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Synthesis of Superabsorbent Polymer based Glucomannan-Polyacrylate by Gamma Irradiation for Personal Care Application

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Abstract

Materials with potential of fast absorption of water or liquid have emerged as very interesting objects for researches. Superabsorbent polymer is a cross linked polymer which has ability to absorb water hundreds to thousands of times the dry weight because it has hydrophilic groups. Owing to this characteristic this polymer gets attention for many applications, one of these is diapers. Superabsorbent polymer was synthesized from the mixture of glucomannan-pottasium acrylic-acrylamide solution by irradiation crosslinking with doses irradiation 10 kGy. It was found that SAP showed super swelling properties in water (~880 g/g) at short time (15 minutes) and in real urine has a good swelling ~110 g/g. Acrylamide was able to increase the swelling ratio in real urine. Therefore, it can be candidate as thin diapers with high sorption. The result of FTIR spectra confirmed that the crosslinking occurs in the hydrogels and SEM images of hydrogels showed large numbers of pores from SEM examination.

Keywords: Superabsorbent polymer; Acrylic acid; Acrylamide; Glucomannan; Irradiation

Abstrak (Indonesian)

Bahan dengan potensi penyerapan air atau cairan yang cepat telah dikenal sebagai objek yang sangat menarik untuk diteliti. Superabsorbent polymer adalah polimer berikatan silang yang memiliki kemampuan menyerap air ratusan hingga ribuan kali lipat dari berat kering karena memiliki gugus hidrofilik. Karena karakteristik ini polimer ini mendapat perhatian untuk banyak aplikasi, salah satunya adalah popok. Polimer superabsorben disintesis dari campuran larutan glucomannan-pottasium acrilyc-acrylamide dengan pengikatan silang iradiasi dengan dosis iradiasi 10 kGy. SAP menunjukkan sifat kemampuan menyerap air yang besar (~880 g / g) dalam waktu singkat (15 menit) dan dalam urin nyata memiliki pembengkakan yang baik ~110 g / g. Acrylamide mampu meningkatkan rasio pembengkakan dalam urin nyata. Oleh karena itu, ia dapat menjadi popok tipis dengan penyerapan tinggi. Hasil spektra FTIR mengkonfirmasi bahwa ikatan silang terjadi pada hidrogel dan gambar SEM hidrogel menunjukkan sejumlah besar pori dari pemeriksaan SEM.

Kata Kunci: Superabsorbent polymer; Acrylic acid; Acrylamide; Glucomannan; Irradiation

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INTRODUCTION

Recently, materials with fast absorption of water or liquid have emerged as very interesting objects for researches. Superabsorbent polymer (SAP) are known as lightly cross linked networks which have ability to swell up hundreds to thousands of times their weight in a relatively short time and have good water-retention capacity. SAP have been widely applied in the field of industry, agriculture, medicine, and remove heavy metal ions [1-2] and azo dyes [3-4]. The super swelling properties can be applied for personal care product, such as infant diapers [5-6] and feminine hygiene products.

Diapers are amongst most popular personnel care products due to simple and disposable nature. Considering the increasing birth rate, personnel care products are likely to become a product that promises to be developed. According to ISO 17190-5 [7], SAP for diapers product should be no less than 46 times the dry weight. So far, commercial diapers are thick type, and mostly unfriendly in environment properties and toxic. Therefore, this calls for the research so as to overcome this problem.

SAP can be synthesized from natural and chemical synthetic polymers having rich hydrophilic groups. While chemical synthetic polymers have good water absorption the cost is high and difficult to degrade. This calls for copolymerization with natural polymers, which have good performance in both water-retaining capacity and rate of water absorption, to get the low cost, low toxicity, biodegradability, and friendly environmental nature products. Glucomannan is a more abundant neutral polysaccharide which have many feature, such as low cost, gelling and filming properties, high viscosity, biodegradable, biocompatible, and bio functional, and bio absorbable [8]. Wu et al. [9] synthesized konjac glucomannan grafted acrylate hydrogels with gamma irradiation methods and got swelling water ~600 times the dry weight. However, so far the focus is on absorption of water, whereas in other cases such absorption of urine is also required. Therefore glucomannan-acrylate hydrogel should be made to swell to real urine.

