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Influences of Neutralization of Superabsorbent Hydrogel from Hydroxyethyl Cellulose on Water Swelling Capacities

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Abstract. In this research, superabsorbent hydrogels were synthesized by graft copolymerization of hydroxyethyl cellulose (HEC) and polyacrylamide (PAM) under the initiation of potassium persulfate (KPS). The polymer networks were constructed using *N,N'*-methylenebisacrylamide (MBA), and the reaction was performed in an aqueous solution. The extent of grafting products was evaluated from grafting efficiency (%GE) and percentage of add-ons at HEC/AM ratios of 1: 10. The water swelling capacities, in terms of swelling capacity and weight loss, of resultant superabsorbent polymers (SAPs) after solvent extraction were determined for swelling behaviors. The result showed that the SAP had poor water absorption of approximately up to 23 g/g. To enhance swelling capacity of SAPs, an alkaline hydrolysis was done by using two types of alkaline bases, i.e., 2 M NaOH and 2 M KOH solution. The obtained treatment SAPs were neutralized by washing with distilled water and 0.5 M HCl until the liquors pH was nearly 7. They were found that the treatment SAPs showed the highest water absorption up to 317 g/g. Influences of various fluids pH values ranging between 4 and 10, on water swelling capacities of SAPs were also investigated. Under optimal pH value, the highest water absorptions of SAP was 382 g/g. To confirm the grafting reaction of PAM onto HEC backbone, FT-IR analysis was used. The results revealed absorption bands of the HEC backbone and new absorption bands from the grafted copolymer. Furthermore, the FT-IR spectrum was proved that washing with distilled water can alter the chemical functional group of SAPs.

INTRODUCTION

The functional materials that can absorb and retain a large amount of fluid comparing to its weight, namely hydrogel or superabsorbent polymers (SAPs). They were basically described as a loose three dimensional network structures of hydrophilic polymer chains [1, 2]. In the 1980s, water absorption materials were derived from cellulosic or fiber-based products. Logical choices were tissue paper, cotton, sponge, and fluff pulp. These types of materials had low water absorption capacity up to 20 times their initial weight.

In the 1960s, the water conservation materials were firstly invented by the United States Department of Agriculture for soils amendment. They worked hard and developed a polymer based on the grafting of polyacrylonitrile onto starch backbone. This new material can absorb a large of water more than 400 times its weight without releasing liquid fluid even under high pressure. The SAPs were originally synthetic crosslinked polyacrylic acid and polyacrylated derivatives of petroleum products which have a tendency to increase the cost endlessly. They are able to absorb large quantities of water without dissolving, even exceeding 1,000 fold of their dry weight [3].

Because of its excellent swelling behaviors, the SAPs have prompted much attention both fields of academic and industries to produce for diverse utilizations. For example they are widely proposed for horticultural purposes over the last five decades with the idea to improve water availability for plants [4]. Several possible applications of SAPs have been described corresponding applications such as in disposable baby diapers, in agriculture as a soil amendment [5], in controlled release of drugs as a carrier [6], in coal dewatering [7,8], in waste water treatment [9], in cosmetic and absorbent pads [10], and in gel electrolyte membranes [11]. According to their structure, SAPs were

definitely divided into three main types, namely natural polymers (polysaccharide derivatives), semi-synthetic polymers (cellulosic primitive derivatives), and synthetic polymers [12]. Most of the commercial SAPs are synthetic polyacrylate-based products, non degradable and considered as potential pollutants for the environments. Because of large attention in environmental protection issues, biodegradable SAPs have stood up interest for potential application in various fields. Although all types of SAP have no direct threat to human life, systematical disposal of synthetic SAPs waste is a source of environmental pollutants [13, 2]. This problem has prompted polymer technologist to produce SAP that reduce the need to have an actual disposal system. The naturally occurring SAPs are attractive route due to their unique renewability and biodegradability. Amongst them, polysaccharides have been employed due to availability in large feedstock, renewability and biodegradability. Hydroxyethyl cellulose (HEC) is modified cellulose with abundant reactive hydroxyl groups, they can be grafted with hydrophilic vinyl monomers to produce materials with excellent properties [14].

In this work, Hydroxyethyl cellulose was finely used to prepare SAP by grafting copolymerization with polyacrylamide, via solution radical polymerization. The aim of this study was to investigate the main factors that affect the swelling capacity of SAP including types of alkaline hydrolysis treatment and neutralization condition after alkaline treatment. Water swelling capacities of obtained SAPs were determined under the different pH values in range of 4-10. FTIR determination was utilized to characterize and confirm successful graft copolymerization.

