

SYNTHESIS OF POLY(ACRYLAMIDE-CO-ACRYLIC ACID)-STARCH BASED SUPERABSORBENT HYDROGELS BY GAMMA RADIATION: STUDY ITS SWELLING BEHAVIOR

Erizal

Centre for the Applications Isotopes and Radiation Technology, BATAN, Jl. Lebak Bulus Raya no. 49, Jakarta 12070

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ABSTRACT

Modification of poly(acrylamide-co-acrylic acid) superabsorbent hydrogels with varying starch concentration (1-3%) via simultaneous gamma radiation have been carried out. The structure and morphology of copolymers were characterization by Fourier transform infra red spectroscopy and scanning electron microscopy. The gel fraction, swelling kinetics and the equilibrium degree of swelling (EDS) of the hydrogels were studied. It was found that the an increase in the starch content present in the hydrogels (1-3%) and with increase irradiation dose from 10 kGy up to 30 kGy, the swelling ratio decreased from 250-100 g/g. Incorporation of 1% starch increases the EDS of the hydrogels up 350 g/g. Under maximum conditions, poly(AAm-co-AA)-starch hydrogels with high gel fraction (~93%) was prepared from aqueous solution containing 5% AAm, 15% acrylic acid and 0-3% starch. The hydrogels were sensitive against salts solution.

Keywords: Radiation; superabsorbent; Acrylamide; Acrylic acid; alginate

ABSTRAK

Telah dilakukan modifikasi hidrogel superabsorben poli(akrilamida-ko-asam akrilat) dengan variasi konsentrasi pati (1-3%) via iradiasi gamma simultan. Struktur dan morfologi kopolimer dikarakterisasi menggunakan Fourier Transform Infra Red (FTIR) dan Scanning Electron Microscopy (SEM). Fraksi gel, kinetika swelling dan derajat kesetimbangan swelling (EDS) hidrogel dipelajari. Diperoleh hasil dengan meningkatnya kandungan pati dalam hidrogel (1-3 %) dan meningkatnya dosis iradiasi dari 10 kGy hingga 30 kGy, rasio swelling hidrogel menurun dari 250-100 g/g. Penggabungan 1% pati meningkatkan EDS hidrogel hingga 350 g/g. Pada kondisi maksimum, diperoleh nilai fraksi gel tertinggi (~93%) hidrogel poli(akrilamida-ko-asam akrilat)-pati yang mengandung AAm 5%, asam akrilat 15 % dan pati 0-3%. Hidrogel ini peka terhadap terhadap larutan garam.

Kata Kunci: Radiasi; superabsorben; akrilamida; asam akrilat; alginat

INTRODUCTION

Hydrogel superbasorbent (HSA) is the type of a cross-linked polymer based which able to absorb some quantity of water. These polymers have a different way to achieve the rate of absorption and very effectively absorb the water. Insoluble in water because of the 3-dimensional structure of the polymer network which the ability to absorb water hundreds of times it's the dry weight [1]. Nowadays, superbasorbent is one of the very interesting materials because of its solubility properties and a unique water transport capacity. When they absorb water up to equilibrium, their form is similar to water caused by almost all parts of the polymer form consisting water. Due to the unique nature, the hydrogel HSA has a wide range of applications such as a urine absorbent material in baby diapers/women with the needs of a fairly large per year worldwide [2].

Furthermore, HSA also can be used for water storage containers for dry areas/agriculture [3], absorbing dyes and metal ions [4-5], a backup water source on horticulture crops [6-7], artificial snow [8], concentration of compounds evaporate [9], absorption of bacteria and fungi in wound dressings [10], elimination water body [11], and immobilization of urea [12].

In recent years research on the preparation of hydrogel superabsorbent have been focused intensively on some types of material based such as cellulose derivatives [13-14], acrylic acid [15] and acrylamide (AAm) [16] monomers. Karadag et al. [16] synthesized HSA copoly (AAM-crotonic acid) in the form of rod with a relatively high swelling containing ammonium nitrate and potassium nitrate which is intended for applications in agriculture as fertilizer. Tomar et al [17] synthesized hydrogel copoly(AAM-AA) based superabsorbent by gamma radiation, and

* Corresponding author.
Email address : izza3053@yahoo.com

obtained a result indicated that an increase in the AAm content present in the hydrogels varied from 38.87% to 64.02%, equilibrium water absorbency decreased from 872 to 402 g H₂O sample. Erizal [18] synthesized HSA copoly (AAM-AA) for application as metal ions adsorbent.

