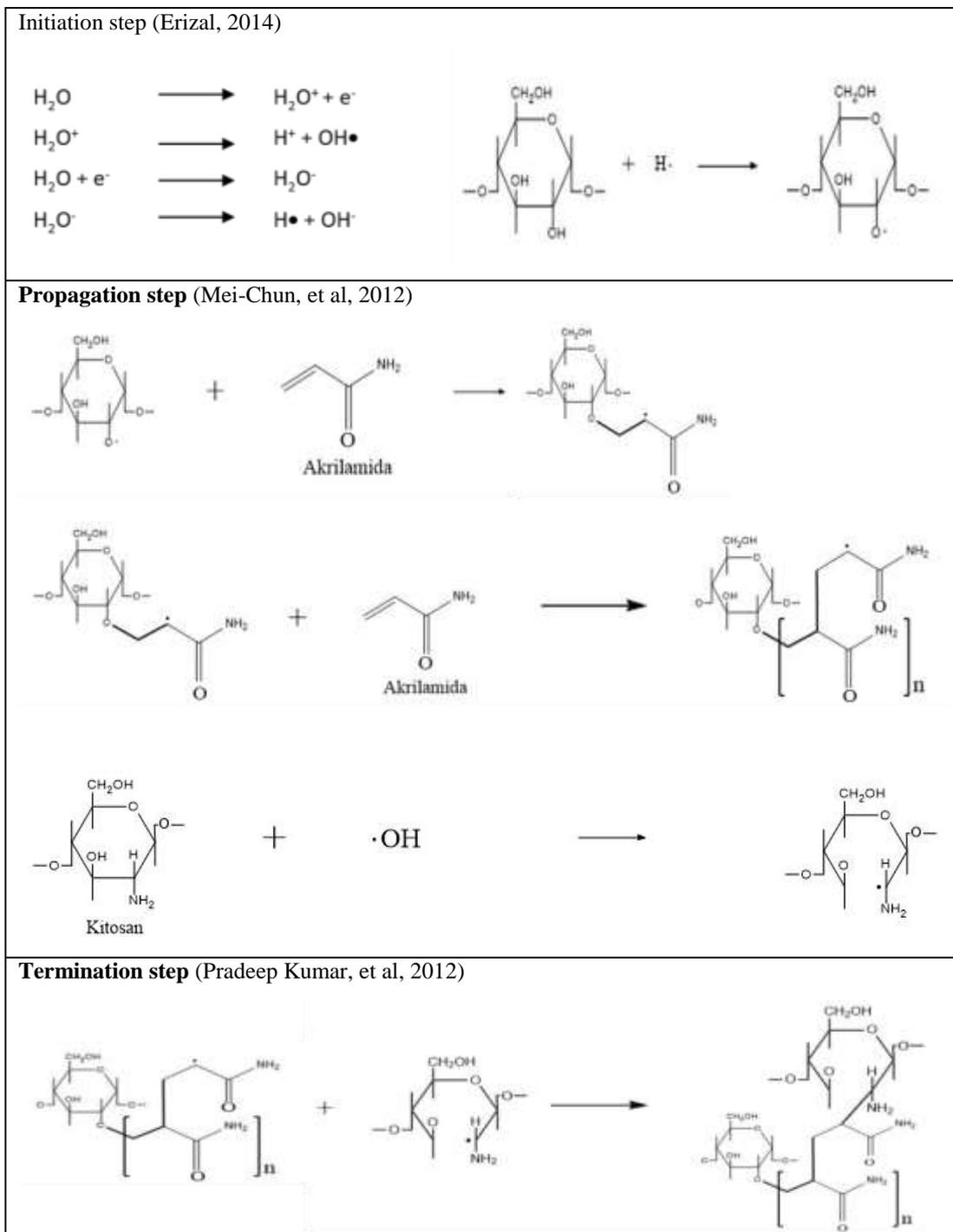


Fig. 1. Mechanism of Copolymerization Reactions of Chitosan-Chitosan-Acrylamide

2. Copolymer Viscosity

The Onggok-Chitosan-Acrylamide mixture was tested the viscosity before and after the radiation, and obtained the viscosity value according to Figure 4.2.

Sampel		Viskositas (cps)	
		Sebelum Iradiasi	Sesudah Iradiasi
5 kGy	AAm 1%	11000	50000
	AAm 3%	13600	80000
	AAm 5%	14600	710 x 10 ⁴
	AAm 7%	15000	50000

Sampel		Viskositas (cps)	
		Sebelum Iradiasi	Sesudah Iradiasi
10 kGy	AAm 1%	11100	70000
	AAm 3%	13100	10 x 10 ⁴
	AAm 5%	15150	Gel
	AAm 7%	16300	Gel

Sampel		Viskositas (cps)	
		Sebelum Iradiasi	Sesudah Iradiasi
15 kGy	AAm 1%	10850	90200
	AAm 3%	13400	Gel
	AAm 5%	15000	Gel
	AAm 7%	16350	Gel

Sampel		Viskositas	
		Sebelum Iradiasi	Sesudah Iradiasi
20 kGy	AAm 1%	10550	13 x 10 ⁴
	AAm 3%	13500	Gel
	AAm 5%	14900	Gel
	AAm 7%	16700	Gel

Fig. 2. Viscosity Value of Each 2% Copolymer-2% Chitosan-Acrylamide (1%, 3%, 5%, 7%) with Different Dose of Irradiation

In Figure 2, from the data before irradiation, the high concentration of acrylamide increased the viscosity value of the synthesized copolymer. Variations of gamma-ray doses in the samples also affected the increasing of viscosity values as well. Based on the theory, it was known that irradiation served as a cross linker agent in copolymer synthesis. The higher radiation dose, the more crosslinking that was formed on the copolymer.

