Preparation and Properties of Konjac Bran-Graft-Poly (acrylic acid) Superabsorbent Polymer

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The Asian Conference on Sustainability, Energy & the Environment 2016
Official Conference Proceedings

Abstract
Biopolymer-based superabsorbent was synthesized by graft copolymerization of partially neutralized acrylic acid (AA) onto glucomannan backbone in konjac bran via a thermal initiator system of potassium persulfate (KPS) and using N,N'-methylenebisacrylamide (NMBA) as a crosslinking agent. The synthesized superabsorbent polymer was characterized by FTIR and SEM. The influence of variables content on the water absorbency property including amounts of AA, KPS, NMBA and konjac bran were investigated. Results obtained from this studied showed that the maximum equilibrium water absorbency was 554 g g^{-1} in deionized water and 56 g g^{-1} in 0.9 wt% NaCl aqueous solution under the optimized conditions. Furthermore, the superabsorbent polymer was good water retention, being biodegradable and low cost that can be used in a various range of applications especially in the horticulture and agriculture industry.

Keywords: Konjac bran; Glucomannan; Acrylic acid; Superabsorbent polymer; Water absorbency

1. Introduction

Superabsorbent polymers (SAPs) are crosslinked hydrophilic polymers chains forming a 3-dimensional network structure that have the ability to absorb and retain large volumes of water and aqueous solutions compared to their dry weight. Because of their excellent properties, superabsorbent polymers are widely used in many fields, such as baby nappies and adult incontinence pads, controlled release medium, agriculture and horticulture, etc. (Elliott, 2004). However, most of SAPs are based on chemical synthetic polymers, which are costly, poorly degradable, and environmentally-unfriendly.

Recent research focused attention on the superabsorbent polymers based on natural polysaccharides for their characteristic properties, including biodegradability, renewability and nontoxicity (Ma, Ran, Yang, Feng, & Lei, 2015). Some natural polysaccharides such as starches, celluloses, gum ghatti, chitosan and alginate can be prepared as superabsorbent polymers via graft copolymerization of vinyl monomers onto the chain of natural polymers.

Konjac bran is a kind of waste from tubers of amorphophallus konjac plant. It is contained the konjac glucomannan (KGM), a more abundant natural polysaccharide, that consist of β-1,4-linked D-mannose and D-glucose in an approximate ratio of 2 : 3 with a low degree of acetyl groups (approximately 1 acetyl group per 17 residues) at the side chain C-6 position (Chen, Zhang, & Li, 2015; Tian et al., 2012). Furthermore, KGM has a large number of hydrophilic groups in the molecular chains. The abundant hydroxyl groups on glucomannan backbone make KGM easily modified in chemical way and a better raw material for synthesis superabsorbent polymer.

The aim of this study is to investigate the synthesis of a novel konjac bran-graft-poly(acrylic acid) superabsorbent polymers (KB-g-PAA) by graft copolymerization reaction of partially neutralized acrylic acid (AA) and konjac bran (KB), using N,N'-methylenebisacrylamind (NMBA) as a crosslinking agent and potassium persulfate (KPS) as a initiator, in aqueous solution. The influent of the amount of reaction parameters (such as monomer, initiator, crosslinking agent and konjac bran) on water absorbency of the KB-g-PAA was studied in both deionized water and 0.9 wt% NaCl solution were investigated and discussed.

2. Experimental

2.1 Materials

Acrylic acid (AA, CP grade) and N, N'-methylenebisacrylamide (NMBA, CP grade) were purchased from Sigma-Aldrich Co. LLC. Potassium persulfate (KPS, AR grade) and Sodium hydroxide (NaOH, AR grade) purchased from Ajax Finechem, Australia. Konjac bran was purchased from Monkey King Food co.,LTD., Bangkok, Thailand. Mixed konjac bran and deionized water (ratio = 1 : 20) and stirred at 50 ˚C for 5 min until the konjac bran's gel was formed.

