SYNTHESIS AND CHARACTERIZATION SUPERABSORBENT HYDROGELS OF PARTIALLY NEUTRALIZED ACRYLIC ACID PREPARED USING GAMMA IRRADIATION; SWELLING AND THERMAL BEHAVIOR

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ABSTRACT

A series of superabsorbent hydrogels were synthesized from partially neutralized acrylic acid with varying degree of neutralization (0-1) using gamma radiation. The effects of degree neutralization of acrylic acid on swelling ratio were studied. DSC measurement was performed to understand the type of end products resulting from irradiation. The morphologies of the hydrogels were examined using SEM. The chemical changes of the hydrogels were characterized using FTIR. At optimum conditions (10 kGy, 15 min), the hydrogels with neutralization degree 0.5 exhibited rapid swelling with the highest swelling ratio ~1000 g/g. The results of DSC studies confirmed the possible formation of the type hydrogels from irradiated partially neutralized acrylic acid, and the hydrogels showed large numbers of pores from SEM examination.

Keywords: *hydrogel; superabsorbent; acrylic acid; irradiation; crosslinking*

ABSTRAK

Satu seri hidrogel superabsorben asam akrilat yang dinetralkan sebagian dengan variasi derajat netralisasi (0-1) disintesis menggunakan iradiasi gamma. Pengaruh derajat netralisasi terhadap rasio swelling dipelajari. Pengukuran sifat termal hidrogel dilakukan menggunakan DSC untuk mengkonfirmasi jenis produk hasil iradiasi. Scanning elektron mikroskop dilakukan untuk menguji morpologi hidrogel. Perubahan kimia hidrogel diukur menggunakan FTIR. Pada kondisi optimum (10 kGy, 15 menit), hidrogel dengan derajat netralisasi 0,5 menunjukkan rasio swelling yang tinggi (~1000 g/g). Hasil pengujian DSC mengkonfirmasi jenis produk yang mungkin terbentuk dari hasil iradiasi asam akrilat yang dinetralkan sebagian, dan hasil pengujian SEM menunjukkan hidrogel berpori.

Kata Kunci: *hidrogel; superabsorben; asam akrilat; iradiasi; ikatan silang*

INTRODUCTION

Hydrogel superabsorbent (HSA) is a type of polymer-based ability to absorb some quantity of water. Each type of polymer HSA has different way of achieving superabsorbent behavior. HSA is essentially a cross-linked polymer which ability to absorb water hundreds of times of their dry weight, insoluble in water because of the 3-dimensional structure of the polymer network [1]. HSA is a very attractive material because of its solubility properties and a unique water transport capacity. When they absorbed water almost all parts of their network consists of water, they form is similar to the polymer caused by water. Due to the unique nature, the hydrogel HSA has a wide range of applications ranging from a urine absorbent material in baby diapers/women to drug delivery system. Furthermore, HSAs can also be used for other purpose such as water storage containers for dry areas/agriculture [2], absorbing dyes and metal ions [3-4], a backup water source on horticulture crops [5-6], artificial snow [7], concentration of compounds evaporate [8], absorption of bacteria and fungi in wound dressings [9], elimination water body [10], and immobilization of urea [11].

Hydrogels of acrylic acid-based have been reported demonstrate special properties because of the presence of carboxylate acid as anion side groups in their network. When they are dissolved in water, the ionic hydrogels interaction with solvent/polymer, the polymer chains charges repeal each other, expands polymer coil and increase water uptake. To maintain the presence of anion groups of acrylic acid after polymerization can be done by neutralization of acid groups in the liquid phase (usually with sodium or

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potassium hydroxide solution), and then followed with crosslinking for polymerization.

Polymerization of acrylic acid can be carried out by various methods including chemical and radiation induced crosslinking, respectively. The radiation technique seems to be superior to chemical crosslinking. The advantages of radiation technique application are easy process control, simultaneously hydrogel formation and sterilization in one step process, no need any initiators and crosslinkers ect. This makes irradiation, as one of the best choice for the preparation method of hydrogels [12]. However, some researchers have been reported on the radiation of acrylic acid aimed to prepare hydrogels [13]. Besides, the mechanisms poly(acrylic acid) radiolysis in water has been well studied. However, up to now only limited information about swelling and characterization of hydrogels synthesized by radiation partially acrylic acid have been published [14-18]. The objective of this work was to investigate the swelling behavior of acrylic acid hydrogels partially neutralized from 0 up 1 neutralization degree (Dn) and its thermal behavior synthesized by using gamma radiation crosslinking in aqueous solution. The types of end products resulting from irradiation were examined using Differential Scanning Calorimetry (DSC). In addition, the chemical changes of hydrogels were measured using Fourier Transform Infra Red (FTIR) and the morphology of hydrogels were examined using Scanning Electron Microscope (SEM).