3. Gel Fraction

The synthesized copolymer was gel fraction test. The test aimed to determine the amount of the starting material changed into gel. In addition, this test was also to determine the amount of crosslinking that were formed on each copolymer sample (Erizal et al., 2011).

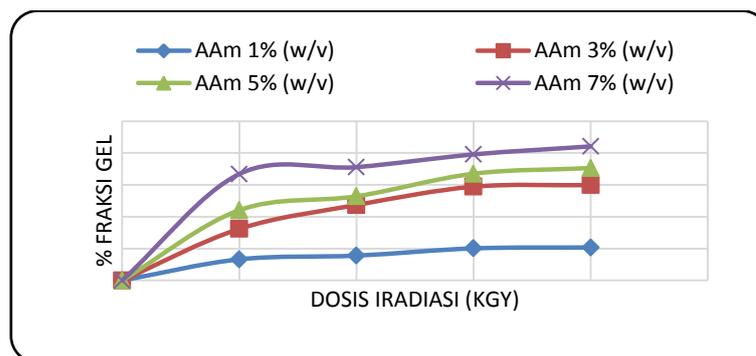


Fig. 3. The effect of Radiation Dose on the Value of Gel Fraction in Sample with Free Variation of Acrylamide, 2% (w / v) Stacked Variation of Onggok and 2% Chitosan (w / v).

Based on the gel fraction test data above, it was obtained that the increase of irradiation dose that was given to the sample also increased the % of gel fraction. The low gel fraction values at low dose and concentrations of acrylamide were due to the small amount of insoluble ingredients, consequently a non-rigidly formed matrix. This was because at low radiation doses the number of crosslinks that were formed only slightly. While on the high gel fraction value, the amount of insoluble material were much so that the matrix that was formed more rigid. However, the optimum copolymer characterized was sample IV (AAm 7%) at a dose of 15 kGy, with a gel fraction value of 79.13%. This sample was chosen because at the higher gel fraction value it has been solidified, while the desired copolymer phase was semi solid.

4. Capacity of Development

Development is one of the peculiar abilities of gel copolymers in absorbing water. The ability of these gels to absorb water is influenced by the free functional groups contained in the hydrogel, such as is -OH and -NH₂ (Erizal et al., 2002). The development properties possessed by this copolymer gel can be used as a determination of the swelling ability of the copolymer, based on the value of the development ratio to the maximum extent of the swell gel at a particular immersion time. The value of this development ratio was obtained through the mass ratio between the gel that has been absorbed by water immersion with dry

gel. In each sample the copolymer was tested for development in aquadest, acid solution, alkaline solution, phosphate fertilizer solution and KH_2PO_4 solution.

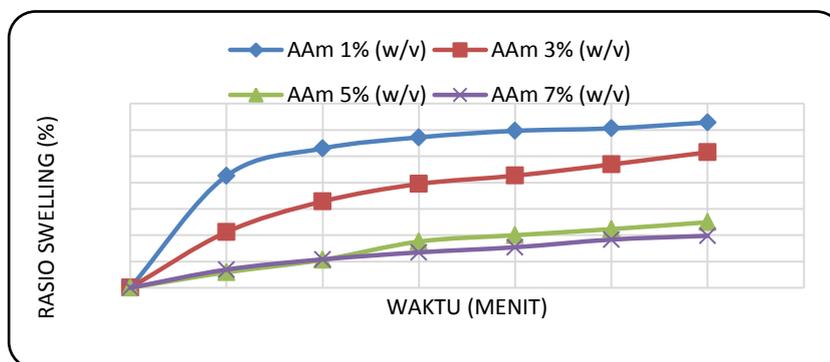


Fig. 4. The relation between time of immersion to the swelling ratio of sample 15 kGy with Onggok 2% (w / v) -Titrate 2% (w / v) and% Acrylamide 1%, 3%, 5%, 7%

The increased radiation dose caused the sample development capacity decreased, but the copolymer capability reached maximum immersion time. At low doses, pore size was big, but the number of pores that were formed was still very small so that the pore space to enlarge was still quite large compared to the higher doses due to a lot of pores but in small size. When it was associated with the gel fraction test results, samples with high development values have low gel fraction values. The rigid / non-rimed copolymer matrix caused a large amount of absorbed water with a lower optimum absorption time. The absorption process of the phosphate solution by the copolymer was due to the diffusion process and hydrophilic groups that were contained in copolymer. The phosphate fertilizer solution contained a large amount of PO_4^{3-} -anion, whereas in the copolymer there was no such anion allowing for diffusion. By its definition, the diffusion was an event of the solutes transfer in a particular solvent from high concentration to low concentration through a semipermeable membrane (nptel.ac.id). This will cause the water-bound phosphate molecule entered the copolymer membrane by itself due to diffusion. Then, the water molecules were bound into the copolymers as a result of the hydrophilic group derived from the monomers and the copolymer polymers.