In the present work, synthesized glucomannan-Acrylate, which is in copolymerization with other polymers, namely acrylamide, was investigated. Acrylamide hydrogels have found extensive commercial applications as sorbent in personal care. Synthesize hydrogel poly (acrylic acid-acrylamide) had swelling in the urine 50 g/g [10]. Therefore, composite of acrylamide polymer is expected to increase the ability to absorb urine, so that it can become a candidate as thin diapers and dry surface after sorbing.

^{60}Co γ-irradiation is the most potential method for the formation of hydrogels with simple sample preparation, higher emissions energy, and low cost [11], without the addition of chemicals such as initiators, linker cross, and the activator so that the product obtained is more pure. In addition, the cross-link process does not require the addition of heat, and the reaction is easily controlled [12]. These techniques aim to obtain homogeneous crosslinking. Until now, synthesis of glucomannan using two monomers, namely acrylic acid and acrylamide using gamma irradiation, has not been reported. Therefore, the purpose of this study is to synthesize SAP from glucomannan-acrylic acid-acrylamide solution as well as to determine its ability of swelling in real urine. The SAP is expected to be applied as environment friendly diapers and having a thin shape and dry surface even after absorption. SAP products are characterized using Fourier Transform Infra-Red (FTIR) spectrophotometer and Scanning Electron Microscopy (SEM).

MATERIALS AND METHODS

Materials

The monomers used included acrylic acid and acrylamide were procured from E.Merck. Glucomannan was obtained from local industry. Alginate, sodium hydroxide and potassium hydroxide were purchased from E.Merck, Distilled water was used for the synthesis of the hydrogel, and real urine for swelling application.

Methods

Neutralization of acrylic acid. A series of acrylic acid solution were prepared from 15mL acrylic acid was neutralized KOH at different neutralization degree of 25%, 50%, 75%, and 100%. The mixture added 1g glucomannan and volume of the mixture was made up to 100 ml with destillated water. The mixture was stirred at 200 rpm at room temperature until homogenous. Then, the reaction mixtures were packed in polypropylene (PP) plastic bags, sealed and then irradiated at single dose of 10 kGy. The hydrogels were dried at 60°C for 48 h, and milled up to 60-80 mesh.

Preparation of Glucomannan-Poly(Potassium akrylic) Hydrogel. Acrylic acid solution (15%) was neutralized with optimum KOH and added 0,5- 2 g glucomannan. The volume of the mixture was made up to 100 ml with destillated water. Subsequently the mixture was stirred until it become homogeneous and packed in polypropylene (PP) plastic bags, sealed and then irradiated at single dose of 10 kGy. The hydrogels were dried at 60°C for 48 h, and milled up to 60-80 mesh.

Composite of Glucomannan-Poly(Potassium akrylic-Acrylamide) Hydrogel. Acrylic acid solution (15%) was neutralized with optimum KOH and added optimum glucomannan. The variations acrylamide 0,25-1g was added to the mixture, the volume of the mixture was made up to 100 ml with destillated water. The mixture was stirred at 200 rpm at room temperature until homogenous. Then, the reaction mixtures were packed in polypropylene (PP) plastic bags, sealed and then irradiated at single dose of 10 kGy. The hydrogels were dried at 60°C for 48 h, and milled up to 60-80 mesh.

Determination of Composite Hydrogel. Composite hydrogel was evaluated for gel content, swelling ratio, chemical structure and morphology properties. Fourier Transform Infrared spectrophotometer (FTIR) Shimadzu Prestige-21 model was amplified to analyze the functional group of cross-linked copolymer. The microstructure of a dry

SAP sample was investigated by means of a scanning electron microscope (SEM).

RESULT AND DISCUSSION

Effect of Neutralized acrylic acid with KOH.

The first step of this work was neutralization of acrylic acid with KOH to protect anions of acrylic acid when swelling. Acrylic acid was neutralized with varying concentration KOH from 25%-100% of neutralization degree, then irradiated with gamma rays a dose of 10 kGy. There are three steps for the polymerization reaction such as initiation, propagation and termination [13]. In first stage, radiolysis of water is resulted in H and OH radicals and attacks the double bond of acrylic acid and potassium acrylic acid to produce their radicals, respectively. These radicals reaction are continued to the second stage (propagation), and finally produces a stable product.