Based on the above description, hence in this study the modification copoly(AAM-AA) copolymer by addition of starch via simultaneous radiation processing have been carried out. The use of starch for modification of poly(AAm-co-AA) in this research was intended to study its effect on swelling behavior of HSA. Copoly(AAM-AA) based superabsorbent was synthesized containing 5% acrylamide, 15% acrylic acid (which has been neutralized) and starch concentration of 1-3%, were irradiated at doses of 20.30, and 40 kGy. Effect of starch content and irradiation dose on the swelling ratio, gel fraction, EDS hydrogels and effect salt solution were studied. In addition, changes in chemical structure and morphology of hydrogels were characterized by FT-IR and SEM.

EXPERIMENTAL SECTION

Materials

Starch of edible potatoes was obtained from local industry. Acrylic acid (AA), and acrylamide (AAm) were purchased from E. Merck Ltd. All other reagents were of analytical grade and used without further purification, distilled water used for as solvent in all experiments.

Instrumentation

FT-IR spectrophotometer, Shimadzu, Prestige-21, Scanning Electron Microscope (SEM), JEOL.

Procedure

Synthesis of the hydrogels poly(acrylamide-co-acrylic acid)-starch hydrogels

A series of 1, 2, and 3 g starch powder were mixed with 50 mL distilled water, respectively, stirred at 400 rpm and heated at approximately 85 ± 3 °C at the same time for 1 h to form a paste-like slurry. Furthermore, the gelatinized starch was cooled at room temperature. Into each the viscous solution was poured 15 mL acrylic acid which has been neutralized and then 5 g of acrylamide, the volume of the mixture was made up to 100 mL by adding distilled water. The mixture was stirred at 400 rpm at room temperature for 30 min. The gelatinized starch-monomer mixture was transferred into 30 cm³ a plastic bag, sealed, and then irradiated using gamma rays at doses of 10, 20, and 30 kGy (dose rate of 7 kGy/h).

Gel fraction

The hydrogel samples (1 cm x 1 cm) were taken in a 300 mesh of stainless steel bags and extracted with methanol for 24 h to remove the soluble fraction. The gels were dried to constant weight under vacuum to determine the soluble fraction in the samples gravimetrically

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

where W_g is the weight of dry gels after extraction and W_o is the initial weight of the gel

Swelling studies

The degree of swelling was determined by gravimetric method. The gel samples (dried to constant weight) were immersed in excess distilled water (and other test solutions) at room temperature. The hydrogels were periodically weighed after the excess surface water was removed with a filter paper. The swelling ratio was calculated as

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

where W_t is the weight of the swollen gel at time t and W_o is the initial weight of the dried gels. The equilibrium degree of swelling (EDS) was calculated by changing W_t to W_e which is the equilibrium weight of the swollen gel.

FT-IR Characterization

The poly(AAm-co-AA) hydrogel and poly(AAm-co-AA)-starch were placed on the flat plate crystal sample stage and a tip ATR (Attenuated Total Reflectance) tool was pressed on the samples. Starch powder was mixed with solid KBr 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 700 cm⁻¹.

SEM Analysis

For scanning electron microscopy, samples were coated with 100 Å thick layer of gold by using a Denton II (Denton vacuum) vacuum sputter coater to minimize 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 obtained using SEM 515/RDAX PV 9900.