In its distribution, water was not freely entering into the copolymer, but it was affected by the phosphate anion that binds the water. Water-bound phosphate molecules were larger than free water. It caused slower movement rates. However, in this research results, it was obtained that the ratio of copolymers' development in water was smaller than in the solution of fertilizer. It may be due to a water-soluble assay performed only for 30 min different in a phosphate solution of 180 minutes. So that, there would be a chance of fluctuation in the ratio of the development in water after 30 minutes, then the ratio of development in water and in the solution of fertilizer could not be compared.

The differences in the ratio of development' value between each sample was expected as a result of differences in pore size in the sample. The smaller pore size would be covered by the PO_4^{3-} -anionic molecule, while if the pore size was larger, the PO_4^{3-} anion could enter into the cross linking network of copolymers and water molecules bounded to the anion would enter in larger quantities. The possible interaction was the ionic interaction between the PO_4^{3-} anion with the functional groups ($-\text{NH}_2$, $-\text{OH}$, $-\text{C} = \text{O}$) present in the copolymer as well as the intra- and inter-molecular interactions and even the hydrogen bonds between the water bonded to the anions with the $-\text{NH}_2$ functional group and $-\text{OH}$ from chitosan (Xiaodi et, al., 2015).

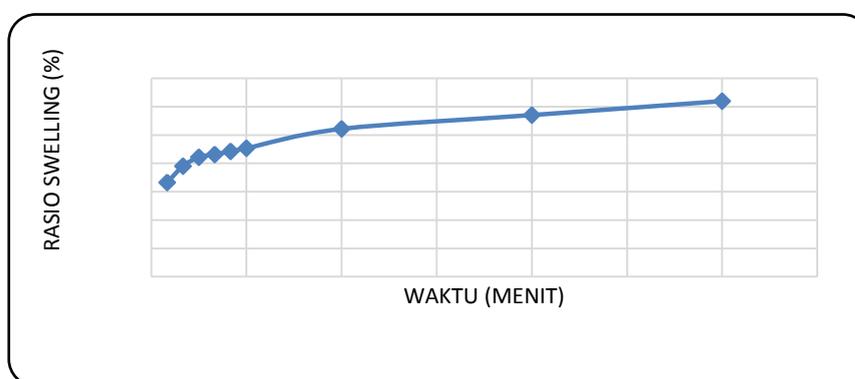


Fig. 5. The Curve of Development Ratio in KH_2PO_4 on 2% for Onggok Samples (w / v) Chitosan 2% (w / v) AAm 7% (w / v) Dose 15 kGy

For knowing the optimization of optimum copolymer in absorbing PO_4^{3-} , at Onggok sample 2% (w / v) 2% (w / v) -AAm 7% (w / v) dosage 15 kGy was tested absorption to KH_2PO_4 with ratio of development that obtained was 619.58%. The value of this development capacity was greater than when the copolymer absorbed phosphate fertilizer where the value of its development ratio was 583.52%. This difference in value could be caused by the use of phosphate fertilizers which the content was not only PO_4^{3-} , so the copolymer could absorb other elements in fertilizers such as Nitrogen and Potassium.

5. Slow Release Phosphate

5.1 Effect of pH on Phosphate Release in Fertilizer

Slow-release test was performed on three samples of each radiation dose by the desorption-absorption method initiated by the absorption process, which was contacted the copolymer into a 20% phosphate fertilizer solution for 3 hours. The desorption process was carried out by contacting the copolymer with a solution of pH 3.45; PH 7; and pH 10 for 6 hours. The amount of phosphate that was absorbed and discharged on the copolymer, was measured chemically by the molybdate-vanadate method. The percent value of phosphate release was the ratio between the amount of phosphate that exited (g) at any given time with the total amount of phosphate (g) absorbed on the copolymer during absorption process.

Slow-release testing was performed on three samples of each radiation dose by the desorption-absorption method initiated by the absorption process, which contacted the copolymer into a 20% phosphate fertilizer solution for 3 hours. The desorption process was carried out by contacting the copolymer with a solution pH: 3.45; 7; and 10 for 6 hours. The amount of phosphate that was absorbed and discharged on the copolymer, was measured chemically by the molybdate-vanadate method. The percent value of phosphate release obtained was the ratio between the amount of phosphate that exits (g) at any given time with the total amount of phosphate (g) absorbed on the copolymer during absorption process.