2.2 Preparation of KB-g-PAA superabsorbent polymer

Grafted copolymerization of superabsorbent polymer was prepared by slowly neutralizing AA (0.1 – 0.2 mol) with 5 M NaOH solution (degree of neutralization 65%) during which the temperature was keep < 20 ˚C by a cool water bath and put solution in a 500 mL four-necked flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. Then, added the NMBA and konjac bran's gel to the acid solution sequentially. The mixture was heated to 70 ˚C and stirred for 30 min under nitrogen atmosphere and oil bath to completely dissolve konjac bran's gel into solution. Then, the initiator KPS (dissolved into 5 mL deionized water) was added to the mixture to initiate the polymerization. After 4 h, the resulting product was cut into small pieces and dried in an oven at 60 ˚C to a constant weight to evaporate the solvent. The dried product was milled and screened. All samples had a particle size in the range of 40 – 60 mesh.

2.3 Water absorbency measurement

The water absorbency of the prepared KB-g-PAA superabsorbent polymer was determined in deionized water and in saline solution of 0.9 wt% NaCl by tea bag method (Tian et al., 2012) as follow: accurately weighted 0.1 ± 0.001 g samples were put into a tea bag and immersed in excess medium at room temperature for 2 h. After that the water unabsorbed into swollen gels was removed by putting the tea bag in air for a short time. Then wiped with filter paper and weighed tea bag containing the swollen gels. The water absorbency was calculated by the following equation:

$$Q = \frac{m_2 - m_1 - m_0}{m_0} \tag{1}$$

where m_2, m_1, and m_0 were the weight of the wet tea bag containing the swollen gels, the tea bag, and the dried samples, respectively.

2.4 Characterization

2.4.1 FT-IR spectroscopy. The structure of the superabsorbent polymer was characterized by a Fourier Transform Infrared Spectrophotometer (Perkin Elmer spectrum one) in the range from 400 to 4000 cm^{-1}. KBr pellets of the samples were prepared.

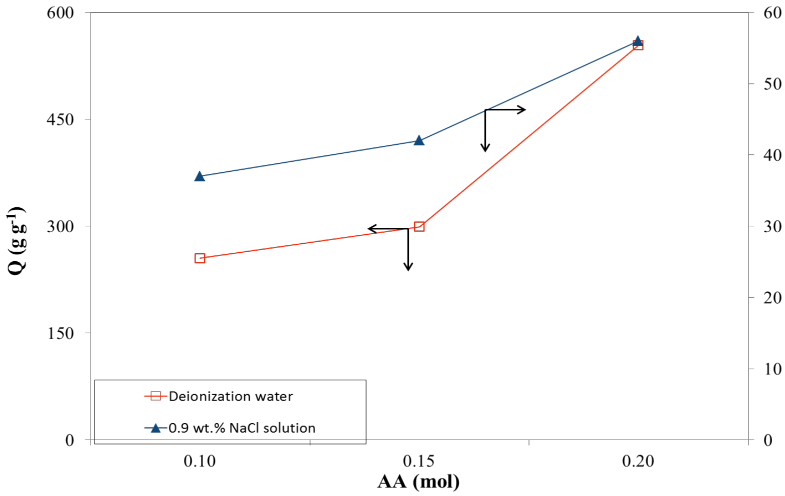
2.4.2 SEM examination. The surface morphologies of the KB-g-PAA superabsorbent polymer were examined using a scanning electron microscope (JSM-6610LV). The samples were coated with Au before SEM examination.

3. Results and discussion

3.1 Effect of initial monomer content on water absorbency

The effect of initial monomer content on water absorbency of superabsorbent polymer was studied by varying the acrylic acid content from 0.1 to 0.2 mol, and keeping constant other parameters such as initiator (KPS, 0.35 mmol), crosslinking agent

(NMBA, 0.1 mmol), neutralization degree (65 %) and konjac bran (0.4 g). As shown in Fig.1, The water absorbency of KB-g-PAA SAP in both deionized water and 0.9 wt% NaCl solution was increasing with the raising of monomer content. The maximum absorbency (554 g g^{-1} and 56 g g^{-1} in deionized water and 0.9 wt% NaCl solution, respectively) was obtained at 0.2 mol of AA. The increase in water absorbency may be attributed to increase in the diffusion of AA molecules into the polysaccharide backbones and enhances the hydrophilicity of superabsorbent polymer



(Pourjavadi, Soleyman, & Barajee, 2008).