EXPERIMENTAL

Materials

Hydroxyethyl cellulose (HEC) (92% purity), Merck KGaA Corporate (Germany); acrylamide (AM) for synthesis (99% purity) Merck K GaA Corporate (Germany); potassium persulfate (KPS) assay (99% purity, radical initiator), Ajax Finechem; N,N'-methylenebisacrylamide (MBA) (98% purity, crosslinker), Fluka (Switzerland); Bentonite, Sigma Aldrich, (USA); sodium hydroxide (99% purity), Fluka (Switzerland).

Preparation of SAP

The reaction took place under nitrogen gas atmosphere and HEC was firstly dried in a hot air oven to constant weight, 12.0 g was dissolved in 400 mL of distilled water in a four-neck reactor, equipped with a mechanical stirrer, nitrogen gas channel, condenser and dropping funnel. They were at ambient temperature and stirred at 100 rpm for 30 minutes until slurry forming and ensure that oxygen gas, which would rapidly form radicals, clearly removed. The slurry was continuously heated to 60° C and kept constant for 30 minutes. Subsequently, 10.0 g of KPS as initiator (0.3 mol/100 g HEC) was added and stirred continuously for 10 minutes to exactly generate radicals onto HEC backbone. To prevent immediately undesired reaction, the temperature was decreased to 50° C then the solution of 120 g AM with MBA crosslinker (0.1 mmol/100 g HEC) in dropping funnel was further added, the temperature was raised to 70° C to initiate the actual reaction. This reaction temperature was constantly kept until the graft copolymerization reaction absolutely archived.

Purification of grafted copolymer

The crude product in gel form was cut into small pieces and subjected to Soxhlet extraction for 24 hrs using acetone, and using 40% ethanol/water as the solvents, to remove the homopolymer (PAM), and unreacted AM, respectively. The percentage of grafting efficiency (%GE) and percentage of add-on were calculated using equations (1) and (2) [15].

$$\text{Grafting efficiency}(\%) = \frac{M_2 - M_0}{M_1 - M_0} \times 100 \quad (1)$$

$$\text{Add - ons}(\%) = \frac{M_1 - M_0}{M_2} \times 100 \quad (2)$$

Where M_0 , M_1 and M_2 are the masses (in gram) of initial HEC backbone, HEC-g-PAM sample before extraction of homopolymer, and after extraction of homopolymer, respectively.

Alkaline treatment

Two types of alkaline base i.e., NaOH and KOH, were used to hydrolyze SAP. The resultant grafted copolymer with amide form had poor water swelling capacity of approximately up to 23 g/g. To improve the swelling capacity of the SAPs, approximately 50 g of grafted copolymer was transferred into round bottle reactor and treated separately with 1.0 L of 2 M NaOH solution and 1.0 L of 2 M KOH solution, stirred at 100 rpm, temperature at 70° C for 120 minutes. The final concentration of purified grafted copolymer in both type alkaline solution were calculated as percentage (w/w) of the total mass. The obtained SAPs were neutralized by washing three times with distilled water and 0.5 M HCl until the liquors pH was nearly 7. The treated SAPs were tested for water swelling capacity.

Measurements of swelling capacity and weight loss of SAP

For swelling capacity measurements, the dried powdery SAP of approximately 0.2 g in a tea bag was immersed in distilled water (pH=7), allowed to reach swelling equilibrium, the resultant SAPs that gave the highest water absorption was chosen for testing at various pH values ranging from 4 to 10 at room temperature and the final state was measured to determine the degree of water absorption (S_w) using equation (3). When measurement percentage of weight loss (% L_w), the swollen state SAP was dried to unchange and determine using equation (4) [9].

$$S_w = \frac{W_2 - W_1}{W_1} \quad (3)$$

$$L_w(\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (4)$$

Where W_1 and W_2 denote the weights of the sample before and after water absorption and W_3 are the dried weight of sample after first water absorption.

Measurements deswelling of SAP

For the deswelling measurements, the SAP equilibrium swollen in each various pH values of aqueous solution (ranging from 4-10) were transferred and placed on watch glass at ambient temperature (29° C) for 48 hrs. The weight change of SAPs was measured gravimetrically after time rested. The water retention was calculated in terms of the percentage of water retention (WR%) by using equation (5) [16].

$$WR(\%) = \frac{(W_t - W_d)}{(W_e - W_d)} \times 100 \quad (5)$$

Where W_d is the weight of the dry SAP, W_e and W_t denote the weights of the swollen SAP at equilibrium and deswollen SAP at time t, respectively.