RESULT AND DISCUSSION

Gel fraction

Fig. 1 shows the variation of gel fraction of poly(AAm-co-AA)/starch hydrogels with the dose and varying starch content in the hydrogels. It is seen that with increased starch content, the gel fraction of

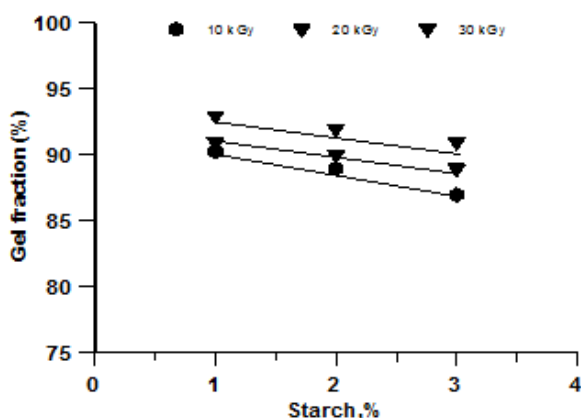


Fig 1. Effect of starch content on gel fraction of hydrogels at various irradiation doses

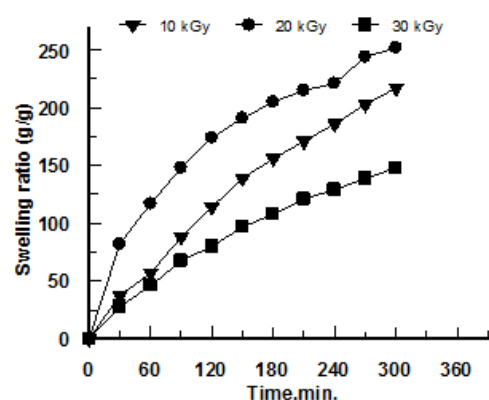


Fig 2. Swelling behavior of poly(acrylamide-co-acrylic acid) containing 1% starch hydrogel irradiated at the doses of 10, 20, 30 kGy

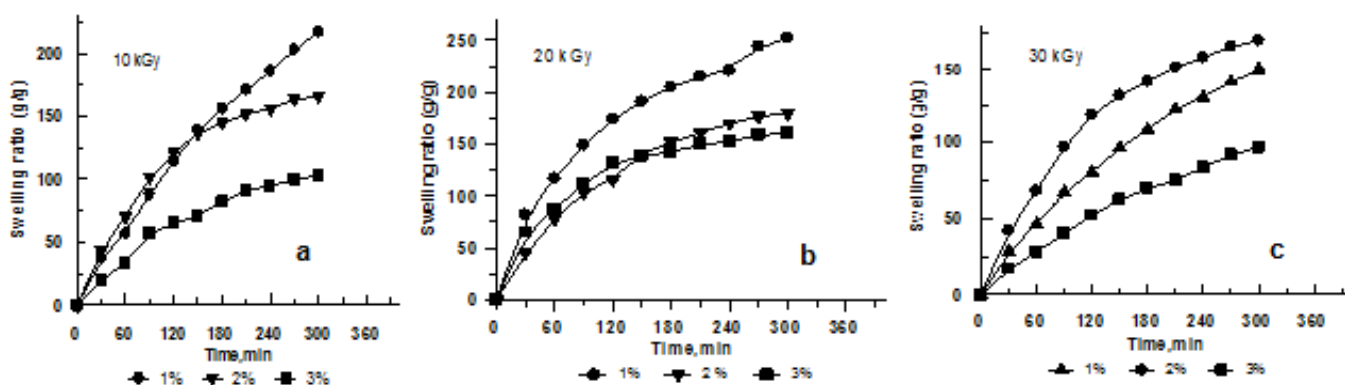


Fig 3. Effect of starch content on swelling ratio of hydrogels at various irradiation doses; (a) 10, (b) 20, and (c) 30 kGy

hydrogels decrease. At a dose 10 kGy, with increasing starch content from 1 to 3%, the gel fraction of hydrogels decreases from 93 to 88%. In contrast, with increasing irradiation dose, the gel fractions increase. It is known that starch is a natural polysaccharide, which degrades on irradiation like the common natural polymers by breakdown of the main chains [19], 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 [20]. As a result with increasing starch content, the amount of starch entrapped in the hydrogel matrices increase.

