

## Fast Swelling Superabsorbent Hydrogels Starch Based Prepared by Gamma Radiation Techniques

Erizal<sup>1,\*</sup>, D. P. Perkasa<sup>1</sup>, Sudirman<sup>2,3</sup>, E. Budianto<sup>3</sup>, R. Yudianti<sup>4</sup>

<sup>1</sup> Centre for Application Isotopes and Radiation Technology, National Nuclear Energy Agency, Jl. Cinere Raya, Jakarta 12070, Indonesia; izza3053@yahoo.com

<sup>2</sup> Centre for Material Nuclear Industry Technology, National Nuclear Energy Agency, Serpong 15314, Tangerang Selatan, Indonesia

<sup>3</sup> Department of Chemistry, University of Indonesia, Kampus UI Baru, Depok, Indonesia

<sup>4</sup> Research Center for Physics, Indonesian Institute of Science, Jl. Sangkuriang 154D, Bandung, Indonesia

**Abstract.** Fast swelling superabsorbent hydrogels starch based were synthesized by radiation crosslinking of the mixture acrylamide (AAM)-acrylic acid (AA)-starch (15: 5 : 1 w/v) solution using  $\gamma$  rays from Co-60 with varying irradiation doses (7.5-12.5 kGy) at ambient temperature. The copolymers were characterized by Fourier transform infra red spectroscopy (FT-IR) and differential thermal analysis (DSC). It was found that hydrogels showed superabsorbent behavior with higher swelling capacities (~300 g/g) and reached at a very short time (15 sec). The maximum gel fraction was ~90 % which achieved with increasing irradiation dose up to 12.5 kGy. There was no significant difference of the effect of irradiation on swelling of hydrogels. The hydrogels were also found sensitive to the NaCl and methylene blue solution. The FTIR spectra of hydrogels showed crosslinking occurs between AAM and AA. This super-absorbent is promising as a biodegradable additive to be used in health care.

**Keywords:** Radiation; superabsorbent; acrylamide; acrylic acid; sodium alginate; gel fraction; swelling

### Introduction

Nowadays, the need for materials that have good performance in absorbing a large amount of water or liquid has become an interesting subject for researchers. One of these materials is the synthetic hydrogel matrices, which comprise water-insoluble, but water-swelling crosslinked hydrophilic polymers. These materials are known as hydrogel superabsorbent (HSA), originated in the United States as water retention agents in agriculture, and developed in Japan in the middle 1970s in personal care and hygienic products such as surgical pads, hot and cold therapy packs, medical waste solidification, disposable diapers, sanitary napkins, etc. [1]. Moreover, they are used as artificial soils for

hydroponics in soil conditioning, as drug delivery systems agents for pharmaceuticals or agrochemicals and the numerous applications [2-5].

In recent years, research on HSA has been intensively focused on some types of basic materials such as acrylic acid (AA) and acrylamide (AAM) monomers and its copolymers [6-8]. However, the disadvantage of HSA based on monomers/polymers synthetic is not biodegradable which will cause environmental problems. Hence, the development of multi-component superabsorbent derived from natural polymer and eco- friendly additives is subject of great interest due to their unique commercial and environment advantages and such materials have also been honored as the material families of “in greening the 21<sup>st</sup> century materials world” [9].

Biodegradable polymers have been recently giving more attention used for the preparation of hydrogels using natural polymers due to their safety, biocompatibility, hydrophilicity, and biodegradability. Among these compounds, starch as naturally occurring polysaccharides is very attractive because its may form physical gels under specific conditions. Using starch-based hydrogels has some advantages such as it has a high swelling capacity in water, applicable to a variety of process, available in many countries, abundant natural biopolymer, and easy to prepare with fairly inexpensive reagents. Therefore, it is expected that the new of HSA with improve structure and performance can be developed by the effective combination of AAM-AA with starch via gamma irradiation technique.