EXPERIMENTAL SECTION

Materials

Acrylic acid, in glacial form was purchased from Merck, Darmstadt Germany and was stored in a refrigerator before use. Potassium hydroxide (KOH) was obtained from Merck and used for neutralization. Potassium chloride (KCl), Sodium chloride (NaCl), Calcium chloride ($CaCl_2$) were also purchased from Merck. Distilled water was used in the polymerization and swelling experiments. All chemical were used as a received. All of the reagents were analytical grade used without purification.

Instrumentation

To confirm the crosslinking of the hydrogels was performed using Differential Scanning Calorimetry (DSC) Shimadzu, Japan. Approximately ± 5 mg samples for each measurement were heated from room temperature up to 600 °C with heating rate 10 °C/min. The surface morphology of hydrogels was studied by field emission scanning electron microscope (SEM), using JSM 6510 equipment (JEOL, Japan), with operating voltage of 30 kV. Samples of hydrogels were immersed in distilled water at room temperature until maximum swelling, then frozen at -80 °C and lyophilized. The freeze-dried hydrogel were fixed on brass holder and coated by sputtering with a thin Au layer in order to avoid charging effects. The chemical changes of hydrogels were measured using Fourier Transform Infra Red (FTIR) Shimadzu IR-Prestige-21 spectrometer model 800 series, Japan.

Procedure

Preparation of hydrogels

Crosslinked HSA were prepared using gamma γ- irradiation from cobalt -60 A series acrylic acid solution were prepared from 15 mL acrylic acid dissolved in 75 mL distilled water, and then partially neutralized with KOH solution at different neutralization degree of 0, 0.25, 0.50, 0.75 and 1. The mixtures were stirred with 200 rpm at room temperature until homogeneous, Then, the reaction mixtures were packed in polypropylene (PP) plastic bags, sealed and then irradiated at single dose of 5 kGy (dose rate 5 kGy/h) at room temperature in the irradiator Panorama, CAIR BATAN, Jakarta. The hydrogels were dried at 60 °C for 48 h, and milled up to 60-80 mesh.

Swelling measurements

Swelling ratio of HSA were determined gravimetrically. The dried HSA (Wo) in distilled water (or other solution), shake with 400 rpm rate at different time interval at room temperature. At predetermined time interval, the water containing the swollen HSA were filtered using stainless steel tea sieves (± 200 mesh) and the hydrogel was hanging for approximately 1 h until no more water drop off. The remaining volume of water was collected and measured as W_t. Swelling ratio of hydrogels calculated as follows;

$$Swelling\ ratio = Wt/W_0 \quad (1)$$

Where W_0 and Wt are the weights of dried hydrogel and swollen hydrogel at time t.

Equilibrium degree of swelling (EDS) hydrogels were determined using equation 1 and all the samples were measured triplicates.

RESULT AND DISCUSSION

The Main Mechanisms of Radiation-Induced Partially Acrylic Acid

The first a step of the reaction in this work was to partially neutralization of acrylic acid with varying concentration KOH solutions from 0 to 1 of neutralization degree, then exposure to gamma rays at a dose of 10 kGy, respectively. The radicals

polymerization reaction will be taken place in these solutions with the following the radiation mechanism stages such as initiation, propagation and termination [19]. In the initiation stage, radiolysis of water is occurred and resulted H and OH radicals. The radicals are recombined to produce H_2 and O_2 gases. In addition, the H or OH radicals are attack the double bond of acrylic acid and potassium acrylic acid to produce their radicals, respectively. These radicals reaction are continued to the propagation stage, and finally produced a stable product, generally.

For acrylic acid monomer solution with Dn = 0, is meant that the solution containing mostly monomer acrylic acid. Thus, the final radiation products will be homopolymer of acrylic acid and the reaction can be illustrated Fig. 1.