In case acrylic acid solution was not neutralized (Dn=0), the solution containing mostly monomer acrylic acid. The final radiation products will be homopolymer of acrylic acid. Meanwhile, acrylic acid solution gets partially neutralized (25%, 50%, and 75%) by KOH, in the mixture contain acrylic acid molecules and its anions in the equilibrium state (Fig.1). And for acrylic acid solution with 100% neutralization (Dn=1), acrylic acid anions predominates the solution and will be polymerized by radiation to its homopolymers of potassium acrylate salt in the final product.

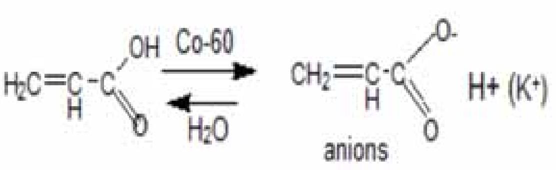

Figure 1. Equilibrium state of acrylic acid monomer in aqueous solution

The effect of immersing time on swelling kinetics of partially neutralized acrylic acid hydrogels with the neutralization degree (Dn) in the range 25%-100% are illustrated (Fig.2). As the neutralization degree of acrylic acid hydrogels increased, the equilibrium swelling ratio of hydrogels significantly decreased. The swelling ratio hydrogels increased with the increase of the immersing time up to 15 minutes. The swelling ratio of hydrogels with neutralization degree of 25% was approximately 303 g/g and the optimum swelling ratio of hydrogel reached 693 g/g from acrylic acid with Dn=50%. For hydrogel with neutralization 75% and 100% the swelling ratio was low 219 g/g and 59 g/g, respectively. It is revealing that the prepared homo-polymer acrylic acid hydrogels with 100% is a result of irradiation composed of a small amounts of crosslinking acrylic acid hydrogels which can absorb and retain small quantities of water. For acrylic acid hydrogels with neutralization partially of 25%; 50%; and 75% are composed of the mixtures of syndiotactic and atactic forms of acrylic acid hydrogels [14].

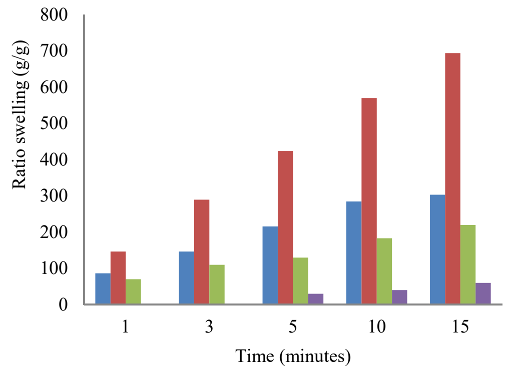

Figure 2. Swelling ratio of glucomannan-poly (potassium acrylic) hydrogels in distilled water of irradiated partially neutralized acrylic acid with different Dn

When hydrogels are immersed in water, the carboxyl anions from polymer backbone were exposed into water. Rapidly swelling hydrogels cause the repulsive forces between carbonyl anions and the porosity size of the hydrogels increased following water diffusion into the pores of hydrogels. Finally, the swelling ratio of hydrogels increased significantly, and the optimum swelling ratio is obtained from hydrogel. Partial neutralization (50%) caused the highest possibility of replacing carboxylate anions in the hydrogel networks

The effect of adding glucomannan.

Having known the partially neutralization of acrylic acid was 50%, then synthesis again with the varying of weight glucomannan 0.5-2 g to determine the optimum weight of glucomannan. The purposed mechanism for the synthesis of glucomannan-poly potassium acrylic hydrogel is shown in Fig.3. First step, radiolysis of water is resulted H and OH radicals and attack the double bond of glucomannan molecules and produce glucomannan radicals. The glucomannan radicals initiated the crosslinking of acrylic acid onto glucomannan. Crosslinking between macromolecular radicals should be formation of 3D network that will keep the water in the matrix [9].

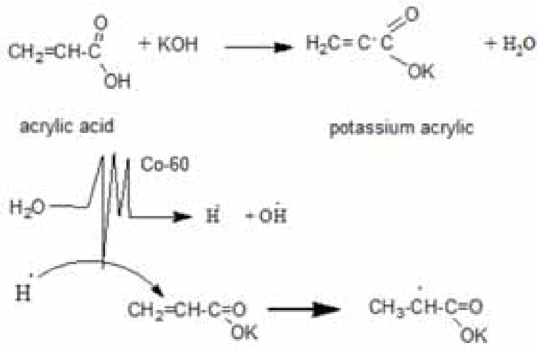

Figure 3. Simple mechanism for the synthesis of glucomannan-poly potassium acrylic hydrogel.