In previous work, the swelling behaviour of poly(AAM-AA)-starch hydrogels containing AAm,AA with varying starch concentration (1-3%) synthesized by gamma radiation at different doses (10- 30 kGy) were studied [10]. We found that incorporation of 1% starch content present in hydrogel irradiated at a dose 10 kGy, the maximum swelling ratio of hydrogel in the granular form was 350 g/g and reached at 24 h. For the application, especially as absorbents incorporated in the baby napkins, this HSA is not applicable because its swelling rate is a low. Following our previous works, we have recently emphasized mostly on the swelling rate enhancement through reducing irradiation dose. In addition, formation of powder form in the final products provides a certain way to improve swelling rate of hydrogels.

In the present work, a series hydrogel superabsorbent of poly(AAM-AA)-starch containing 5% AAM, 15% AA with 1 % starch were irradiated using gamma radiation at a low radiation range of dose 7.5 - 12.5 kGy (dose rate 7.5 kGy/h). An effect different

irradiation dose on swelling ratio was investigated. The possibility applications of copoly(AAM-AA)-starch HSA in health care is an important aim of this work.

## Experimental

### *Materials*

Cassava starch was obtained from local Industry. Acrylic acid (AA) and acrylamide (AAM) were purchased from E.Merck. All the other reagents were of analytical grade and used without further purification. Distilled water was used for the synthesis of the hydrogels.

### *Instrumentation*

FTIR spectrophotometer, Shimadzu, Prestige-21. Differential scanning calometry (DSC), Shimadzu, DSC 60.

### *Procedure*

#### *Preparation of poly (acrylamide-co-acrylic acid)-starch hydrogels*

One gram of starch powder was mixed with 50 ml distilled water, stirred at 200 rpm at approximately  $85\pm 3^{\circ}\text{C}$  for 1 h to form paste-like slurry. Furthermore, the gelatinized starch was cooled at room temperature. Into the viscous solution was poured 15 ml acrylic acid which has been neutralized and 5 g of acrylamide, the volume of the mixture was made up to 100 ml with distilled water. The mixture was stirred at 200 rpm at room temperature for 30 min. The gelatinized starch-monomer mixture was transferred into 30  $\text{cm}^3$  a plastic bag, sealed, and then irradiated by  $\gamma$ -radiation from a  $60\text{ Co}$  source (dose rate 7.5 kGy/h) with the doses of 7.5 kGy; 10 kGy; and 12.5 kGy at room temperature. The hydrogels obtained were vacuum dried at  $60^{\circ}\text{C}$  till constant weight and then milled to averages 60-80 mesh.

#### *Gel fraction determination*

The hydrogel powder were taken in a 300 mesh of tea bags and extracted with distilled water for 24 h to remove the soluble fraction. The gels were dried to constant weight under vacuum at  $60^{\circ}\text{C}$  to determine the soluble fraction in the samples gravimetrically

$$\text{Gel fraction (\%)} = \text{Wg} / \text{Wo} \times 100 \quad (1)$$

Where Wg is the weight of dry gels after extraction and Wo is the initial weight of the gel.

#### *Swelling Rate Studies*

The swelling rate of hydrogels was determined by gravimetric method. The dried gel samples (Wo) were immersed in 50 ml distilled water (and other test solutions) and

dispersed with magnetic stirring at 200 rpm at room temperature. The swollen sample was filtered at desired time through weighed mesh wire gauze (sieve). The excess water was removed by hanging the sieve for 1 h till no water was dropped off. Then water absorbed by hydrogels were weighed (Wt). The swelling ratio was calculated as

$$\text{Swelling ratio} = (W_t/W_o) / W_o \quad (2)$$

Where  $W_t$  is the weight of the swollen gel at time  $t$  and  $W_o$  is the initial weight of the dried gels.

#### *FTIR Characterization*

The poly( AAM-co-AA)-starch hydrogels prepared at the doses of 7.5 kGy, 10 kgy, and 12.5 kGy were mixed with solid KBr in stainless steel sample cup and recorded with DRS system, respectively. A spectrum for each sample was obtained using Shimadzu IR Prestige-21 spectrometer model 800 series from 4000 to 400  $\text{cm}^{-1}$  with scan speed 20  $\text{cm}^{-1}$  and all spectra were displayed in multipoint base line correction.