For acrylic acid with Dn = 1, in which the acrylic acid anions predominate in solution and will be polymerized by radiation to its homopolymers of potassium acrylate salt in the final product, and the reaction can be illustrated as Fig. 2.

For acrylic acid with Dn 0.25, 0.50, and 9.75, in which the acrylic acid solution has been partially neutralized by KOH and resulted the solutions contain the mixture of acrylic acid molecules and its anions in the equilibrium state such as Fig. 3.

When these solutions are irradiated using gamma rays, the radiation polymerization reaction is occurred with following radiation mechanism reaction stages. Thus, the results of irradiation will be a crosslinked copolymer of acrylic acid and potassium acrylate and the reaction can be illustrated as Fig. 4.

Besides, the dissolved peroxides and homopolymers in minor amounts are present as irradiation side products.

DSC Characterization

Thermal behavior of the hydrogels was studied using DSC to confirm the type end products that might be produced from irradiating of acrylic acid partially neutralized and their thermogram are presented in Fig. 5 and decomposition temperatures (td) summarized in Table 1. Fig 5(a) shows the DSC scan of dried sample hydrogels with neutralization degree of 0. It is observed that the thermogram of dried hydrogel made from the resulting partially neutralized acrylic acid via gamma irradiation with Dn = 0, appeared with three glass transition peaks and a single sharp peak at Td 461 °C in the exothermal process is shown in Fig. 5(a). In addition, Fig 5(b) shows the DSC scan of dried sample of acrylic acid hydrogel with neutralization degree of 1 (Dn = 1) appeared with a single broad decomposition temperature peak at 426.63 °C. Based on the characteristics of DSC thermogram peaks [20], it can be assumed that hydrogels with neutralization degree of 0 (Dn = 0) and 1 are presence in the crystalline and amorphous form of the dried hydrogels, respectively. The DSC curve of dried sample of acrylic acid hydrogels with neutralization degree of 0.25, 0.50, and 0.75 in Fig 5(b-d) shows two decomposition peaks, respectively. The first peak ranging from 340.40-358.75 °C and the second peak ranging from 385.0-450.45 °C.

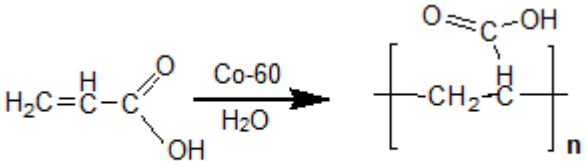

Fig 1. Radiation induced homopolymerization reaction of acrylic acid in aqueous solution

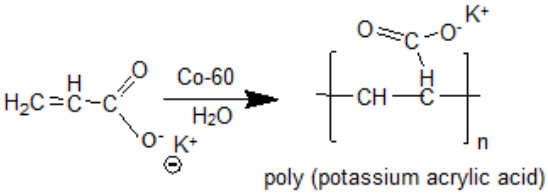

Fig 2. Radiation induced homopolymerization reaction of potassium acrylic acid in aqueous solution

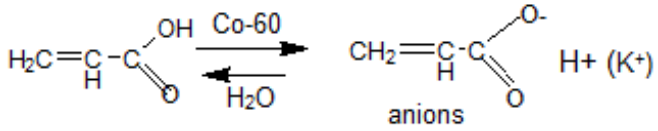

Fig 3. Equilibrium state of acrylic acid monomer in aqueous solution

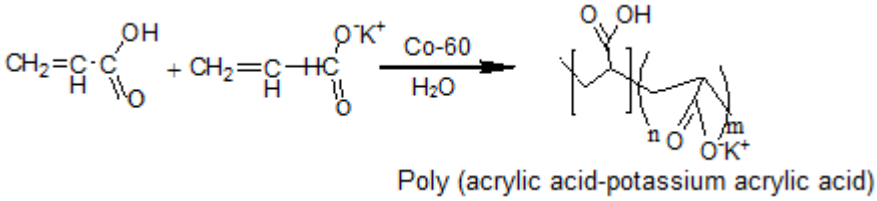

Fig 4. Radiation induced copolymerization reaction of potassium acrylic acid and acrylic acid in aqueous solution

