



Partially Hydrolyzed Biocopolymer Based on Carboxymethylcellulose/Alginate-Graft-AAm and Effect of pH, Salinity onto Swelling Capacity

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In this paper, after synthesis a series of highly swelling hydrogels based on sodium carboxymethylcellulose (NaCMC)/sodium alginate (NaAlg) and polyacrylamide (PAAm) and then partially hydrolyzed by NaOH solution to yield hydrogel, H-CMC/Alg-g-PAAm, the effect of alkaline hydrolysis conditions (*i.e.*, NaOH concentration, hydrolysis time and temperature) were systematically optimized to achieve a hydrogel with swelling capacity as high as possible. Absorbency in various aqueous salt solutions also indicated that the swelling capacity decreased with an increase in the ionic strength of the swelling medium.

Key Words: Carboxymethylcellulose, Alginate, Acrylamide, Hydrogel, Swelling behaviour.

INTRODUCTION

Super absorbent polymers (SAPs) are defined as hydrophilic, three-dimensional networks with ability to absorb large values of water, saline solutions, or physiological fluids^{1,2}. They are widely used in various applications such as hygienic, foods, cosmetics and agriculture³⁻⁵. Thermo-sensitive hydrogels are known to exhibit phase separation properties in aqueous solution when the temperature is increased above a certain level. This phase separation temperature is referred to as the lower critical solution temperature (LCST)⁶. This kind of material could be highly useful in many fields. For example, as an on-off switch function by the change of temperature for the pulsatile controlled release of drugs⁷. In general, the properties of the swelling medium (*e.g.*, pH, temperature and ionic strength) affect the swelling characteristics. Super absorbent polymers responding to external stimuli such as heat, pH, electric field, chemical environments, *etc.*, are often referred to as "intelligent" or "smart" polymers.

Vinyl graft copolymerization onto polysaccharides and proteins is a well-known method for synthesis of natural-based super absorbent hydrogels⁸⁻¹⁰. The first industrial super absorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized by reported method¹¹.

The chosen polysaccharides for modification, *i.e.*, carboxymethylcellulose (CMC) and sodium alginate (NaAlg), are the most well-known and most important type of polysaccharides. These polysaccharides are widely used in various applications such as chelating and thickening agents, emulsifiers,

stabilizers, encapsulation, swelling and suspending agents, or used to form gels, films and membranes¹²⁻¹⁴. Most studies of alginate chemistry have focused on structural characterization such as conformation, ion selectivity or mechanical and rheological properties¹⁵, but among unique properties of alginates, gelation in the presence of multivalent metal cations is important. However, ionic-crosslinked alginate gels show low absorbencies due to high crosslink density. Therefore, "chemically" crosslinking of alginate salts would be better than "ionic" crosslinking, due to facile control of crosslinking degree and higher crosslink length. In this work, we attempted to optimization the reaction variables affecting the water absorbency of the hydrogel as well as the salt-, pH- and temperature sensitivity of the hydrogels.

EXPERIMENTAL

The polysaccharides, sodium alginate (NaAlg, chemical grade, m.w. 50000) and sodium carboxymethylcellulose (Brookfield viscosity 30.3 mPas in 1 % aqueous solution at 25 °C) were purchased from Fluka. N,N'-methylene bisacrylamide (MBA, from Fluka), ammonium persulfate (APS, from Fluka), acrylamide (AAm, from Merck), were of analytical grade and were used as received. Double distilled water was used for the hydrogel preparation and swelling measurements.

Alkaline hydrolysis: The graft copolymer (1.0 g) was saponified using 20.0 mL of NaOH (0.5-8.0 N) in a three-neck flask fitted with a mechanical stirrer and a reflux

condenser. The hydrolysis temperatures of 60-120 °C; and hydrolysis times of 15-360 min were studied. The mixture was allowed to cool to room temperature and neutralized to pH 7 by addition of 10 wt % aqueous acetic acid solution. Then the product was poured into ethanol (200 mL) to dewater for 10 h. The hardened particles were filtered off, dried in oven (50 °C, 5 h) and kept in a dry and cool place.

RESULTS AND DISCUSSION

Effect of NaOH concentration: In this series of experiments, swelling capacity of the final hydrogel, H-CMC/Alg-g-polyAAm, was studied as a function of NaOH concentration (Fig. 1). It is observed that the absorbency is increased substantially with increasing the NaOH concentration from 0.5-3.0 N and then it is decreased. Initial increase in swelling values is due to enhancement of the repulsive action of the increasing carboxylate anions. The swelling loss after the maximum can be attributed to residual alkaline, after completion of alkaline hydrolysis. The excess cations shield the carboxylate anions and prevent effective anion-anion repulsion (screening/shielding effect). Additionally, "alkaline degradation" of the polysaccharide backbone can be another reason of the swelling decrease in highly concentrated alkaline hydrolytic media. The proposed mechanism for this alkaline degradation is already reported¹⁶. Similar alkaline degradation behaviours were already reported in the case of other polysaccharides¹⁷.