#### *Thermal Analysis*

Differential scanning calorimetry (DSC) profiles of the samples were recorded using Shimadzu DSC 60. Approximately 5 mg of the hydrogel samples were sealed in an aluminum pan and heated from room temperature to 600°C at a heating rate of 10°C/min.

## **Results and Discussion**

#### *Gel Fraction*

The effect of different irradiation dose on the gel fraction of poly(AA-AAM)-starch is presented in Fig 1. It can be seen that with increasing irradiation dose from 7.5 to 12.5 kGy, the gel fraction of hydrogels increase from 75% to 90%. It is known that starch is a natural polysaccharide, which degrades on irradiation like the common natural polymers by breakdown of the main chains [11], while the mixture of AAm and AA crosslink in aqueous medium by irradiation. When the mixture containing starch, AAm and AA is irradiated an interpenetrating polymer network (IPN) is formed with the chemical crosslinking of poly(AAm-co-AA) and physical crosslinking of starch. As a result with increasing irradiation dose up to 12.5 kGy, the density crosslinking of hydrogels increase and the gel fraction of increase. In addition, some soluble components in water resulted from irradiation such as peroxides, degradation products of starches, acrylic acid and potassium acrylate that caused the gel fraction of the poly (AA-AAM)/starch hydrogel can not be achieved to 100%.

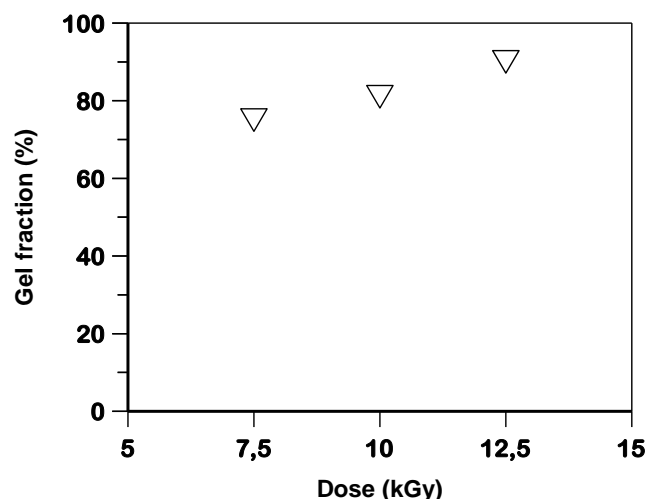


Figure 1. Effects of irradiation dose on gel fraction of superabsorbent hydrogel poly (AAM-co AA)-starch containing 5% AAM, 15% AA, 1% starch.

#### *Effect of immersing of time on the swelling of hydrogel*

The effect of immersing of time on swelling kinetics of copoly (AAM-AA)-starch hydrogels in water is presented in Figure 2. In the initial state at 15 s, the swelling ratio of hydrogels is relatively large attained 300 times of its dried weight. With the increase of immersing of time up to 200 seconds (~3 min), the swelling ratio of hydrogels gradually increased up to 400 g/g. Further increasing of immersing of time up to 1200 seconds, the water absorption of hydrogels is relatively constant in the range of swelling ratio 400-420 g/g. In addition, no significant change on swelling ratio as irradiation dose increased from 7.5 kGy to 12.5kGy. It is strongly suspected as the optimum dose range for the relatively large of the rate of absorption of hydrogels in this study. This is confirmed by our previous studies with increasing irradiation dose above 15 kGy caused the rate of absorption of the hydrogel decreased [10]. This is due to increasing irradiation doses, the density of crosslinked hydrogels increase and decreasing the rate of water absorption.