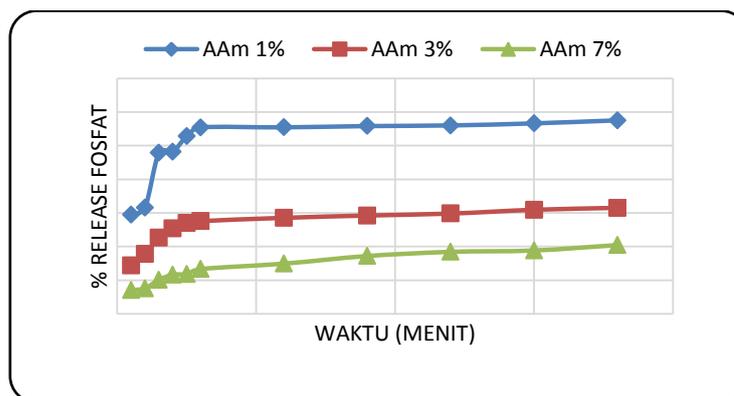


Fig. 6. The Curve of Phosphate Release at pH 3.45 Sample 15 kGy with Acrylamide Free Variation and 2 Mg (w/v) Stochastic Variation of Onggok and 2% Chitosan (w / v)

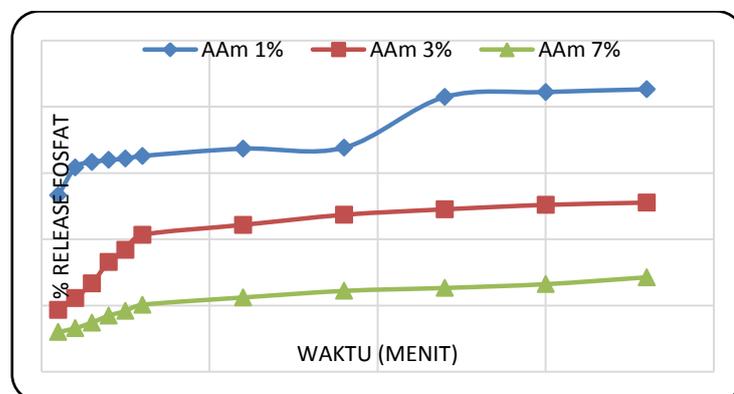
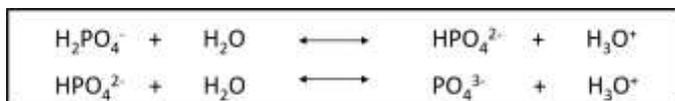


Fig. 7. The Curve of Phosphate Release at pH 10 of Sample 15 kGy with Acrylamide Free Variation and 2% (w / v) Fixed Variation of Onggok and 2% Chitosan (w/v)

In the acidic-alkaline variation, the decreasing amount of H^+ in solution increased the amount of desorption phosphate. Under acidic condition, the reaction moved to the left to form $H_2PO_4^-$, so that the phosphate ions that was released was only slightly, the detached phosphate ion was a phosphate ion that did not bind to H^+ . Conversely, under alkaline condition, the reaction moved to the right to form PO_4^{3-} , since only a small amount of H^+ reacted with phosphate, following the dissociation reaction of the orthophosphate in the fertilizer.



Reaction of Phosphate Dissociation

Furthermore, for the phosphate desorption process at aquadest almost as in pH 3.45 (H^+ high) solution. It was prediction because the ionic interaction of phosphate anions with $-\text{NH}_3^+$ was less due to the amount of H^+ derived only from the natural dissociation of only aquadest. In addition, the interaction of phosphate desorption in copolymers was more dominated by inter and intra-meolecular interactions as well as hydrogen bonds between functional groups in copolymers with phosphate anions.

5.2 Slow Release of Phosphate in KH_2PO_4

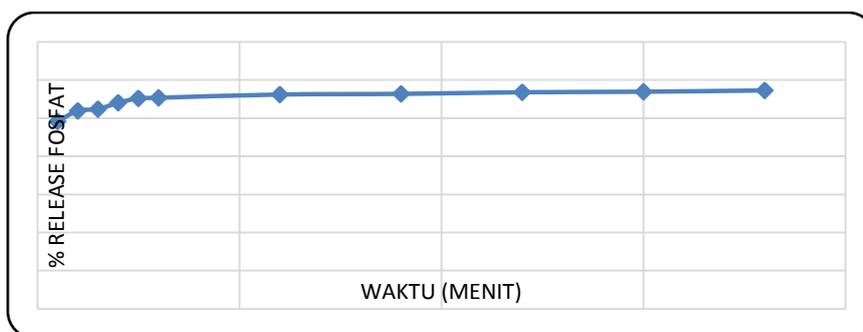


Fig. 8. The % Release of Phosphate from KH_2PO_4 in Sampel: Onggok 2% (w/v)-Chitosan 2% (w/v)-AAM 7% (w/v) Dose 15 kGy in Aquadest (pH 6.6)

Moreover, for knowing optimation of the optimum copolymer in desorbing PO_4^{3-} , in sample: Onggok 2% w / v (w / v) 2% (w / v) -AAM 7% (w / v) dosage 15 kGy was tested for phosphate desorption from KH_2PO_4 with % phosphate release of 11.45%. This value was not much different than when the copolymer was desorbed phosphate fertilizer where the phosphate release value is 11.51%. The selection of the sample with AAM 7% and the 15 kGy irradiation dose was

based on the stable phosphate release curve. The dose of 20 kGy was not selected because the phosphate release was slower than at a dose of 15 kGy.

5.3 The Effect of Temperature to Phosphate Release in Fertilizer

Based on Figure 4.9, it was shown that the increasing temperature, caused more phosphate release. The increased of temperature conditions would affect the copolymer to expand, consequently the fertilizer attached to water that fills the pores of the copolymer was detached due to the expanding pore size. This was the reason that caused more phosphate that were released at higher temperatures.