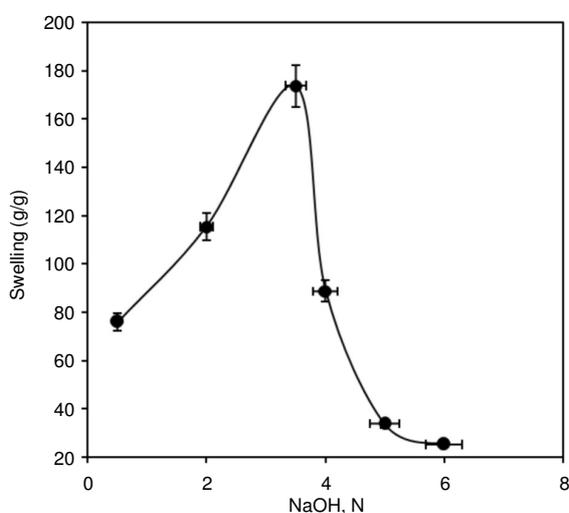


Fig. 1. Influence of NaOH concentration on swelling capacity of H-CMC/Alg-g-polyAAm super absorbent hydrogel

Effect of hydrolysis temperature: Fig. 2 demonstrates the effect of hydrolysis temperature on swelling capacity of H-CMC/Alg-g-polyAAm product. The absorbency is increased *versus* increasing the hydrolysis temperature from 60 to 90 °C and then, it is decreased with a further increase in hydrolysis temperature. By increasing the hydrolysis temperature up to 90 °C, the kinetics of alkaline hydrolysis increased which, in turn, results in carboxylate anions increment and consequently absorbency enhancement. Thereafter, decreasing the swelling capacity may be attributed to alkaline degradation of the CMC-Alg part of the hydrogel.

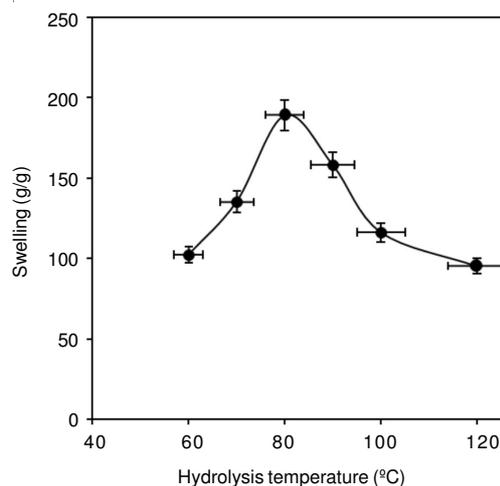


Fig. 2. Effect of hydrolysis temperature on swelling capacity of H-CMC/Alg-g-polyAAm super absorbent hydrogel

Effect of hydrolysis time: The effect of hydrolysis time on swelling capacity of crosslinked H-CMC/Alg-g-polyAAm was studied by varying the hydrolysis time from 15 to 360 min (Fig. 3). As shown in the figure, the absorbency is increased with increasing the hydrolysis time up to 60 min and then it is substantially decreased. The initial increasing in swelling value can be attributed to increase carboxylate-to-carboxamide ratio values. Intensive electrostatic repulsion of the anions leads to higher swelling of the hydrogel. The swelling-loss after the optimum time (1 h) may be attributed to degradation of the CMC-Alg part of the hydrogel under relatively alkaline conditions (3.0 N NaOH, 90 °C).

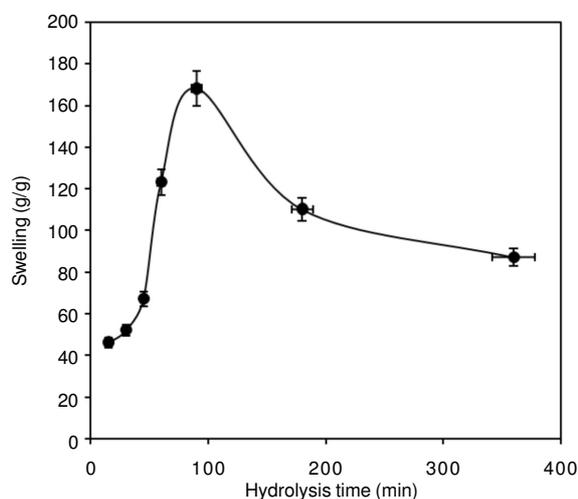


Fig. 3. Effect of hydrolysis time on swelling capacity of H-CMC/Alg-g-polyAAm super absorbent hydrogel

Effect of salinity on swelling capacity: The swelling ratio is mainly related to the characteristics of the external solution, *i.e.*, the charge number and ionic strength, as well as the nature of polymer, *i.e.*, the elasticity of the network, the presence of hydrophilic functional groups and the extent of crosslinking density. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing to the swelling values in distilled water. This well-known undesired swelling-loss is often attributed to a "charge

screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion¹⁸. Therefore, the osmotic pressure resulted from the mobile ion concentration difference between the gel and aqueous phases decreased and consequently the absorbency amounts decreased. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciably decrease in swelling capacity. It is obvious that swelling decrease is strongly depended on the "type" and "concentration" of salt added to the swelling medium. The effect of cation type (cations with different radius and charge) on swelling behaviour is shown in Fig. 4. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency for H-CMC/Alg-g-polyAAM hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations. The effect of cation radius on swelling, may also be observed from Fig. 4. The carboxylate anion interacts with small cations¹⁹, e.g., Li⁺, stronger than with large cations, e.g. Cs⁺. The stronger interactions of carboxylate-small cation have been observed using measurement of activating coefficients of various cations in several salt solutions. As a result, the water absorbency in monovalent and divalent cations salt solutions is in the order of CsCl > KCl > NaCl > LiCl and Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺, respectively.