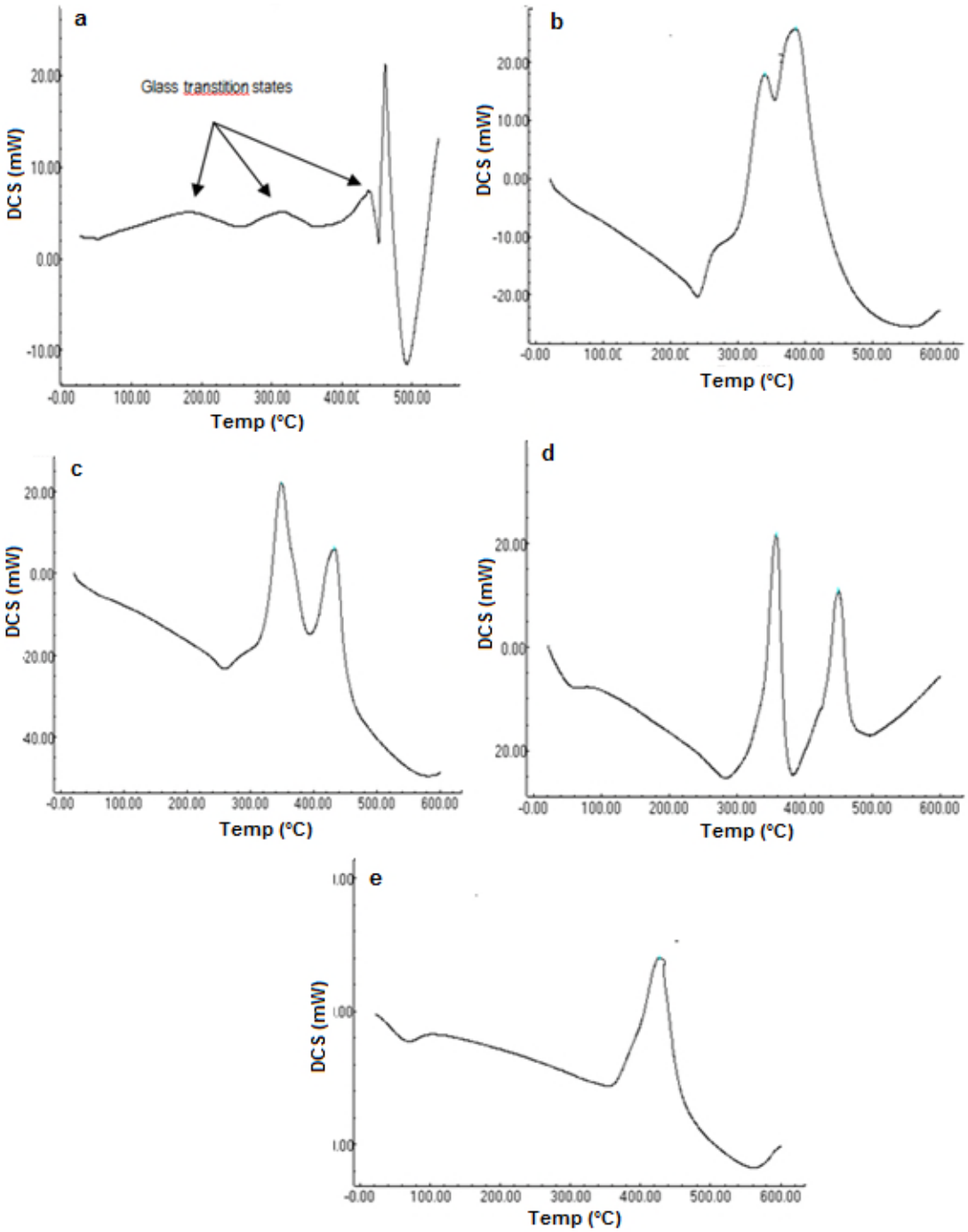

Fig 5. DSC thermogram of HSA of irradiated partially acrylic acid with varying Dn, (a) 0, (b) 0.25 , (c) 0.50, (d) 0.75, and (e) 1

A similar observation has been reported by Chapiro [21] and this has been analyzed that two peaks are presence as syndiotactic and atactic form of acrylic acid polymers.