RESULTS AND DISCUSSION

Infrared spectroscopy

FTIR analysis was utilized to confirm grafting copolymerize of PAM onto HEC backbone by comparison of all FTIR spectra. Figure 1 showed both the FTIR spectrum of HEC backbone and HEC-g-PAM, it was found that some important absorption peaks of HEC were changed after grafted copolymerization. The FTIR of HEC showed broad band absorption around 3560-3320 cm^{-1} was assigned to -OH stretching vibrations with hydrogen bonding and the

strongest absorption peak at 2879 cm^{-1} was ascribed to -O-H bending vibrations. The intense bands around 1020 cm^{-1} was ascribed to -C-OH stretching vibrations of HEC [17, 18]. After graft copolymerization, the broad band around $3560\text{-}3320\text{ cm}^{-1}$ had slightly exchanged due to N-H of amide stretching vibrations emerging as a shoulder band at 3195 cm^{-1} for the graft copolymer. In addition, for HEC-g-PAM the absorption peaks at 1020 cm^{-1} and 2879 cm^{-1} had disappeared and new absorption bands substituted at 1667 and 1120 cm^{-1} were assigned to -C=O stretching vibrations of amide functional group and asymmetric stretching vibrations of ether C-O-C in graft copolymer [19]. Besides of this, the broad band of HEC-g-PAM was emerged strongly at 1443 cm^{-1} due to combining PAM CH_2 bending vibrations.

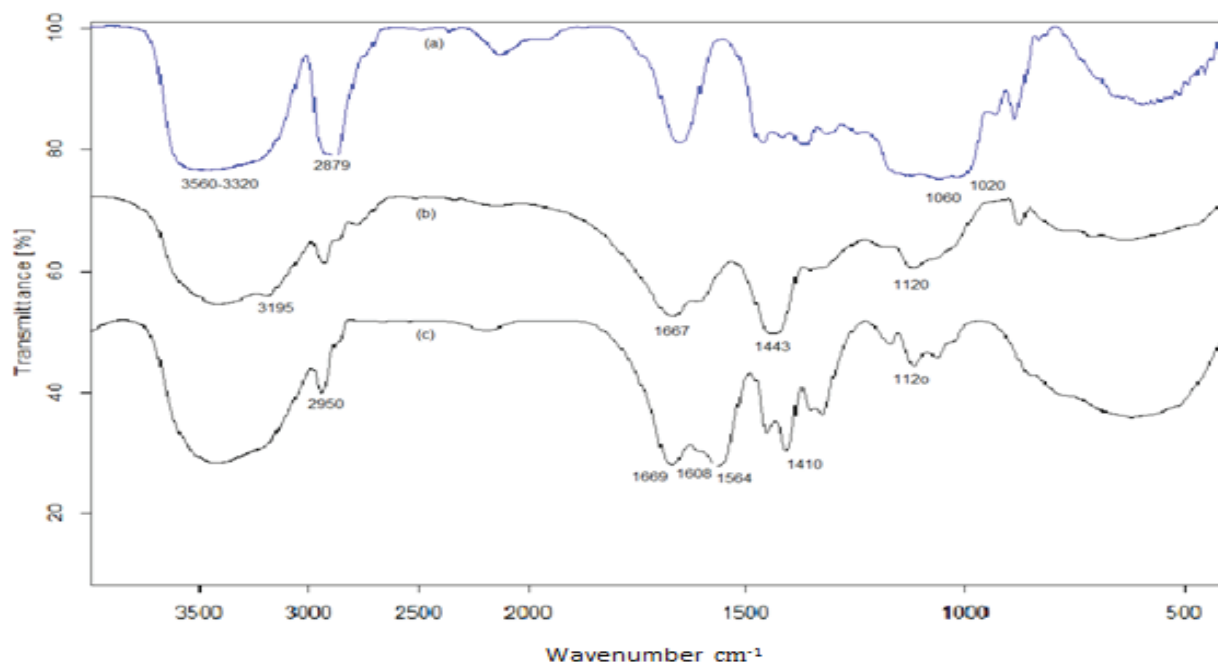


Figure 1. FTIR spectra of (a) HEC, (b) HEC-g-PAM and (c) HEC-g-PAM after hydrolysis alkaline treatment and washing with distilled water

After alkaline hydrolysis, and washing for three times with distilled water, new absorption peaks, especially the fingerprint region, were observed. From figure 2 it can be seen that dominant absorption peaks at 1410 cm^{-1} were assigned to -C-OH bending vibrations of carboxylic groups which was directly emerged interchangeable carboxylate group. The changes attributed to the stretching of C-O-H and the region assigned to stretching of C-O-C confirmed successful PAM moieties graft copolymerized onto HEC backbone.