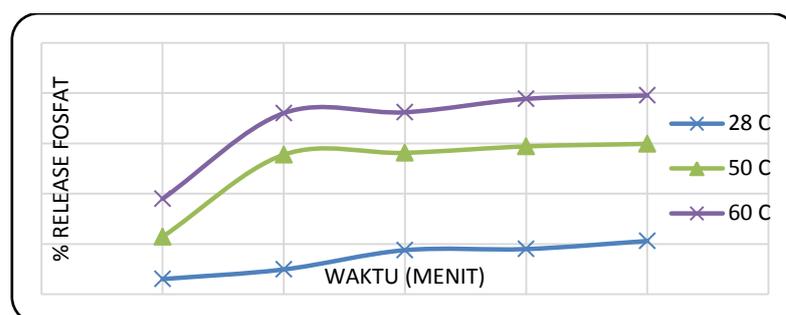


Fig. 9. The % of Phosphate Release at Temperature Variation

6. Kinetics of Reaction

6.1 Determination of Order Reaction in Phosphate Release

Determination of the release reaction order can be found by comparing the phosphate mass released from the chitosan-chitosan-acrylamide copolymers to the total amount of the phosphate absorbed. For knowing the appropriate reaction order, then the phosphate release reaction used first order and second order for higher linearity. At the first order release rate kinetics based on the basic theory of release kinetics, the curve was obtained by plotting the parameters of $S_0 / (S_0 - A)$ on the y-axis and on the x-axis i.e. time. On this curve, it was added a point at $t = 0$ because for this first-order equation was $y = bx$ in the absence of an intercept. Then for second-order rate kinetics can be obtained by plotting the parameters $1 / (S_0 - A)$ on the y-axis and on the x-axis i.e. time.

Table 1. The value of R² on each temperature in determination of rate reactions kinetics in phosphate release by first and second order

Temperature (°C)	R ²	
	First Order	Second Order
28	0.9531	0.9279
50	0.7646	0.6142
60	0.7641	0.6751

Based on the data obtained from the above curve by comparing the regression value at each temperature, it could be concluded that the regression value from the first order was greater than the second order (see Table 4.1). Regression values can be used as indicators to determine the appropriate reaction order. Therefore, the reaction kinetics of phosphate release used first order was obtained from $\ln S_0/S_0-A$ as a function of time. This relationship can be used to find the water-soluble phosphate in a copolymer matrix. Therefore, the equation of the reaction rate bellow.

$$v = k[\text{development}]$$
$$k[\text{development}]$$

6.2 The Effect of Temperature to Kinetics of Reaction

The temperature was related to the reaction kinetics to find out the amount of activation energy required during the reaction, according to the following equation.

$$\ln k = \ln A -$$

The temperature relation to the reaction kinetics was obtained by plotting the first order $\ln x$ as the $1/T$ function.

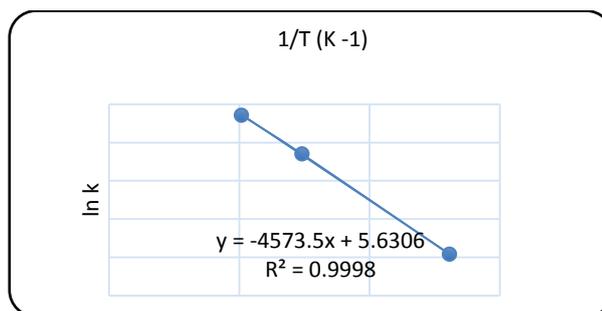


Fig. 10. The Curve of Relation of ln k to 1/T in determination of relation of temperature and Kinetics of Reaction

Based on the curve above, we got the equation of line $y = -4573,5x + 5,6306$ where the gradient of this equation was $-E_a / R$. The R was a constant value of $8,314 \text{ J / mol.K}$ so that it can be calculated the activation energy of the following reaction was 38024.08 J / mol i.e. the energy required by phosphate to desorb from the matrix of the copolymer at a temperature.

7. Characterization of Copolymers

7.1 FTIR

Characterization with FTIR aimed to determine the changing of group peaks of materials that were used as the copolymer constituents. The analysis was done by comparing the result of FTIR acrylamide, onggok, chitosan, sample before irradiated and after irradiated.

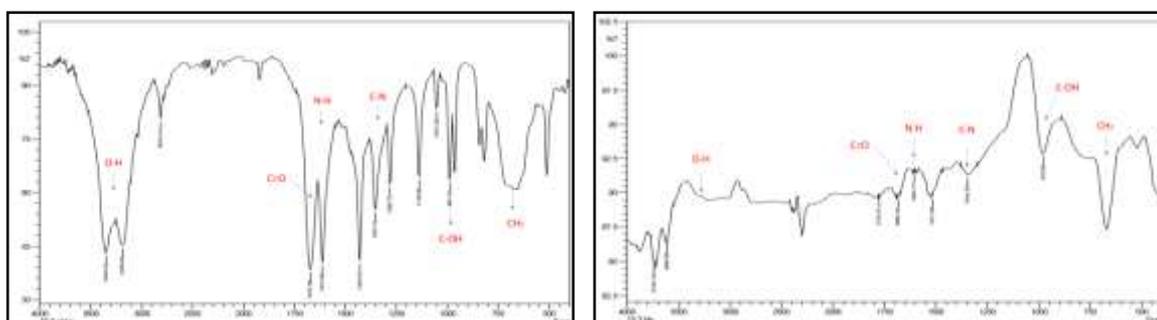


Fig. 11. Result of FTIR Analysis on Mixture of Prior to Irradiated Material (left) and on Copolymer Formed (right)