Effect of irradiation dose on swelling ratio of poly (acrylamide-co-acrylic acid)-starch hydrogels

The effect of irradiation dose on the swelling of hydrogels containing 1% starch as a function of time is illustrated in Fig. 2. It can be seen that with the increase of time up to 300 min the swelling of hydrogels increases and reaches maximum swelling ratio to 250 g/g of its

dried weight. Thus, it is indicated that the poly(AAm-co-AA)-starch shows a remarkable superabsorbent properties with rapidly water absorption. In contrast, the swelling of hydrogels decreased with the increase of irradiation doses. At immersion time up to 300 min, the swelling ratio of hydrogel irradiated at a fixed dose at 10 kGy can reach up to 250 g/g. For hydrogel produced at 20 kGy, the maximum swelling is 220 g/g, and for hydrogel 30 kGy is 130 g/g. The swelling ratio decreased with increasing irradiation doses is due to the formation of more crosslink and tighter structure. Crosslink hinders the mobility of the polymer chain and hence reduces the penetration of water in to the hydrogel structure.

Effect of starch content on the swelling of hydrogel

Various concentration of starch (shown 1-3% wt%) with different irradiation dose were used to enhancement the water absorption capacity of the poly(AAm-co-AA) hydrogels. The swelling behaviors of poly(AAm-co-AA) hydrogels are affected significantly by

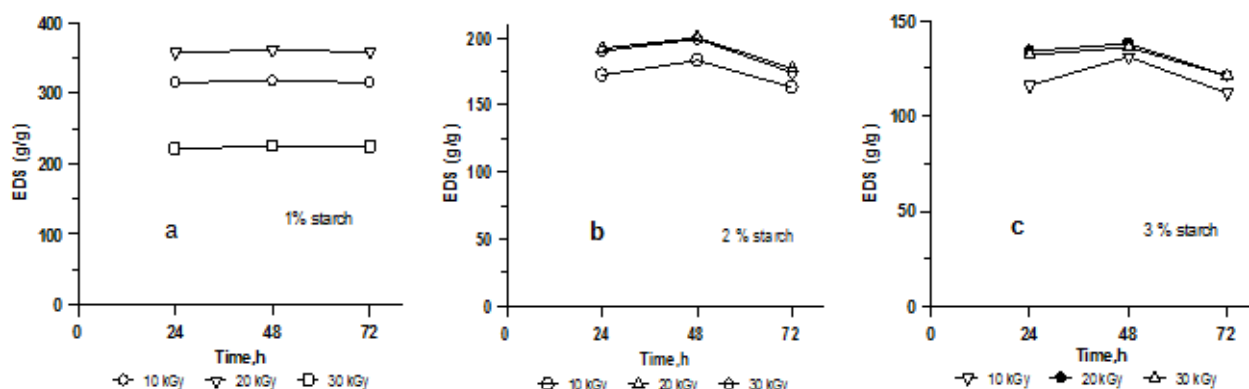


Fig 4. Effect of swelling time on the EDS of the poly(AAm-co-AA)-starch hydrogels synthesized at various irradiation doses and starch content; (a) 1, (b) 2, and (c) 3% starch

changing the starch content of the hydrogels and irradiation doses as shown in Fig. 3a, b, and c. Fig. 3a shows the effect of starch content at irradiation dose of 10 kGy, it can be seen that maximum swelling ratio can be reached up to 220 g/g at 1% starch content, then decrease with increasing starch content. For irradiation 20 kGy (Fig. 3b), at 1% starch content the swelling ratio of hydrogel increase up to 250 g/g and then decrease with increasing starch content. For irradiation 30 kGy (Fig. 3c) the swelling ratio of hydrogels decrease significantly at 1% starch content (148 g/g) and also following with decrease starch content. It is indicated that the swelling ratio of hydrogels at 1% starch content and irradiated at 20 kGy is the optimum condition, and with increasing starch content the swelling ratio of hydrogels decrease, generally. It is clear that amount of starch powder plays an important role in affecting equilibrium swelling ratio of the poly(AAm-co-AA) superabsorbent hydrogels. The decreased of swelling ratio of hydrogels with further increasing starch content and irradiation doses may be attributed to generation of more crosslink points in the polymeric network, inducing an increase in crosslink density of the hydrogels and resulted the decrease water diffusion in matrix hydrogels. On the other hand, the swelling ratio decreased with increasing starch content may be due to that the starch powder are partly physically filled in the hydrogels network, the content of hydrophilic groups is lower and the swelling ratio thus gradually decrease.