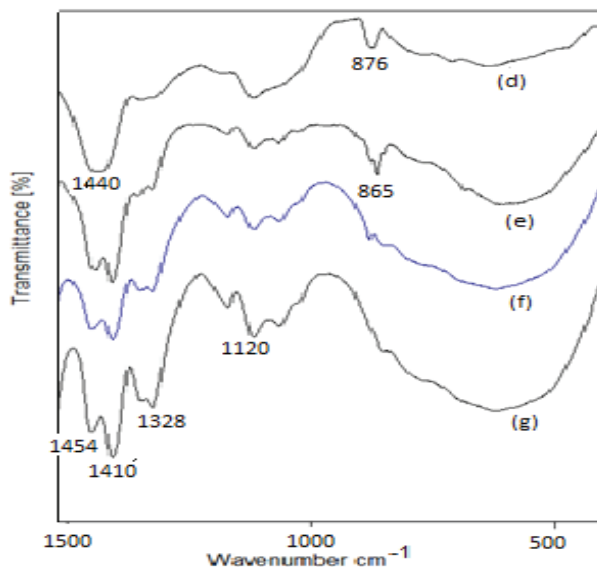


Figure 2. FTIR spectra of (d) HEC-g-PAM and HEC-g-PAM after alkaline treatment were affected by wash cycles with distilled water: (e) one washing, (f) two washings, or (g) three washings.

The effect of types of alkaline treatment and neutralization on swelling capacities of SAP

Studies have showed that the ultimate swelling capacity of SAPs increases dramatically after alkaline treatment [2]. The results showed that the highest swelling capacities of SAP were found after alkaline treatment with 0.5 M NaOH and washing 2 times with distilled water (figure 3). This is due to introduction of alkaline ion, sodium or potassium into the polymer network and subsequent development of negatively charged carboxyl groups. These groups set up an electrostatic repulsion between negative charges which tends to expand the polymer network. In fact the presence of alkaline cation, usually Na⁺ acts as an opposite factor for an exceedingly large electrostatic repulsion. The dissociated sodium carboxylate groups in polymer network increase osmotic pressure in polymer which was effectively increased swelling capacity of SAP.

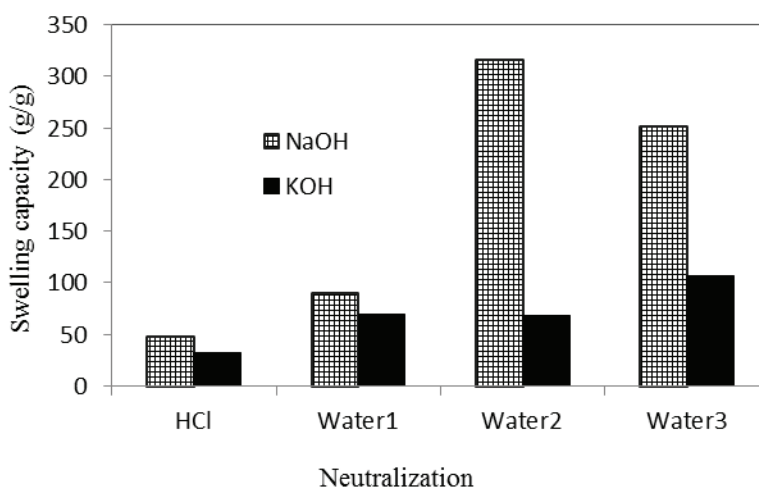


Figure 3. Swelling capacities of SAP after alkaline treatment with 0.5 M NaOH and 0.5 M KOH and neutralized with 0.5 M HCl and wash cycles with distilled water: 1 washing, 2 washings, or 3 washings.

