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ORIGINAL ARTICLE

Optimization of Effective Parameters onto Hydrolyzed Alginate-g-polyAN Hydrogel

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ABSTRACT
The following synthesis of superabsorbent hydrogel,H-Alg-poly(NaAA-co-AAm), by using ammonium persulfate (APS) as an initiator and sodium hydroxide (NaOH) as a crosslinking agent, we investigated the synthetic parameters affecting on swelling capacity of the hydrogel (i.e., the hydrolysis time and temperature, and concentration of NaOH) to achieve maximum swelling.

***Keywords**: Hydrogel, alginate, acrylonitrile, graft copolymerization, optimization.*

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INTRODUCTION

In recent years, increasing interest in natural-based superabsorbent hydrogel has developed mainly due to high hydrophobicity, biocompatibility, non-toxicity, and biodegradability of biopolymers. These materials are defined as crosslinked macromolecular networks that can absorb water or physical fluids up to many times of their own weight in a short time, but are not dissolved when brought into contact with water [1]. The absorbed fluids are hardly removable even under some pressure. Because of excellent characteristics, superabsorbent hydrogels are widely used in many fields, such as agricultural and horticultural, disposable diapers, feminine napkins, pharmaceuticals and medical applications [2-4]. This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996. Nowadays, the worldwide production of SAPs is more than one million tons in year. Hence, synthesis and investigation of specific and new superabsorbent hydrogels with high absorbency, mechanical strength and initial absorption rate, has been the goal of several research groups in the past decades [5-8]. In this work, effect of the parameters and the subsequent hydrolysis reaction variables on the swelling properties as well as temperature and hydrolysis time was investigated in detail.

MATERIALS AND METHODS

Materials

Sodium alginate (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). The monomer, acrylonitrile (AN, Merck), was used after vacuum distillation. Sodium hydroxide and ethanol as reagent grade were used without further purification. Ammonium persulfate (APS) was used without purification. All other chemicals were of analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Graft copolymerization

Graft copolymerization of acrylonitrile onto alginate was carried out with APS radical initiator under argon atmosphere [9, 11]. In a 100 mL flask, alginate (0.50 g) was dissolved in 50 mL of degassed distilled water. The flask was placed in a water bath with desired temperature (35-100 ^{o}C). A given amount of monomer, AN (1.62-4.05 g), was added to the flask and the mixture was stirred for 10 min. Then the initiator solution (7.0 mL) was added to the mixture and continuously stirred for 2 h. The product was then worked up with methanol (200 mL) and dried in oven at 50 °C for 5 h.

RESULTS AND DISCUSSION

Optimization of alkali concentration on swelling

The effect of the alkali concentration on swelling capacity is shown in Figure 1. Alkaline hydrolysis reaction was carried out at 75 ºC for 90 min. It was found that the mixture was discolored faster at higher NaOH concentration. In addition, lower absorbency was achieved when a further concentration of the base (higher than 10 wt %) was applied. This can be attributed to the formation of more crosslinks at higher OH^- concentration. It is known that a higher degree of crosslinking results in a rigid network that can not hold a large quantity of fluid [10, 11]. A similar observation has been reported by Castel et al. [19] in the case of the hydrolysis of starch-g-PAN. Additionally, alkaline degradation of the polysaccharide backbone can be another reason of the swelling decrease in highly concentrated alkaline hydrolytic media. Similar alkaline degradation behaviors were already reported in the case of other polysaccharides [13, 14].

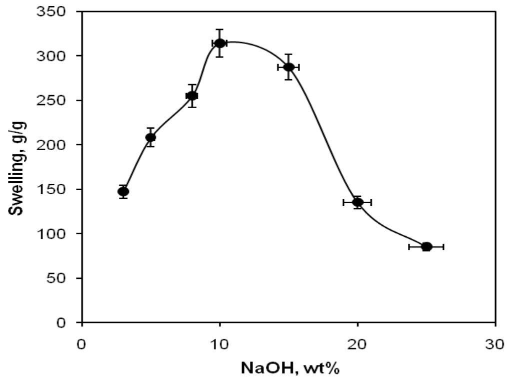

Figure 1. Effect of NaOH concentration on the swelling capacity of H-alginate-g-PAN superabsorbent hydrogel

Effect of bath temperature on swelling capacity

To study the influence of reaction temperature on water absorbency, the graft copolymerization of AN onto alginate was carried out at six temperatures ranging from 50 to 100 °C and the results are presented in Figure 2. Swelling capacity of the hydrogels is increased with increasing the temperature from 50 to 90 °C, and then decreased. At 90 °C, maximum swelling (423 g/g) was obtained.