The swelling ratio of product needs to be investigated by specified intervals. The effect of immersing time on swelling glucomannan-poly potassium acrylic hydrogels with varying glucomannan is presented is shown in Fig.4. The highest swelling was obtained by adding 1 g glucomannan. At the initial state at 1 minute, the swelling ratio of hydrogel was attained 146 g/g. With the increase of immersing time up to 15 minutes, the swelling ratio of hydrogels gradually increased up to 693 g/g. SAP with the addition of 0.5 g glucomannan had good swelling (507 g/g), while the hydrogels with addition of 1,5g and 2g glucomannan provided smaller swelling, i.e. 408 g/g and 282 g/g, respectively. Addition of more than 1g glucomannan decreased the swelling ratio and cause increasing number of hydrophilic group, so that the density of both intramolecular and intermolecular distances in the matrix SAP also increased. As a result, water is difficult to penetrate into the network framework matrix [14].

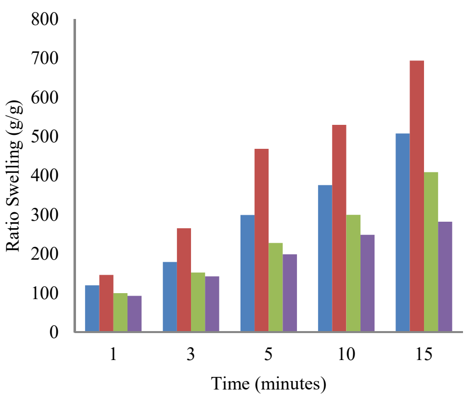

Figure 4. Swelling ratio of HSA glucomannan-poly potassium acrylic).

Factors that influence the mechanism of water absorption into SAP are hydration and hydrogen bonding. The mechanism of absorption of water by hydrogel can be explained from its initial form in dry conditions and when it is in solution media. The structure of hydrogel is in the form of drying up like a scroll folded (Figure 5) which is along the main chain consisting of hydrophilic groups. When SAP immersing into water, hydrophilic groups of acrylic acid dissociated in water to form a carboxyl ions with a negative charge. These ions repel each other along the polymer chain resulting expansion of hydrogel size. The ions are attracted to the polar molecules of water so that the interaction between the polymer and water molecules, namely interaction of hydration. After reaching equilibrium, the adsorbed water will be bound by the COO of forming hydrogen bonds. At the end of the absorbed water will be retained so that the HSA will expands. This resulted increase the swelling ratio [15].

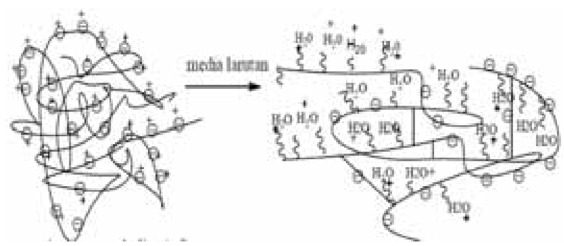

Figure 5. Scheme of SAP swelling process.

Wu et al. [9] produce HSA that have swelling in water is 600 times that of the dry weight with a soaking time of 1 hour. The difference in water absorbency is from the different materials used in preparing reaction mixture glucomannan and acrylic acid. Wu et al. [9] showed that expands swell hydrogel smaller compared with the results of this study, because this study using KOH as an alkaline neutralizing acrylic acid, while them using NaOH. Neutralization with KOH can improve the ability of sorption than NaOH.

HSA Glucomannan-Poly Potassium acrylic-Acrylamide).

Acrylamide is used as a hydrophilic agent in polymer modification, including in the manufacture of hydrogels. When the mixture containing glucomannan, potassium acrylic, and acrylamide is irradiated as an interpenetrating polymer network (IPN) that is formed with the chemical crosslinking of poly(potassiumacrylic-acrylamide) and physical crosslinking of glucomannan. Possibile mechanism is reactions based on the effect of irradiation on the mixture glucomannan-potassium acrylic-acrylamide based on the reaction polymerization of Charlesby [16]. If the solution has two types of polymers/monomers that have different chemical properties (degradation and crosslinking) and irradiated with gamma rays, results of irradiation will result in a product with a more dominant in amount either in crosslinked or degraded form. The Acrylic acid and Acrylamide are known as the crosslinking monomers and glucomannan as degradable polymers. Mechanism reaction of polymerization radical process occurs in three steps such as initiation, propagation and termination reactions. First, initiation reaction wherein free radicals are created, water molecules absorb the rays and break into HO· and H· radicals. The free radical of H· (or HO·) radicals is then transferred to the potassium acrylic monomer, forming active center and attack acrylamide monomer. Copoly (potassium acrylic-acrylamide) radicals was formed. This step is called propagation. In the last step or termination reaction is copoly (potassium acrylic-acrylamide) is crosslinking with the glucomannan molecules via hydrogen bond.