The Effects of pH value on water swelling capacity

Research has indicated that water swelling capacity of SAPs was responsive to environmental pH [20]. So, the swelling behavior of the SAPs was investigated at various pH values ranging from 4 to 10 at ambient temperature. Figure 4. It can be clearly observed that pH value are influence swelling capacity of SAP, highest swelling capacity was found at pH solution 8 up to 382 g/g. This due to solutions containing a lot of ionic species (HCl and NaOH), as the swelling capacity of SAPs are decreased by ionic strength. At low pH, the swelling capacity decreases as its carboxylate group on the polymer network is protonated by HCl, leading the polymer becomes hydrophobic. At high pH, the swelling capacity also decreases by “charge screening effect” of excess Na^+ in the solution, which shields the carboxylate anions and prevents effective anion-anion repulsion. At pH=8, some of carboxylic acid groups are ionized and the electrostatic repulsion between COO^- groups causes an enhancement of the swelling capacity [21].

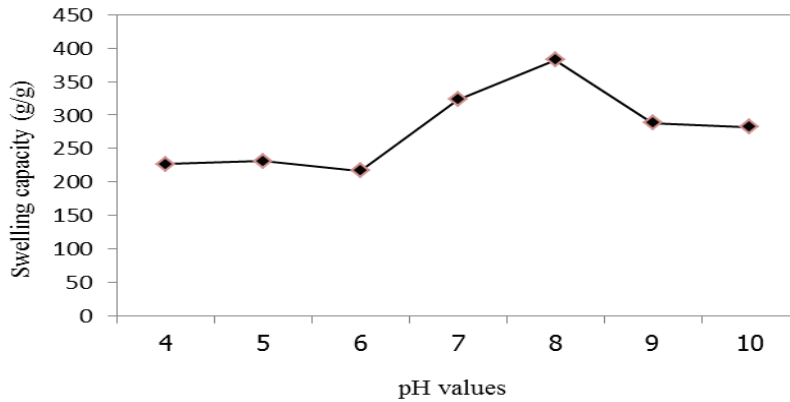


Figure 4. Swelling capacities of SAP measurement at different pH-values after alkaline treatment with 0.5 M NaOH and neutralized with distilled water.

The deswelling of SAP

The deswelling measurements of SAP was determined in terms of the percentage of water retention which of is amount of final water retaining in SAP, after equilibrium swollen in various pH solution and placed on watch glass at temperature of 29° C for 48 hrs. Studies have indicated that the deswelling response rate of the swollen SAP [22]. Figure 5 exhibited percentage of water retention, the result showed that pH value was not directly affected to deswelling of SAP. Some deviations observed can be ascribed to the fact that, as the gel swells it loses strength. As a result, the stresses imposed producing SAP fragmentation leading to erratic results.

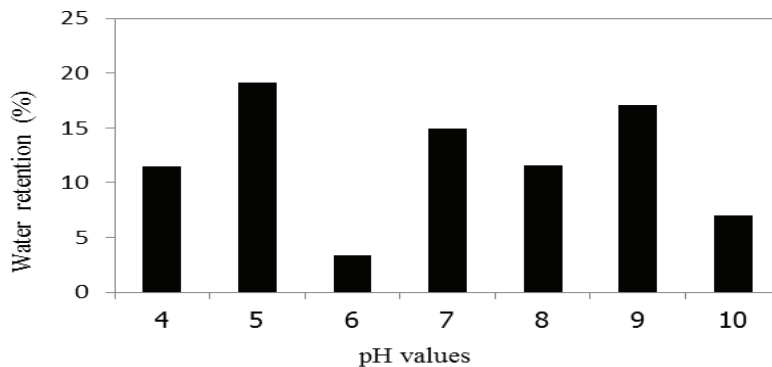


Figure 5. Water retention of SAP measurement after equilibrium swelling in each various pH values at room temperature and 48 hours

CONCLUSION

In summary, superabsorbent polymers were successfully copolymerized by graft copolymerization of polyacrylamide onto hydroxyethyl cellulose in the presence of crosslinker MBA using KPS as an initiator. The resulting SAPs produced at 1: 10 ratios of HEC : AM, was extensively characterized and determined for swelling behaviors including swelling capacity and water retention. The different types of alkaline treatment such as NaOH solution and KOH solution were investigated for swelling behaviors as important as neutralization system. It was found that the SAP with NaOH solution treatment and washing two times with distilled water exhibited highest water swelling capacity up to 317 g/g, while it was significantly increased water uptakes in solution of pH-8 up to 382 g/g. FT-IR determination was confirmed entirely grafted PAM onto HEC backbone. Furthermore FT-IR spectrum was proved that washing with distilled water can alter the chemical functional group of SAPs.

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