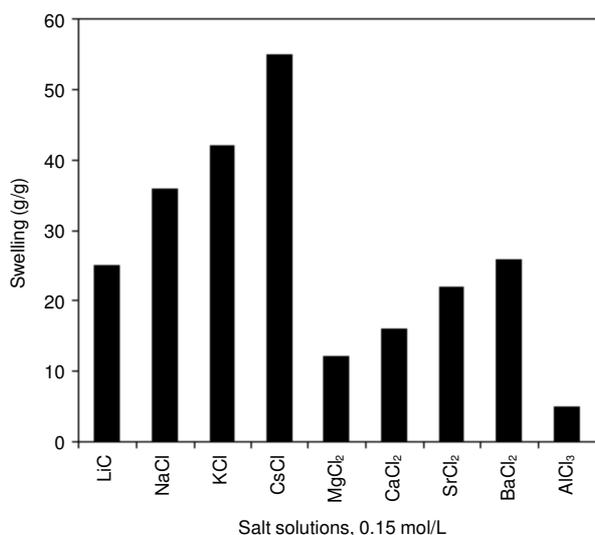


Fig. 4. Swelling capacity of the hydrogel, H-CMC/Alg-g-polyAAM, in different chloride salt solutions (0.15 M)

Fig. 4 illustrates a reverse and power law relationship between concentration of salt solutions (NaCl, CaCl₂ and AlCl₃) and swelling capacity of the hydrogel, H-Alg-g-MAM. Again, charge screening effect and ionic crosslinking are the main explanations for the intense loss of swelling. The known relationship between swelling and concentration of salt solution is stated as following equation²⁰:

$$\text{Swelling} = k [\text{salt}]^{-n} \quad (1)$$

where k and n are constant values for an individual super absorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity. The recorded data indicates that changing of the salt concentrations higher than

ca. 0.2 M has no appreciable influence on super absorbency of the super absorbent.

Equilibrium swelling at various pH solutions: Ionic super absorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, equilibrium swelling for H-CMC/Alg-g-polyAAM hydrogel was measured in different pH solutions ranged from 1.0-13.0 (Fig. 5). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 13.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (58 g/g) was obtained at pH 8. In acidic media, the most of carboxylate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio. At higher pHs (5-8), some of carboxylate groups are ionized and the electrostatic repulsion between COO⁻ groups causes an enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions is "charge screening effect" of excess Na⁺ in the swelling media which shield the carboxylate anions and prevent effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems²¹⁻²⁴.

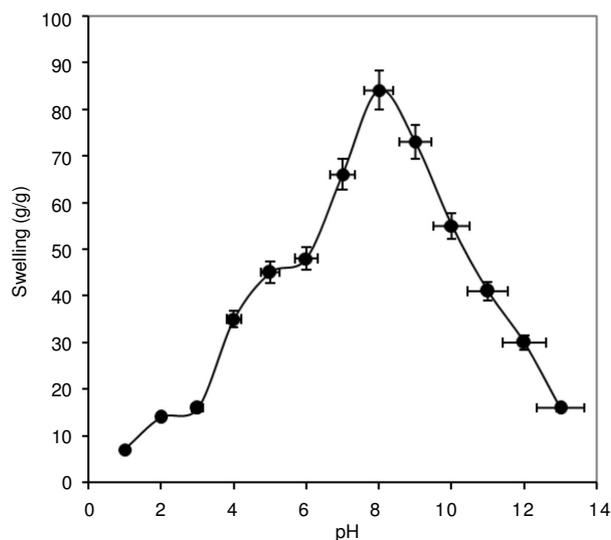


Fig. 5. Effect of pH of solutions on swelling capacity of H-CMC/Alg-g-polyAAM hydrogel

Conclusion

After synthesis of a novel super absorbent hydrogel, H-CMC/Alg-g-PolyAAM, alkaline hydrolysis of the graft copolymer was take placed. The synthesis of super absorbent hydrogel was optimized by varying the reaction parameters affecting the ultimate swelling capacity of the final product. The maximum water absorbency (197 g/g) was achieved under the optimum conditions that found to be: concentration of NaOH 3.0 N, hydrolysis time 60 min and hydrolysis temperature 90 °C. Swelling capacity of H-CMC/Alg-g-PolyAAM hydrogel in various salt solutions, especially in CsCl and KCl solutions is appreciable.

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