Equilibrium Degree of swelling (EDS)

The ability of superabsorbent hydrogels to absorb water is strongly influenced by their porosity and hydrophilicity [21]. The more porous and hydrophilic the hydrogels the faster it absorbs water and reaches equilibrium state known as EDS (Equilibrium Degree of Swelling) which is a swelling time function. The effect of swelling time (24, 48, 72 h) on the EDS hydrogel poly(AAm-co-AA)-starch with various starch content

(1-3%) and irradiation with the doses of 10-30 kGy are presented in Fig. 4a, b, and c. In Fig. 4a, shows that hydrogels containing 1% starch with increasing time at different irradiation doses, the EDS values of all hydrogels did not change significantly. But it changes with increasing irradiation doses. For irradiation dose in the range of 10-30 kGy at fixed starch content (1%), with increasing time up to 72 h, the EDS of hydrogels initially is ± 315 g/g and then increases up to ± 361 g/g at dose of 20 kGy, and finally decreases to ± 225 g/g at 30 kGy. This is indicated that irradiation dose of 20 kGy is an optimum dose of EDS with 1% starch content in the hydrogels. For hydrogel containing 2% of starch with varying irradiation doses, the effect of time is shown in Fig. 4b. It can be seen that with increasing swelling time, the EDS all hydrogels reach an optimum condition at 48 h observation. With increasing time up to 72 h, the EDS of hydrogels decreases from 190 to 178 g/g. For hydrogel containing 3% of starch with varying irradiation doses, the effect of time is shown in Fig. 4c. It can be seen that with increasing time, all hydrogels reach an optimum EDS at 48 h with the range 121-133 g/g. The effect irradiation dose on EDS show did not significant changes. Generally, it can be suggested that with increasing starch content, the EDS of hydrogels decrease.

In early stages of irradiation mainly acrylamide and acrylic acid polymerizes and then crosslinking occurs. During this process, presence of starch reduces crosslinking density by scavenging OH/H radicals and probably physically screening the approach of radicals sites that form crosslinks. The present study indicates that this effect practically gets saturated at about 20 kGy irradiation dose and further increase of irradiation dose results in marginal increase of EDS. Therefore, presence of starch in porous network structure of crosslinked poly(acrylamide-co-acrylic acid) could also contribute for the observed high EDS value. The presence of starch could also modify

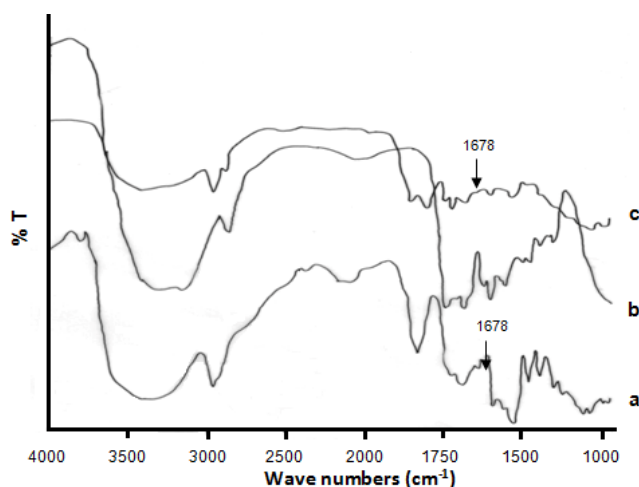


Fig 5. FTIR spectra of starch (a), hydrogel (AAm-co-AA) (b), and poly(AAm-co-AA)-starch hydrogels (c)

the average pore size, the pore size distribution and the pore interconnections due to inter and intra molecular interaction of starch with poly(acrylamide-co-acrylic acid) during irradiation.