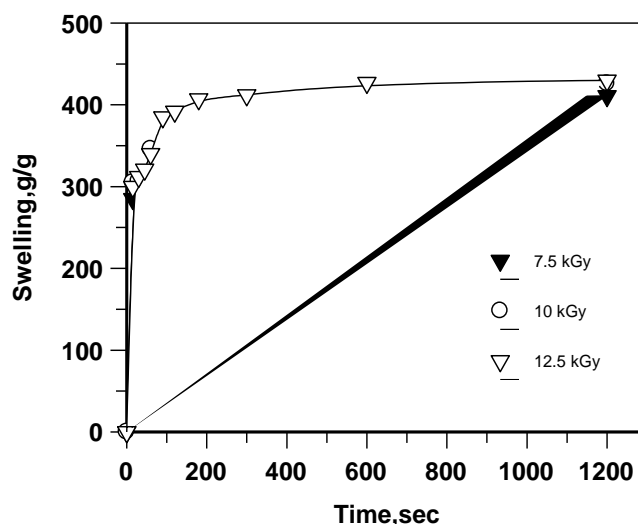


Figure 2. Swelling kinetics poly (AAM-co-AA)-starch superabsorbent hydrogels. with the composition of 5:15;1 (% Wt) irradiated at irradiation dose 7.5 kGy; 10kGy; and 12.5 kG.

The starches are known as cellulose derivate compounds consisting of hydroxyl group (OH) along their polymer backbones which acts as hydrophilic sites. In addition, the acrylic acid containing carboxylic groups (COOH) as hydrophilic groups is easily binding with water molecules to form hydrogen bonds with water. Some researchers reported that acrylic acid-based superabsorbent hydrogel absorbs large amount of water with the rate swelling in the range of minutes, hours and days [10, 12-14]. Hence, it is indicated that the combination of starch with AAM, AA in the powder form of hydrogel prepared at a low irradiation dose (7.5 kGy) when compared with granular form (previous work) were greatly improved the capacity of hydrogels to absorb water.

#### *Swelling of hydrogels in saline solution*

The effect external stimuli such as ionic strength, temperature or solvent composition on the change of swelling ability and structure superabsorbent have been studied extensively. The swelling behavior along with swelling time in different kinds of saline solutions is very important factor for the utilization of the superabsorbent. The swelling kinetics curves of the AA-AAM-starch superabsorbent in water and 0.09 % NaCl solutions are shown in Figure 3.

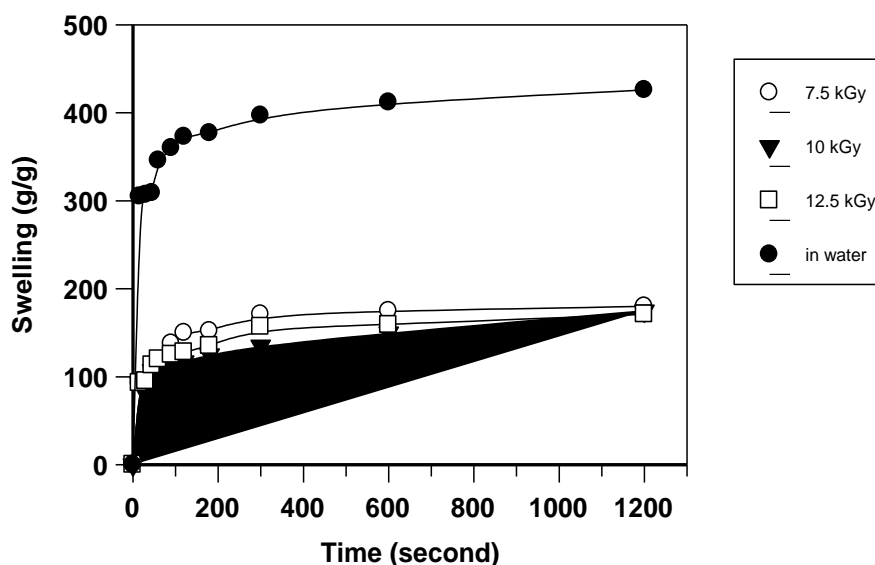


Figure 3. Dynamic swelling curve of the poly (AAM-co-AA)-starch superabsorbent hydrogels with different irradiation doses in 0.09 % NaCl and water.