Based on the FTIR results, with based on spectra of each copolymer constituent it can be concluded in whole that the peak of each cluster was reduced. At the wave number 3000-3600 cm^{-1} the peak of the O-H group has been weak and widened. This can be due to the O-H on the onggok and the chitosan has reacted with acrylamide to form hydrogen bonds. The success of copolymerization reactions can also be seen from the newly emerging peak, at the wave number of 700 cm^{-1} which was the peak of CH_2 of poly-acrylamide. Before the irradiation, acrylamide monomer has a double structure, but after the copolymerization the acrylamide monomer was joined by breaking the double bond and forming a straight chain CH_2 . At wave number 1685,79; 1517,96; And 1344,38 cm^{-1} , indicated the presence of C = O, N-H bending, and C-N stretching respectively and indicating the $-\text{CONH}_2$ group (Arup et al., 2015). In the spectrum about 987 and 979 cm^{-1} , there was a C-OH reduction between the results before irradiation and after irradiation. This was prediction due to the copolymerization with the monomer or polymer in the mixture of the material.

7.2 DSC

The success of copolymerization reaction with irradiation technique can be known through analysis with DSC by comparing the sample before irradiation and after irradiation. The copolymer materials that were used there were two types of acrylamide including monomers while chitosan and onggok were polymers.

Based on Figure 4.12, it was seen that in the sample before irradiation there were three peaks of each constituent which temperature of 100 $^{\circ}\text{C}$ as the peak of the melting point of acrylamide, at temperature of 300-330 $^{\circ}\text{C}$ as the peak crystallization of chitosan, and at temperature of 360-380 $^{\circ}\text{C}$ as Crystallization of onggok. While in the sample after irradiation of the three peaks of each material was not visible. This indicated that all materials used in the manufacture of copolymers have been successfully bonded to each other.

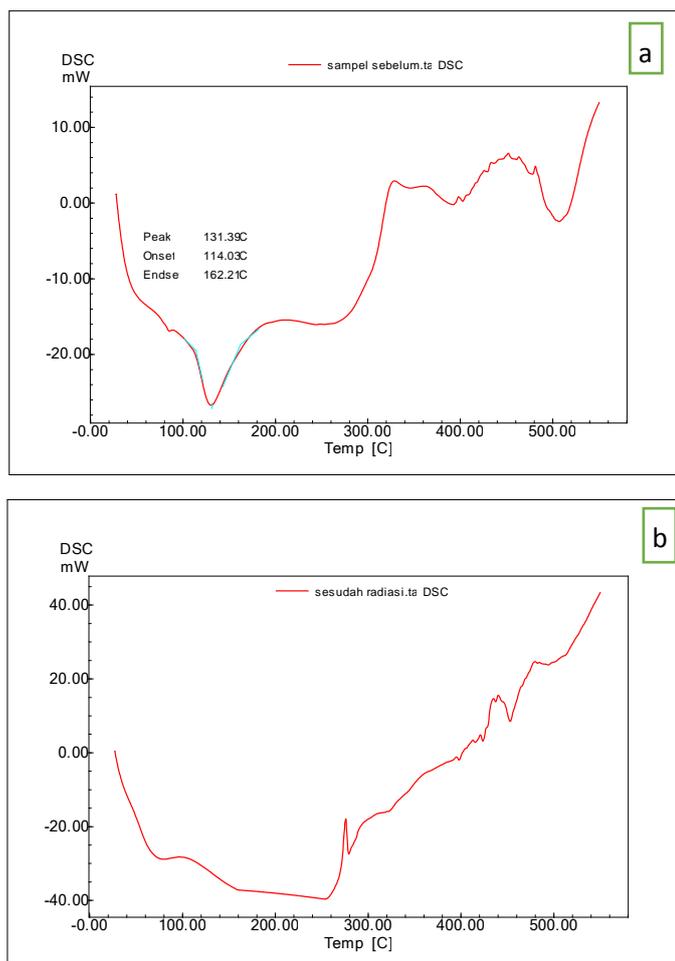


Fig. 12. The Result of DSC (a.) Mixed Materials (b.) Copolymer after Irradiation

7.3 SEM

SEM characterization aimed to determine the surface morphology of the synthesized copolymers. Characterization was only done on 2% -good samples-2% -AAm 7% dosage of 15 kGy because based on previously obtained and observed data this sample has better physical and chemical properties which can be applied as material of slow release phosphate fertilizer. Based on Figure 4.13, the added Onggok into the crosslinked copolymer network material enter into the crosslinks forming bonds and making pores in the crosslinking network. However, the uniform distribution and size of these pores can be due to uneven

size of the pieces and the less homogenous synthesized copolymers resulting in uneven distribution of pores.