SEM Photograph of HSA

The SEM photograph provides the pores geometry and size related to their specific location of the hydrogels. Therefore, it gives relevant information the homogeneity and heterogeneity of the hydrogels network. For this purpose SEM pictures of hydrogel prepared from 0.75 Dn with higher swelling ratio (~1000 g/g) were taken at the surface and interior of the hydrogels and shown in Fig. 6. It can be seen that the hydrogel is covered by irregular pores with sizes ranging from 7.5–100 μm, and in some places covered

Table 1. Decomposition (Td) temperature of HSA acrylic acid based with different Dn prepared by gamma irradiation at a dose of 10 kGy

Sample(s) HSA of partially acrylic acid with Dn	Td_1 (°C)	Td_2 (°C)
0	461.51	---------
0.25	340.40	385.90
0.50	349.55	433.13
0.75	358.74	450.48
1.00	426.63	---------

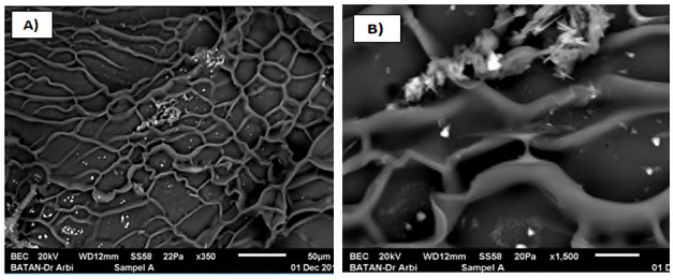

Fig 6. Scanning micrograph of the surface of HSA prepared from irradiated of 0.75 Dn of acrylic acid with swelling ratio ~1000g/g. The micrographs of the surface hydrogels were taken with a magnification, a) 350 x and b) 1500 x (the scale bar are 50 µm and 10 µm)

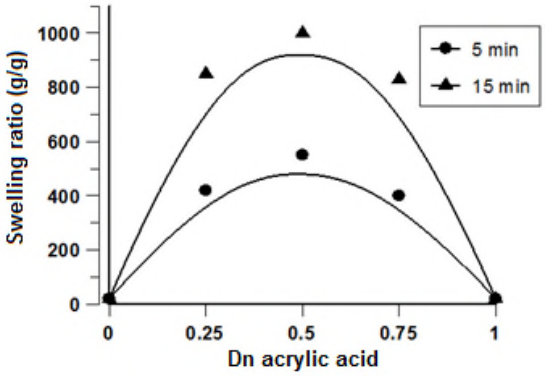

Fig 7. Swelling ratio of HSA in distilled water of irradiated partially neutralized acrylic acid with different Dn

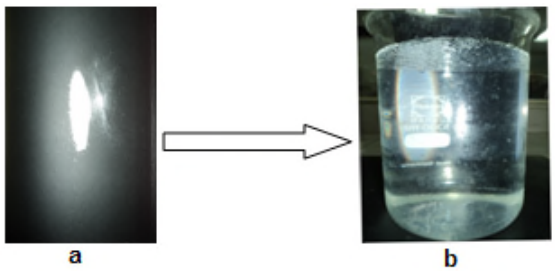

Fig 8. The swollen of HSA irradiated acrylic acid (Dn=0.5) in water with a high *swelling* capacity of 1000 g/g as super absorbent hydrogel a) Dried hydrogel (1g), b) swollen hydrogel in 1 L (1000 g) of water

by a thin skin of polymer. The presence of a polymeric skin has been describe for other hydrogel, and is probably related to the collapse of surface pores by a freeze drying process mainly in the hydrogels with large pores and thin walls.

Swelling Properties of Partially Neutralized Acrylic Acid Hydrogels

The effect of immersing time on swelling kinetics of partially neutralized acrylic acid hydrogels with the neutralization degree (Dn) in the range of 0–1 are presented in Fig. 7. It can be seen that as the neutralization degree of acrylic acid hydrogels increased, the equilibrium swelling ratio of hydrogels significantly decreased. While with the increase immersing time from 5 min to 15 min, the swelling ratio of the hydrogels increased. The swelling ratios of hydrogels with neutralization degree of 0.25 and 0.75 was approximately 450 and 600 g/g, respectively and the optimum swelling ratio of hydrogel was reached 1000 g/g (shown in Fig. 7) from acrylic acid with Dn = 0.5. In contrast, for hydrogels with Dn = 0 and Dn = 1, the swelling ratio was low (~20 g/g). It is indicated that the prepared homopolymer acrylic acid hydrogels with D = 0 and D = 1.00 as a results of irradiation composed a small amounts of crosslinking acrylic acid hydrogels which can absorb and retain small quantities of water. In addition for acrylic acid hydrogels with Dn in the range of 0.25–0.75 are composed of the mixtures of syndiotactic and atactic forms of acrylic acid hydrogels [21]. When they are dissolved in water, the carboxyl anions in the polymer backbone were exposed into water, the hydrogels rapidly swell due to the repulsive forces between carboxyl anions and the porosity sizes of the hydrogels increased with following water diffusion into the pores of hydrogels. Finally, the swelling ratio of the hydrogel increased significantly, and the optimum swelling ratio is obtained from hydrogel with Dn = 0.50 caused the highest possibility of repealing carboxylate anions in the hydrogel networks.