In water, the swelling ratio increased with prolongs immersing time. The superabsorbent reached swelling equilibrium ~400 within 600 seconds. Further increase of immersing time did not influence of swelling ratio of the superabsorbent. However, a distinct swelling was observed in NaCl solution. The swelling of superabsorbent increased gradually from 92 to 175 g/g of equilibrium state at 600 seconds. Thus, the swelling ratio of superabsorbent in saline solution is low compared with swelling in water. The behaviour can be explained on the basis of osmotic pressure developed due to unequal distribution of ions in the medium and the polymer network. The ions attached to the polymer network are immobilized and considered to be separated from the external solution by a semipermeable membrane. When the hydrogels are placed in water, there is maximum swelling. When the polymer is in NaCl solution the osmotic pressure developed is much lower because the external solution contains Na<sup>+</sup> and Cl<sup>-</sup>.

#### *FTIR Analysis*

To understand the formation and crosslinking of hydrogel obtained from the mixture AAM,AA and starch prepared by gamma irradiation with the doses of 7.5 kGy,10 kGy, and 12.5 kGy , their FT-IR spectra of poly (AAM-co-AA)-starch are presented in Fig. 4. In the spectra of poly(AAM-co-AA)-starch prepared at a dose 7.5 kGy (curve 4a), the peaks observed at 3666 cm<sup>-1</sup>, corresponding to the carboxylic acid groups from AA, hydroxyl from starch and the NH stretching of acrylamide units [15]. The absorbance at 2926 cm<sup>-1</sup> is assigned to –C-H stretching of all polymers, and the absorbance at 1489 cm<sup>-1</sup> is assigned to the –COOK group [6]. A weak band at 2926 cm<sup>-1</sup> is indicated the presence

of C-H stretch and a characteristic peak at  $1731\text{ cm}^{-1}$  is attributed to tightly bound water present in the starch. The absorption at  $1029\text{ cm}^{-1}$  is typical of the system (C-O-C), skeletal mode vibration of  $\alpha$ -1,4-glycosidic linkage and the peaks at 1489, 1193 and  $1029\text{ cm}^{-1}$  were assigned as the peaks contributed from starch [16]. In comparison of curve a (7.5 kGy) against the curve b (10 kGy) and curve c (12.5 kGy), it can be seen that the peaks at  $1489\text{ cm}^{-1}$ ,  $1193\text{ cm}^{-1}$ , and  $889\text{ cm}^{-1}$  (curve a) were shifted to higher wave numbers with the broadening peaks. This is indicated that the starch entrapped in the poly(AA-co-AAM) matrices by crosslinking or grafting with increasing irradiation dose.