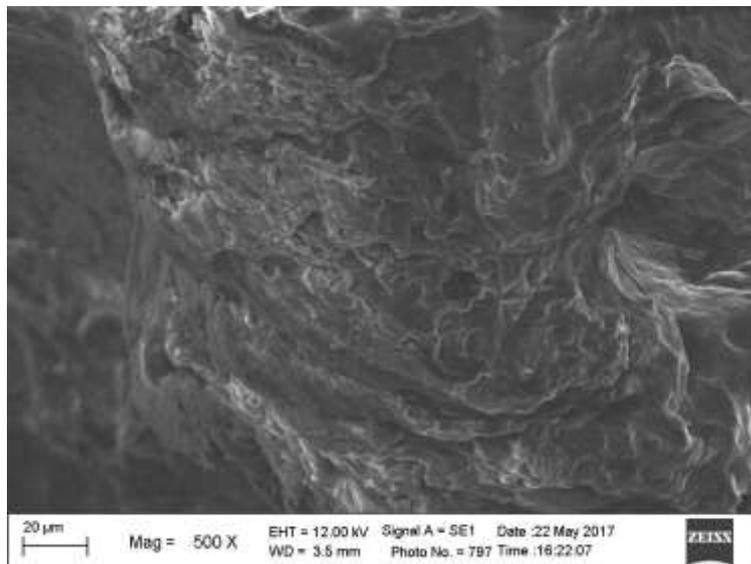


Fig. 13. Result of SEM Analysis Copolymers of Onggok 2%-Chitosan 2%-AAm 7%.

Conclusions

In this study, copolymers of chitosan-acrylamide have been successfully synthesized using gamma irradiation techniques. The resulting copolymer may be used to modify phosphate fertilizer into slow release fertilizer by looking at the parameters of success from the gel fraction value, development capacity, and from the phosphate release test on the fertilizer. The results obtained that the increased of radiation dose and acrylamide concentration affect the matrix structure formed on the more rigid copolymers. The matrix's influence of each copolymer was seen in the swelling capacity when the 5 kGy irradiation dose tends to be larger and faster to reach the optimum swelling point compared with the doses of 10, 15, and 20 kGy. The effect of pH by increasing the least amount of H⁺ in the solution, then the percent value of phosphate release increases. The increase in temperature is proportional to the amount of phosphate released from copolymers more and more. Sample IV (AA 7% concentration with 15 kGy irradiation dose) was selected as the optimum copolymer with gel fraction percent value of 79.13%, absorption of 20% phosphate phosphate solution and IV phosphate KH₂PO₄

sample having swelling capacity of 583.52% and 619.59%,% phosphate release for IV samples for 6 hours under pH 3.45, aquadest (pH 6.6), and pH 10 conditions of 10.22%; 11.51%; 14.25%, with a fairly rigid matrix form seen from its physical form. The relation between the temperature and the kinetics of the phosphate release reaction was the rate of phosphate release with the greater temperature. From the relation temperature obtained energy value of activation equal to 38024,08 J/mol. The order of kinetics of the phosphate release reaction was obtained from the comparison of the regression values of the first and second order curves, it was found that the reaction kinetics of the phosphate release follows the first order. FTIR, DSC, and SEM results showed that copolymerization reactions with irradiation techniques on synthesized copolymers have been successfully seen from the reduced clusters of each material and the pores formed on the copolymer.

Suggestion

Chitosan-acrylamide had great potential as new copolymer materials, especially in modifying phosphate fertilizers to have slow release properties. Therefore, it was expected that the development and improvement of the copolymer in synthesis method. Where all the ingredients and fertilizers were mixed entirely and made in pellet form. This will improve the performance of the copolymers as well as to avoid moldy copolymers. Then the biodegradation test on the copolymer determines the copolymer resistance to the microorganisms in the soil. In testing of slow release properties, for variations in temperature and pH adjusted to soil conditions of the tropics as initial simulations before the copolymers were developed on a wider scale, as well as the addition of variations in water and soil release times over 6 hours to determine the optimum release time of the samples by Dose irradiation 15 kGy upwards.

References

- A. S., Dieter, et al. (2012). *Synthesis of Polymers: New Structure and Methods*. Wiley -VCH.
- Adi Suryo, Gurit. (2015) <http://lipi.go.id/berita/single/Eutrofikasi-Penyebab-Kematian-Massal-Ikan/10464> Accessed on 28 January 2017 at 17.53 WIB.