FTIR Characterization of HSA

The FTIR spectra of superabsorbent of partially neutralized acrylic acid with having 50% neutralization degree as a result gamma irradiation is presented in Fig. 9. It can be seen that at wave numbers of 3,700–3,000 cm^{-1} there is a broad absorption band which corresponds to the stretching vibration of –OH groups, -CH stretching vibrations of the acrylate groups on the chain give absorption at 2,962 cm^{-1}. At the 1,674 range, is a peak corresponding to deformation vibrations of –C-OH, the peak at 1,570 cm^{-1}

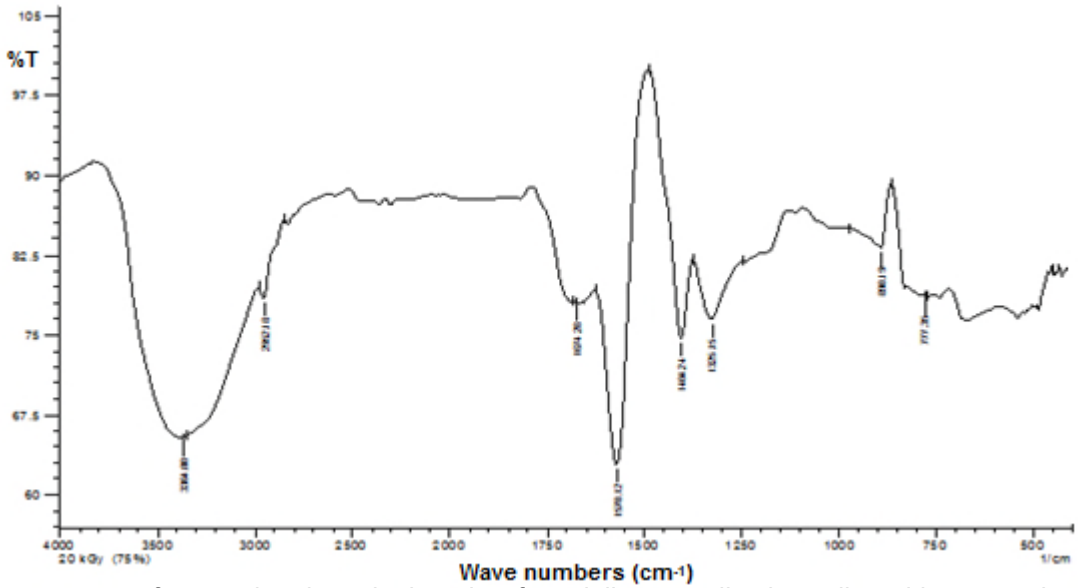

Fig 9. FTIR spectrum of superabsorbent hydrogels of partially neutralized acrylic acid prepared using gamma irradiation

is a peak corresponding to asymmetrical vibrations of $–COO^-$ groups and the peak at 1,325 cm^{-1} is a peak of symmetrical vibrations of $–COO^-$. Based on this FTIR spectrum it can be proven that crosslinking of acrylic acid occurs at its double bond caused there is no double bond of acrylic acid appeared in the FTIR spectrum.

CONCLUSION

Superabsorbent hydrogels (HSA) with rapid swelling and a large capacity water absorption based on partially neutralized acrylic acid can be synthesized through gamma irradiation technique. The swelling behavior of HSA dependent on Dn of acrylic acid. The highest swelling capacity (~1000 g/g) of HSA can be reached in 15 min of irradiated partially neutralized acrylic acid with having Dn = 0.50. The thermogram DSC confirmed possibilities of the type end products resulting from irradiated of partially neutralized acrylic acid. From SEM examination, the hydrogels had large numbers of pores. Spectra FTIR supported the role of double bond in radiation polymerization of acrylic acid.

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