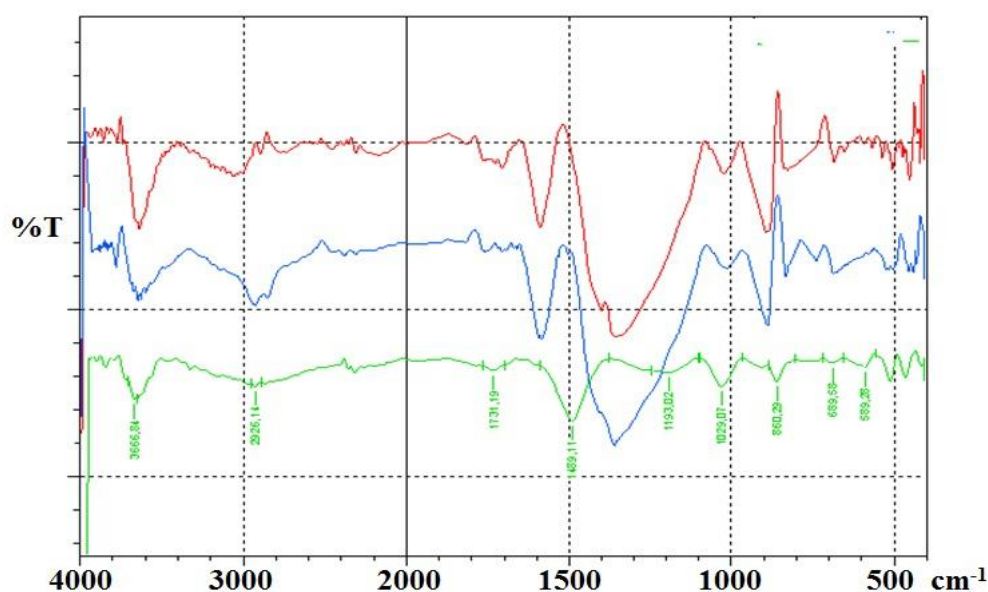


Figure 4. FTIR spectra of superabsorbent hydrogel poly(AAM-co-AA)-starch at different irradiation doses of, a) 7.5 kGy, b) 10 kGy, and c) 12.5 kGy.

#### *DSC measurements*

To characterize thermal properties of all samples in the present work, the heating run of DSC was taken into account. The results from DSC and the characteristics observed for pure starch and the prepared hydrogels containing starch are shown in Fig. 5-8 and summarized in Table 1. Fig. 5 shows the DSC of pure starch, it can be seen that there is one endothermic peak at  $65.06^{\circ}\text{C}$  is that gelatinization temperature ( $T_p$ ), two glass transition temperature and one exothermic peak at  $354.83^{\circ}\text{C}$  is decomposition temperature of the starch in the cassava [17]. Structural relationships between the amorphous regions and crystallites within the starch granule are responsible for the sharpness of the transition and the temperature at which it occurs [18]. Fig. 6 shows the thermogram of poly(AAM-co-AA) starch prepared at irradiation dose of 7.5 kGy with endothermic gelatinization peak at  $66.23^{\circ}\text{C}$ . In addition to this a broad exothermic decomposition peak was obtained



at 408.39°C showing the crystallinity of hydrogel in different form. Fig. 7 shows the thermogram of poly(AAM-co-AA) starch prepared at irradiation dose of 10 kGy with endothermic gelatinization peak at 66.23°C. and two endotherm glass transition peak at 349.40°C and 387.90°C, respectively. There is a single sharp exothermic peak at 423.82°C, which indicated homogeneity of the crystallinity of hydrogel. Fig. 8 shows the thermogram of poly(AAM-co-AA) starch prepared at irradiation dose of 12.5 kGy with endothermic gelatinization peak at 65.02°C and two endotherm glass transition peak at 349.72°C and 402,78°C, respectively. There was one a sharp exothermic peak at 437.22°C due to the decomposition of hydrogel with the homogenous crystalline structure. However, it can be concluded that with increasing irradiation doses from 7.5 kGy to 12.5 kGy (Table 1) the decomposition temperature of hydrogels increase from 408.39°C to 437.22°C because of the crosslinking, which will disturbs the intra and inter molecular hydrogen bonds of starch.

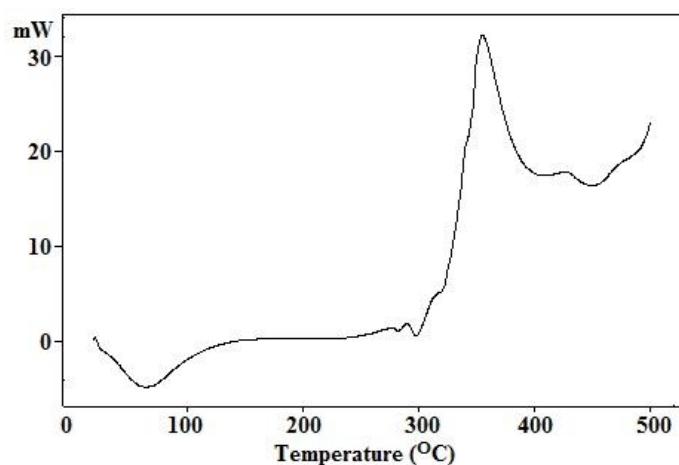


Figure 5. DSC thermogram DSC of starch.