Glucomannan-poly(potassium acrylic-acrylamide) hydrogel that have been synthesized to investigating the swelling by adding acrylamide. The effect of immersing time on swelling of glucomannan-polypotassiumacrylic hydrogels with varying addition of acrylamide is illustrated in Fig.6. The swelling ratio was obtained by addition of 0,5 g of acrylamide that is equal to 885 g/g with 15 minutes immersion time. SAP with addition 0,25g of acrylamide gave swelling ratio was 733 g/g, while the addition of 0,75g acrylamide decreased swelling ratio, ie 780 g/g. This was because the number of hydrophilic groups increased, so the density of both intramolecular and intermolecular distances in the matrix SAP also increased. As a result, water is difficult to penetrate into the network framework matrix.

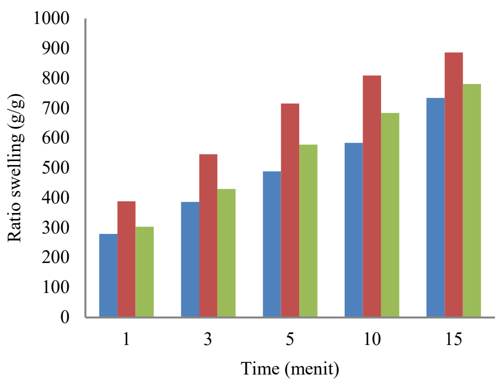

Figure 6. Swelling ratio of HSA glucomannan-poly potassium acrylic-acrylamide

Application of SAP in real urine.

The most important property of a commercial superabsorbent used in personal care applications is the extent of swelling. According to ISO 17190-5:2001, an acceptable swelling capacity for diapers is 46 g of urine per gram of polymer. In general, the swelling of hydrogels in real urine is much lower than the swelling obtained in distilled water. The reduction in polymer swelling in urine can be effected by urinal salts on the macromolecules network, which may cause a swelling reduction. The amount of urine absorbed by dry hydrogels was investigated and the results are shown in Fig. 7 and 8.

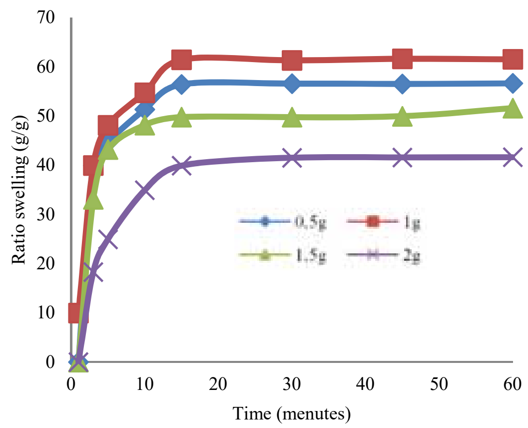

Figure 7. Swelling ratio of HSA glucomannan-poly potassium acrylic in real urine.

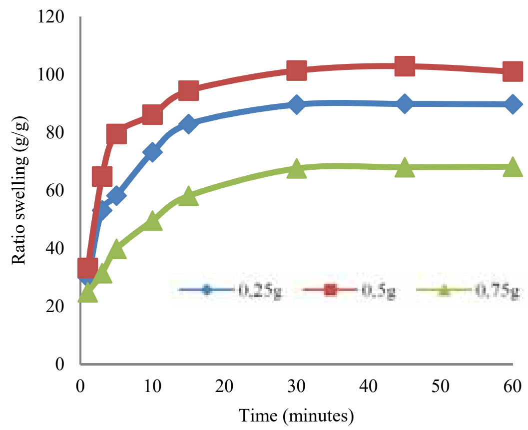

Figure 8. Swelling ratio of HSA glucomannan-poly potassium acrylic-acrylamide in real urine.