Fig.1. Effect of initial monomer content on water absorbency. Reaction conditions: KPS 0.35 mmol, NMBA 0.1 mmol, Konjac bran 0.4 g, neutralization degree 65%

3.2 Effect of initiator content on water absorbency

The effect of initiator content on water absorbency of superabsorbent polymer was investigated (Fig.2). The water absorbency was decreased versus increasing the initiator content from 0.35 to 1.05 mmol. This water absorbency loss can be attributed to an increase the terminating step of reaction via bimolecular collision which causes to enhance crosslinking density of SAP (Hosseinzadeh, Sadeghzadeh, & Babazadeh, 2011). In addition, the free radical degradation of glucomannan backbones by sulfate radical-anions is an additional reason for abatement of swelling at higher KPS content.

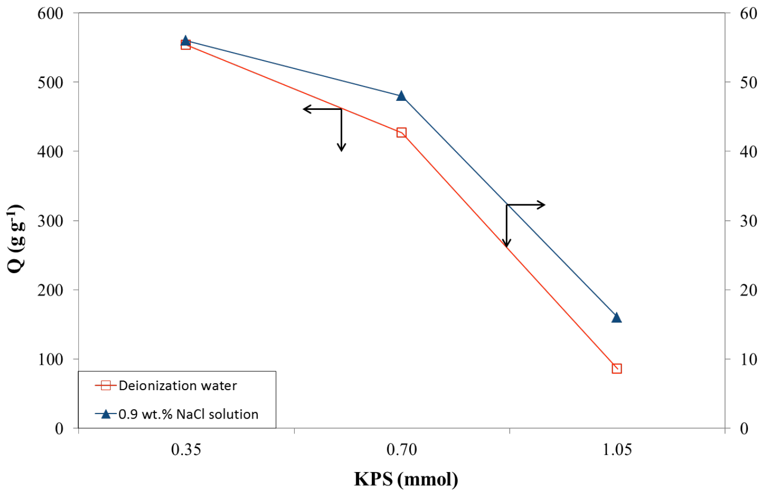


Fig.2. Effect of initiator content on water absorbency. Reaction conditions: AA 0.20 mol, NMBA 0.1 mmol, Konjac bran 0.4 g, neutralization degree 65%

3.3 Effect of crosslinking agent content on water absorbency

A crosslinking agent is used through SAP preparation to provide crosslinks between polymer chain to form a network structure and prevent the SAP swelling to infinity. The effect of NMBA content on water absorbency of KB-g-PAA SAP was studied by varying the NMBA content from 0.1 – 0.5 mmol and the results were shown in Fig.3. The water absorbency was decreased with increasing crosslinking agent. The high cross-linking density, contributed to a decreased space between polymer chains, that according to Flory's theory (Li & Wang, 2005).

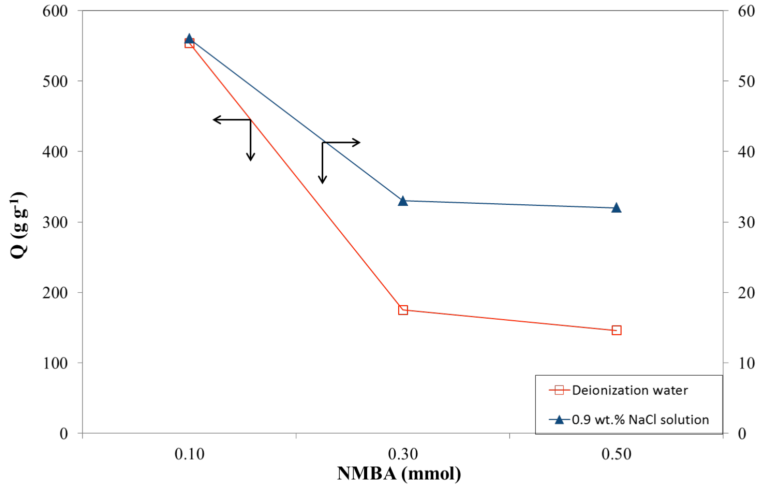


Fig.3. Effect of crosslinking agent content on water absorbency. Reaction conditions: AA 0.20 mol, KPS 0.35 mmol, Konjac bran 0.4 g, neutralization degree 65%

3.4 Effect of konjac bran content on water absorbency

The swelling capacity of the KB-g-PAA SAP in deionized water and 0.9 wt% NaCl solution with difference contents of konjac bran was investigated. As shown in Fig.4, the water absorbency of samples in deionized water was increased with increasing the konjac bran content up to 0.4 g and then it was considerably decreased with a further increase in the content of konjac bran. On the other hand, the water absorbency of samples in 0.9 wt% NaCl solution was decreased with increasing the konjac bran content.