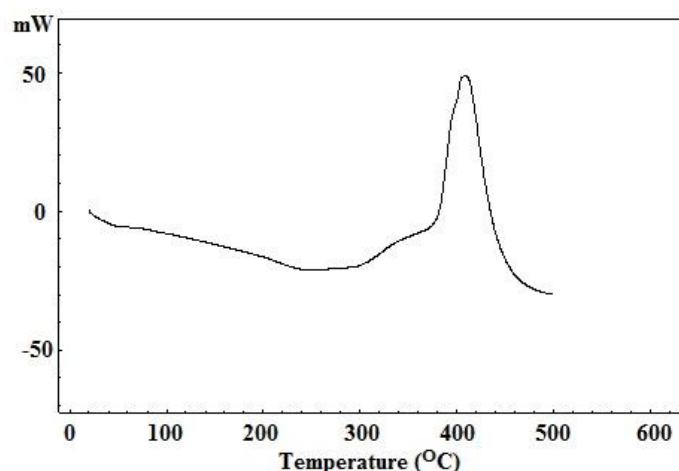


Figure 6. DSC thermogram of poly(AAM-co- AA)-starch (7.5 kGy).

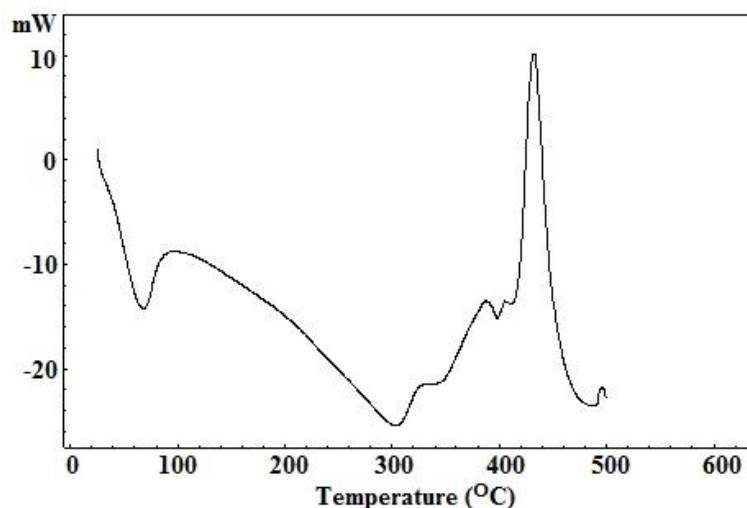


Figure 7. DSC thermogram of poly(AAM-co-AA)-starch (10 kGy).

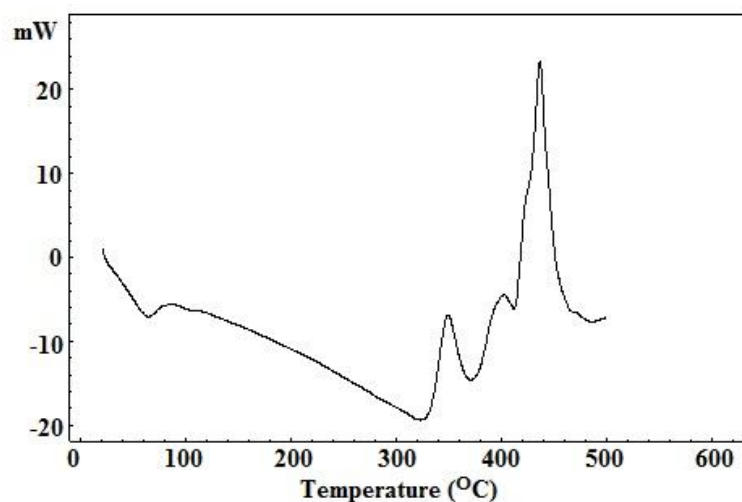


Figure 8. DSC thermogram of poly(AAM-co-AA)-starch (12.5 kGy).