Corresponding increase in water absorbency up to 90 °C could be attributed to the following factors: increased the number of free radicals formed on the alginate backbone, increased propagation of the graft copolymerization onto alginate, enhanced diffusion of monomer and initiator into and onto backbone structure, and increased in mobility of the monomers molecules and their higher collision probability with the backbone macroradicals [18]. However, swelling capacity decreased as the bath temperature was raised beyond 90°C. This can be accounted for in terms of chain radical termination at higher temperatures [12].

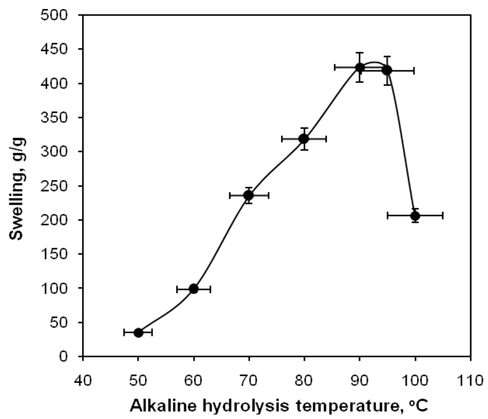

Figure 2. Effect of hydrolysis temperature on swelling capacity of H-alginate-g-PAN superabsorbent hydrogel.

Effect of alkaline hydrolysis time

Figure 3 presents the relationship between the reaction time and swelling capacity. It is obvious that the higher the reaction time leads to more carboxamide and carboxylate groups generated from alkaline hydrolysis. As shown in Figure 3, swelling capacity is decreased with further increase in hydrolysis time after 45 min. The lower absorbency at longer hydrolysis times can be explained by the formation of a higher crosslinked, rigid structure. In addition, degradation of the hydrogel, specially the polysaccharide part [15, 16], under relatively alkaline conditions at 90 °C may be other possible reason for the decreased swelling capacity versus higher reaction times.

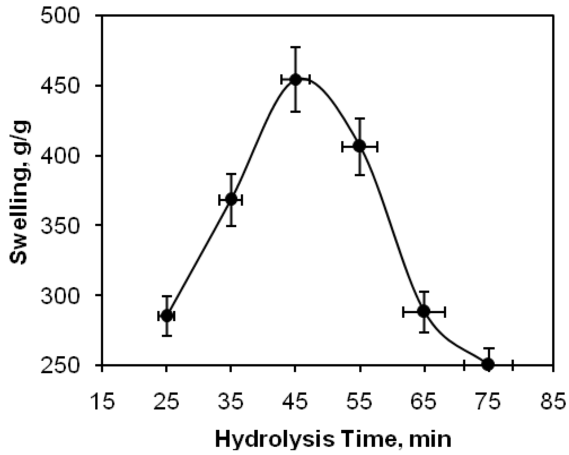

Figure 3. Effect of hydrolysis time on the swelling capacity of H-alginate-g-PAN superabsorbent hydrogel

CONCLUSION

A novel superabsorbent hydrogel, H-alginate-g-PAN, was prepared by graft copolymerization of AN onto alginate followed by alkaline hydrolysis of the graft copolymer. The swelling capacity of the synthesized hydrogel was affected by NaOH concentration, hydrolysis temperature, and hydrolysis time. Therefore, the maximum swelling capacity (423g/g) was achieved under the optimum alkaline hydrolysis conditions that found to be NaOH concentration (10 wt %), hydrolysis temperature 90 °C, and hydrolysis time 45 min.

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