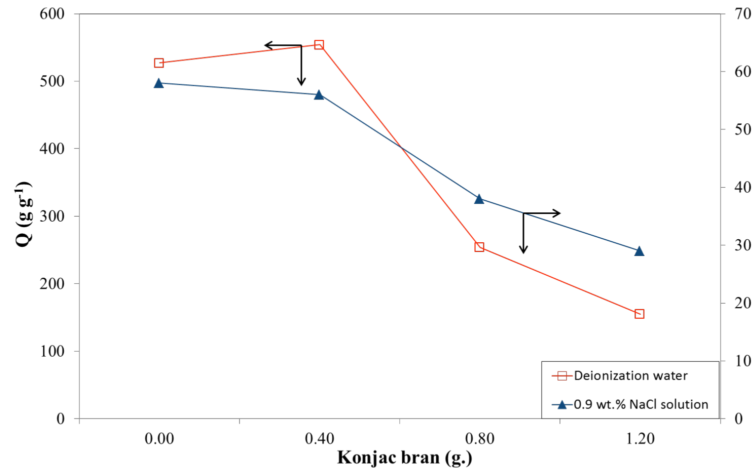


Fig.4. Effect of konjac bran content on water absorbency. Reaction conditions: AA 0.20 mol, KPS 0.35 mmol, NMBA 0.1 mmol, neutralization degree 65%

By increasing the amount of konjac bran up to 0.4 g, the number of active free radicals was enough to react with the glucomannan backbone. In addition, glucomannan structure contains a large number of hydrophilic groups in the molecular chains could attracted to water molecules and reacted with PAA-COO^- groups to enhance the polymeric network resulting in an increased water absorbency value (Mukerabigwi et al., 2015). However, the konjac bran content higher than the optimum value, water absorbency of samples was decreased, may be attributed to an increase in viscosity of the medium, which hinders the movement free radicals and monomer molecules in reaction system (Hosseinzadeh et al., 2011).

3.5 FTIR analysis

The structure changes of konjac bran and KB-g-PAA SAP were confirmed by FT-IR spectroscopy (presented in Fig.5). In the FTIR spectrum, a very broad between 3700 and 3200 cm^{-1} was observed. Fig.5a shows the FTIR spectrum of konjac bran, the peak at 3429 cm^{-1} was assigned to the stretching vibration of –OH groups of the methyl, the characteristic absorption peak in 1727 cm^{-1} was attributed to C=O stretching vibration of acyl groups in the glucomannan. Meanwhile, compared with the spectrum of KB-g-PAA SAP (Fig.5b), the peak at 3444 cm^{-1} was attributed to the –OH stretching vibration of the carboxylic groups and the intensity of the peak at 1719 cm^{-1} was stronger than the spectrum of konjac bran and assigned to the stretching of the C=O of the carbonyl of acetyl groups in KB-g-PAA SAP after the reaction.