Table 1. Gelatinization temperature ( $T_p$ ), transition temperature ( $T_g$ ) and decomposition temperature ( $T_d$ ) of starch and poly (AAM-co-AA)-starch hydrogels prepared by gamma irradiation with different irradiation doses.

Sample	Gelatinization Temp. ( $T_p$ ) (°C)	$T_g$ (°C)	$T_d$ (°C)
Starch	65.06	289.76; 320.36	354.83
Poly(AAM-co-AA)-starch (7.5 kGy)	66.23	370.18;	408.39
Poly(AAM-co-AA)-starch (10.0 kGy)	64.73	349.40; 387,90	423.82
Poly(AAM-co-AA)-starch (12.5 kGy)	65.02	349.72;402.78	437.22

## Conclusion

A superabsorbent of poly(AAM-co-AA)-starch was synthesized by radiation copolymerization reaction of AAM, AA and starch in aqueous solution at varying irradiation doses (7.5 kGy-12.5 kGy). Experimental results show that the hydrogels can absorb water (swelling) very fast with swelling ratio was higher (~400 g/g) attained at 3 min. There was no significant different on swelling ratio among irradiation doses of hydrogels. Due to ionic strength, the swelling ratio of poly (AAM-co-AA)-starch hydrogel was low compared to its swelling in water. From FTIR and DSC measurement, it was shown that the crosslinking occurs in the hydrogels.

## Acknowledgments

The authors are grateful to all staff at IRKA Irradiator facility that are very helpful for samples irradiation.

- [1] F. L. Bucholz, T. Graham, "Modern Superabsorbent Polymer Technology", Wiley-VCH, New York, 1998, p.151.
- [2] H.A. Abd El-Rehim, E. S. A. Hegazy, H. L. Abd El Mohdy, *J Apply Polym Sci*, **2004**, 93,1360.
- [3] M. Bakass, A. Mokhlisse, M. Lalleman, *J. Appl. Polym. Sci*, **2002**, 83, 234.
- [4] C. Chang, B. Duan, J. Cai, L. Zhang, *Eur. Polym. J.* **2010**, 46, 92.
- [5] G. Flores, M. Herraiz, M.L. Ruiz del Castillo, *J. Sep. Sci.* **2006**, 29, 267.
- [6] R.S. Tomar, I. Gupta, R. Singhai, A.K. Nagpal, *Des. Monomers Polym.* 2007, 10,49.
- [7] Erizal, 2010, A Scientific J. Appl.Isot. Radiat., 6,2,105.
- [8] D. Solpan, S. Duran, D. Saraydin, O. Guven, *Rad. Phys. Chem.* **2003**, 66, 117.
- [9] K. Kurita, *Prog. Polym. Sci.* **2001**, 26, 1921.
- [10] Erizal, *Indonesian J.of Chem.* **2012**. 12, 2, 113.
- [11] A. Charlesby, "Atomic Radiation and Polymers", Pergamon Press, Oxford, 1960.
- [12] N. C. Defader, S. Ganguli, M. A. Sattar, M. E. Haque, F. Akhtar, *Malaysian Polym. J.* 2009, 4,2, 37.
- [13] F. Khoylu, F. Naimian, *Radiat. Phys. Chem.* **2009**, 78,195.
- [14] S. Francis, M. Kumar, L. Varshney, *Radiat. Phys. Chem.* **2004**, 69,481.
- [15] C. Elvira, J. F. Mano, J. San Roman, R. L. Reis, *Biomaterials.* **2002**, 23, 1955.
- [16] Erizal, Sudirman, B. Emil, V. M. Anggara, R. Yudianti, *Adv. Mater. Res.* **2013**, 746, 88-96.
- [17] J. M. Fang, P. A. Fowler, J. Tomkinson, C. A. S. Hill, *Carbohydr. Polym.* **2002**, 47, 245.
- [18] Colette,F.Q., TA Instrument , Water LLC, 2011.
- [19] B. R. Krueger, C. E. Walker, C. A. Knutson, G. E. Inolett, *Cereal Chem.* **1987**, 64, 187.