Glucomannan-poly potassium acrylic hydrogels with added 1g of glucomannan has qualified as a hydrogel that can be applied to diapers because it has a absorption capacity of 60 times the dry weight of the urine. However, when a small amount of acrylamide polymer (0.5g) was added, there was an increase in the absorption of urine which was high enough to reach 100 times the weight of the polymer.

This is caused because acrylamide has a hydrophilic group such as $-CONH_2$. It is well known, the order of ability to absorb water for the hydrophilic groups is as follows: -COOH > $-CONH_2$ > -OH. Acrylamide hydrogels have found extensive commercial applications as sorbents in personnel care products (e.g. infant diapers). El-Rahim [10] has synthesize hydrogel poly (acrylic acid-acrylamide) using gamma irradiation with urine absorption capacity of 50 g/g. Therefore, with the added acrylamide monomer in the solution one can enhance the ability of urine swelling by double.

Analysis spectra FTIR.

Evaluation of FTIR spectrum of the mixture glucomannan-potassium acrylic-acrylamide provided understanding of binding and crosslinking of the sample during the polymerization (Fig.9). FTIR spectra of glucomannan-poly potassium acrylic-acrylamide showed the absorption peak at 3450cm^{-1} (-COOH of acrylic acid, -OH of glucomannan, and –NH of acrylamide), 2926cm^{-1} (–CH of all polymers), 1707cm^{-1} ($-CONH_2$) and the crosslink copolymer gives rise to two characteristics bands at 1575cm^{-1} and 1400cm^{-1}, which belong to the symmetric and the asymmetric vibration absorption of -COO. These are the proofs that both potassium acrylic and acrylamide have been cross linked onto glucomannan.

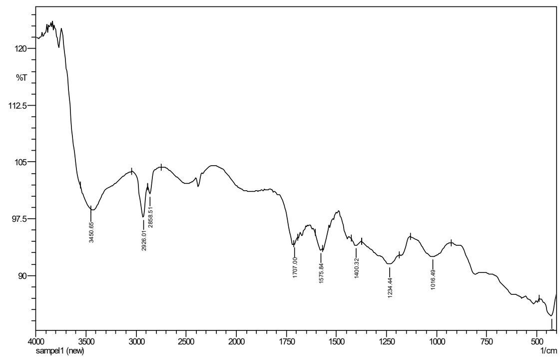

Figure 9. FTIR spectra of Glucomannan-poly potassium acrylic-acrylamide hydrogel

SEM morphological analysis.

The SEM images of the surface of glucomannan-poly potassium acrylic-acrylamide hydrogel particles are shown in Fig.10. The micrographs of the SAP cross section of glucomannan-poly (potassium acrylate-acrylamide) after attainment of equilibrium at 100x magnification (Figure 10) show a highly porous structure with sufficiently large pores and wide pore size distribution. The structure of the pores has a shape like a sponge and interconnected tissue. This shows that there is a cross link in the HSA structure. The large pore size (macro porous) in this HSA causes water to easily enter the HSA structure so that the resulting inflating ratio is quite large.

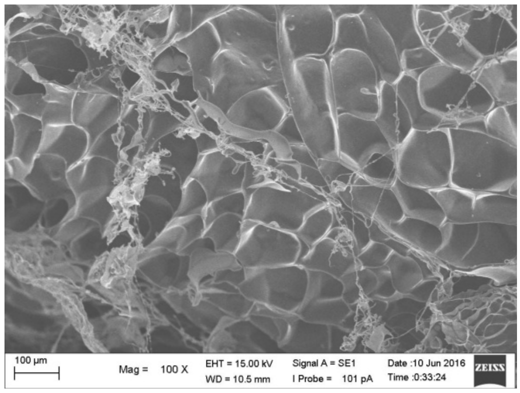

Figure 10. SEM images of glucomannan-poly potassium acrylic-acrylamide).

CONCLUSION

A biodegradable hydrogel superabsorbent of glucomannan-poly(potassium acrylic-acrylamide) was synthesized by radiation copolymerization reaction of glucomannan, potassium acrylic, and acrylamide in aqueous solution. Experimental results revealed that the superabsorbents can absorb water (swelling) very fast with higher swelling ratio (~880 g/g) and swelling of real urine is obtained (~100 g/g). Therefore, it is recommended as a good candidate for thin diapers with higher sorption. The results of FTIR spectra confirmed that the crosslinking occurs in the hydrogels and SEM images of hydrogels showed large numbers of pores from SEM examination.

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