- Andriyanti, Wiwien, et. al. (2012) Pembuatan dan Karakterisasi Polimer Superabsorben dari Ampas Tebu. Jakarta: <http://digilib.batan.go.id> Accessed on February 9, 2017.
- Balai Besar Pelatihan Pertanian. (2014) <http://bbppbinuang.info/index.html> Accessed on 30 January 2017 at 16.38 WIB.
- Damardjanti, D. S. (1995). *Karakteristik Sifat Standardisasi Mutu Beras sebagai Landasan Pengembangan Agribisnis dan Agroindustri Padi di Indonesia. Inaugural Oration of Expert Researcher*. Bogor: Balai Penelitian Bioteknologi Tanaman Pangan.
- Erizal, Abidin Z, Deswita, Sudirman. (2011). Super absorben poli(akrilamida-ko-kalium akrilat) dengan Teknik Radiasi dan Penciriannya. *JlIm Aplik Isot Rad*. 6(2): 105-116
- Erizal, Dewi S.P., dan Darmawan D. (2002). Sintesis dan Karakterisasi Hidrogel Poli (Akrilamida) Hasil Iradiasi Gamma. Jakarta: Accessed on May 20, 2017.
- Erizal, Sudirman, Zainal A. (2014). Efek Dosis Iradiasi dan Konsentrasi Pada Sintesis Superabsorben Hidrogel Poliakrilamida Berikatan Silang menggunakan Iradiasi Gamma. *APISORA*.
- Jamnongkan, T dan Kaewpirom, S. (2010). Controlled-Release Fertilizer Based on Chitosan Hydrogel: Phosphorus Release Kinetics. *Science Journal Ubonratchathani University*, Vol. 1, No. 1, 43-50.
- Kumar, Pradeep, et al. (2012). Novel High-Viscosity Polyacrylamidated Chitosan for Neural Tissue Engineering: Fabrication of Anisotropic Neurodurable Scaffold via Molecular Disposition of Persulfate-Mediated Polymer Slicing and Complexation. *Int. J. Mol. Sci.* 2012, 13(11), 13966-13984.
- Li, Mei-Chun, et al. (2012). Emulsion Grafting Monomers onto Starch for Reinforcement of Styrene-Butadiene Rubber. *Macromolecules Research* DOI: 10.10007/13233-01301052-3.
- Li, Xiaodi, et al. (2015). Characterization, Swelling, and Slow Release Properties of a New Controlled Release Fertilizer Based on Wheat Straw Cellulose

- Hydrogel. Jakarta : www.elsevier.com/locate/jtice Accessed on May 20, 2017.
- Lv, Shenghua, et al. (2011). Preparation and Properties of Copolymer of Methacrylic Acid and Acrylamide onto Degraded Chitosan Initiated by HRP/H₂O₂/ACAC. *Applied Mechanics and Materials* Vols. 80-81 pp 396-399.
- Mandal, Arup dan Debabrata Chakrabarty. (2015). Characterization of Nanocellulose Reinforced Semi-Interpenetratingpolymer Network of Poly(vinyl alcohol) & Polyacrylamide Compositefilms. www.elsevier.com/locate/carbpol Accessed on January 30, 2017 at 21:40 pm.
- Nasih. (2008). Penetapan Kadar Fosfor dalam Buah Apel. Jakarta : <http://repository.usu.ac.id/bitstream/123456789/14443/1/09E0086.pdf> Accessed on February 9, 2017.
- Rekso, Gatot Trimulyadi dan Anik Sunarni. (2007). Karakteristik Hidrogel Polivinilalkohol-Kitosan Hasil Iradiasi Sinar Gamma. Depok : http://jusami.batan.go.id/dokumen/materi/15Apr11_155745_Gatot.pdf Accessed on February 9, 2017.
- Rekso, Gatot Trimulyadi. (2014). Kopolimerisasi Cangkok dan Karakterisasi Lembaran Kitosan Teriradiasi. Pusat Aplikasi Teknologi Isotop dan Radiasi BATAN.
- Rekso, Gatot Trimulyadi. (2015). Fraksi Padatan dan Nilai Swelling Campuran CMC-Pati-Kitosan dengan Akrialmida yang Diiradiasi dengan Sinar Gamma sebagai Bahan Pelapis Pupuk. *Proceeding.Seminar Nasional Kimia dan Pendidikan Kimia VII UNS*.
- Retnowati, D dan R. Susanti. (2009). Pemanfaatan limbah padat ampas singkong dan lindur sebagai bahan baku pembuatan etanol. *Thesis*. Semarang: Teknik Kimia Universitas Diponegoro.
- Syahputra, Akhmad Rasyid. (2016). Kopolimerisasi Iradiasi Pati Akrilamida dan Polivinil Alkohol dengan Penambahan Oligokitosan sebagai Bahan

- Penginduksi Pertumbuhan Bayam Hijau. *Thesis*. Depok : Kimia FMIPA UI.
- Tusseau-Vuilleman, M.H. (2001). Do food processing industries contribute to the eutrophication of aquatic systems? *Ecotoxicol. Environ. Saf.* 50: 143-152.
- U, Shavit, et al. (2002). Wetting mechanisms of gel based controlled release fertilizers. *Journal of Controlled Release*.88:71-83.
- Wang, Jinlei, Zheng,Yian and Wang, Aiqin. 2010. Synthesis and Swelling Behaviors of Poly (sodium acrylate) / Hydroxyapatite Superabsorbent Nanocomposit. Beijing, Cina.
- Wu L, et al. (2008). Preparation and Properties of Chitosan-Coated NPK Compound Fertilizer with Controlled-Release and Water-Retention. *Bioresource Technology*. 99 (2): 547-554.
- Yulianti, Wina. (2013). *Sintesis-Kinetika Swelling Selulosa Jerami Padi-Cangkok-Poli (Asam Akrilat-ko-Akrilamida)*. Depok: Departemen Kimia Universitas Indonesia.