FTIR Spectra of hydrogel

To understand the formation and crosslinking of hydrogel obtained from irradiation of the mixture of AAm-AA monomers and starch, an FT-IR spectrum of poly(AAm-co-AA) hydrogel is presented in Fig. 5. In the spectra of starch (curve a), the peaks observed were at 3423 cm^{-1} for the OH groups, and at 2927 cm^{-1} , corresponding to the CH stretching. The peaks at 1149 cm^{-1} , 1078 cm^{-1} and 1000 cm^{-1} are assigned to $\text{C}=\text{O}$ stretching, C-C stretching, and COH vibration, respectively. The peak at 858 cm^{-1} corresponds to the C-O-C symmetric stretching.

In the spectra of (AAm-co-AA) hydrogel (curve b), the peaks were observed at 3338 cm^{-1} , corresponding to the NH stretching of acrylamide unit. -CH_2 groups on the chain give absorption at 1452 cm^{-1} . The absorbance at 2927 cm^{-1} is assigned to -C-H stretching of the acrylate unit, the peak at 1678 cm^{-1} corresponds to the $\text{C}=\text{O}$ of acrylate unit. The absorbance at 1678 cm^{-1} can be attributed to the $\text{C}=\text{O}$ group of the acrylamide unit, the absorbance at 1178 cm^{-1} corresponds to the -C-O-O stretching of the acrylate unit and the absorbance at 1550 cm^{-1} is assigned to the -COOK group.

When the mixture of starch –AAm-AA irradiated, the poly(AAm-co-AA)-starch hydrogel was produced, and its FTIR spectra presented in Fig. 5 (curve c). It was found that the same peaks corresponding to AAm, AA, and starch all appear in the spectra, but the intensity of peaks at 1678 cm^{-1} decreased compare to the peaks of starch alone. It is suggested that starch crosslinked

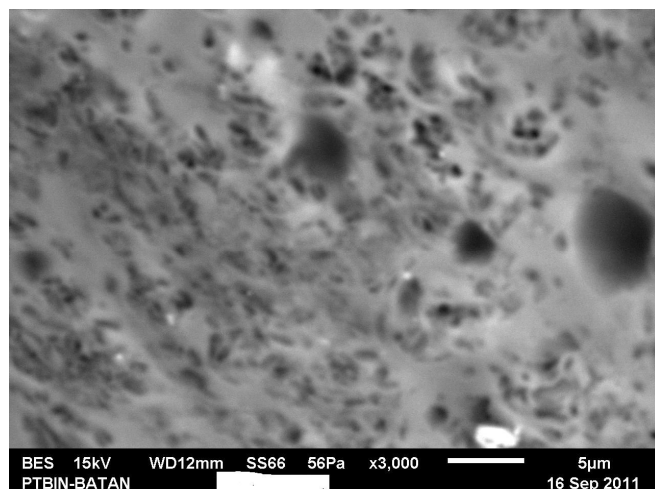


Fig 6. SEM of poly(AAm-co-AA-starch hydrogel)

through hydrogen bonding and entrapped in poly(AAm-co-AA) hydrogel with IPN network.

Surface morphology of the hydrogel

The surface appearance and structure of hydrogel were observed using scanning electron microscopy (SEM). The SEM photographs of poly(AAm-co-AA)-starch which are polymers of good absorbency, illustrated in Fig. 6, show that the hydrogel have a porous structure and with the white color of the starch appearance on the flat surfaces. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the copolymers.

CONCLUSION

Superabsorbent polymers of acrylamide-co-acrylic acid)-starch were synthesized by a simultaneous irradiation technique using gamma-rays as an initiator. We found that the concentration of starch (starch content) in the superabsorbent polymer is a parameter of utmost importance for water absorption. The copolymer produced with starch content 1% and irradiated at 20 kGy gave the highest gel fraction as high as 93%, and the copolymer produced with starch content 1% and irradiated at 20 kGy gave copolymer the highest swelling ratio in distilled water as 250 g/g as its dry weight. All hydrogels with different starch content and irradiated up 30 kGy, attained EDS at 48 h with the values in the range of 150-350 g/g. The hydrogels were sensitive against salts solution.

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