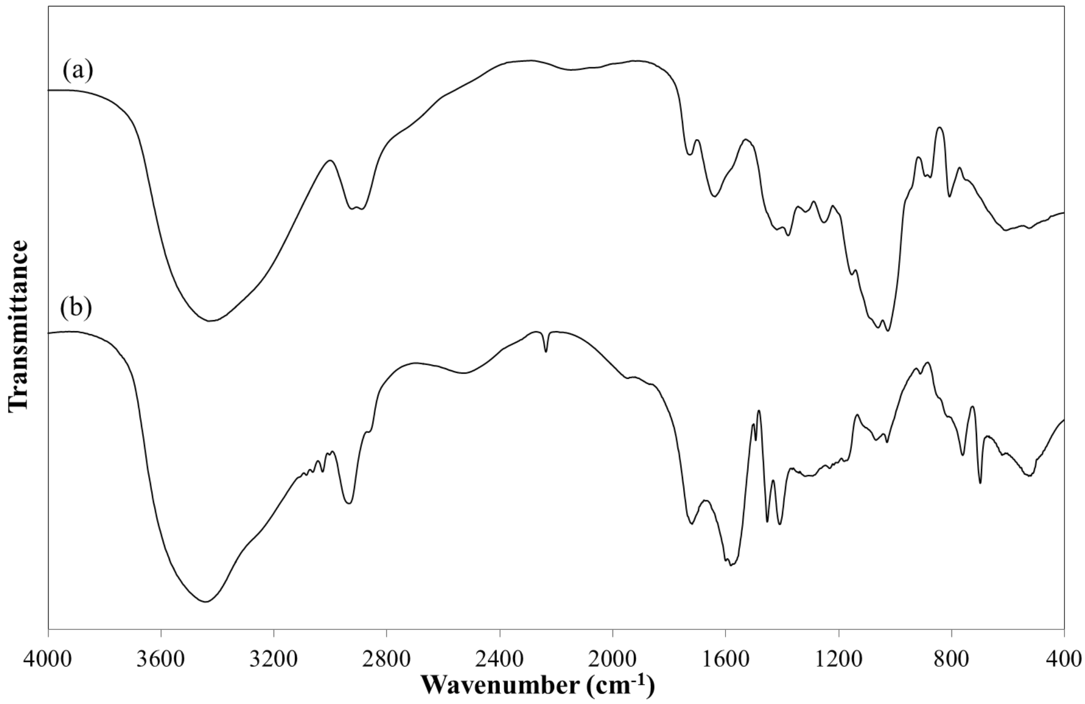


Fig.5 FTIR spectra of (a) konjac bran and (b) KB-g-PAA SAP

3.6 SEM observations

The morphology of microstructure was one of the most important factors which should be considered. Fig.6 shows the scanning electron microscope images of the superabsorbent polymer without konjac bran (PAA SAP) and superabsorbent polymers with different contents of konjac bran (KB-g-PAA SAP). Obviously from

Fig.6a, the surface morphology of the PAA presents a smooth and tight surface without any pores. However, the superabsorbent polymers containing konjac bran (Fig.6b – 6d) display an undulant, rough and tight surface without any pores.

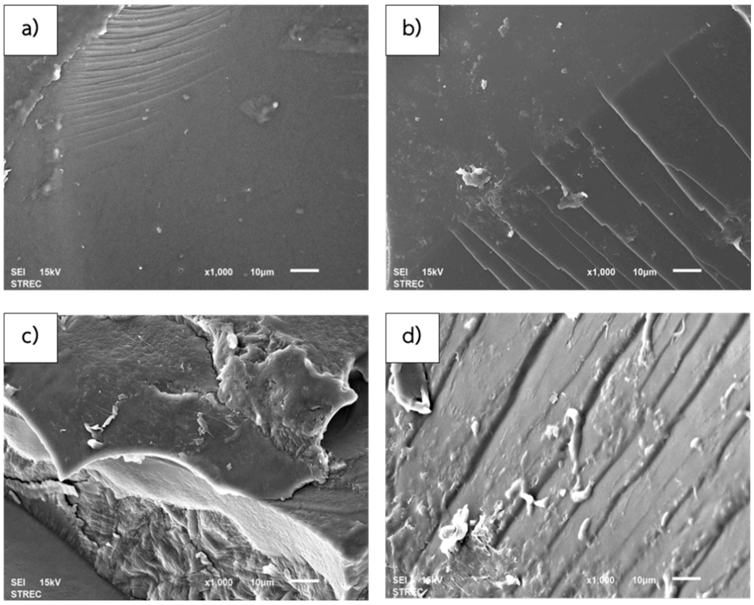


Fig.6 SEM images of PAA SAP (a) and KB-g-PAA SAP with difference contents of konjac bran: (b) 0.4 g, (c) 0.8 g, and (d) 1.2 g

4. Conclusions

In the present study, a novel superabsorbent polymers based on konjac bran was prepared by graft copolymerization of acrylic acid in the presence of a crosslinking agent. Under the optimized conditions, AA = 0.2 mol, neutralization degree = 65%, KPS = 0.35 mmol, NMBA = 0.1 mmol, and konjac bran 0.4 g, the water absorbency of KB-g-PAA superabsorbent in deionized water and 0.9 wt% NaCl saline solution was 554 g g^{-1} and 56 g g^{-1}, respectively. Furthermore, the superabsorbent polymer was good water retention, being biodegradable and low cost that can be used in a various range of applications especially in the horticulture and agriculture industry.

Acknowledgements

This research was supported by Research and Researchers for Industries (Grant No. MSD57I0003) and Thailand Research Fund (TRF).

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