



Preparation and Swelling Behaviour of Carboxymethylcellulose-g-Poly(sodium acrylate)/Kaolin Super Absorbent Hydrogel Composites

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In this paper, a novel biopolymer-based superabsorbent hydrogel composite based on carboxymethylcellulose (CMC) has been prepared *via* graft copolymerization of acrylic acid in the presence of kaolin powder using methylenebisacrylamide as a crosslinking agent and ammonium persulfate as an initiator. The synthetic variables *i.e.* acrylic acid, methylenebisacrylamide and ammonium persulfate concentration, as well as the kaolin amount affecting on water absorbency of the resulted superabsorbent composite were studied. Evidence of grafting and kaolin interaction was obtained by comparison of FTIR spectra of initial substrates and superabsorbent composite. The effect of various salt media and solutions with different pHs on the swelling of the super absorbent was also studied.

Key Words: Carboxymethylcellulose, Kaolin, Poly(acrylic acid), Hydrogel, Composite.

INTRODUCTION

Super absorbent polymers (SAPs) are special soft and pliable polymeric materials that can absorb large quantities of water, saline or physiological solutions while the absorbed solutions are not removable even under pressure^{1,2}. Because of their superior properties, they have found extensive applications such as disposable diapers, feminine napkins, drug delivery systems and soil for agriculture and horticulture³⁻⁵.

Because of their exceptional properties, *i.e.* biocompatibility, biodegradability, renewability and non-toxicity, polysaccharides are the main part of the natural-based super absorbent hydrogels⁶⁻⁹. The higher production cost and low gel strength of these super absorbents, however, restrict their application widely. To improve these limitations, inorganic compounds with low cost can be used. The introduction of inorganic fillers to a polymer matrix increases its strength and stiffness properties. Among inorganic compounds, special attention has been paid to clay minerals in the field of nanocomposites because of their small particle size and intercalation properties. Mineral powders are hydrated layered aluminosilicate with reactive -OH groups on the surface. The interaction of mineral powders, reactive site of natural polymers and monomers result in a super absorbent composite. Super absorbent composites based on synthetic polymers^{10,11} or natural polymers^{12,13} have been reported.

In this work, we attempt to synthesize and characterize new super absorbent composites based on carboxymethylcellulose (CMC) in the presence of kaolin particles. The preparation of the biopolymer-based super absorbent composites can also improve the mechanical properties of materials and can lower the cost of the finished product compared with the synthetic counterparts as well as providing biodegradable characteristics. The reaction variables affecting the water absorbency of the CMC-g-poly(acrylic acid)/kaolin as well as the salt- and pH-sensitivity of the hydrogels were investigated.

EXPERIMENTAL

The polysaccharide, carboxymethylcellulose (CMC) (chemical grade, m.w. 50,000, DS 5 0.50), was purchased from Merck Chemical (Germany) and used without further purification. Acrylic acid (from Merck) was used after vacuum distillation. Methylenebisacrylamide (MBA) (from Fluka), ammonium persulfate (APS) (from Merck) and kaolin (from Khorassan Co., Iran, KPS grade, particle size < 5 μm) were used as received. All other chemicals were of analytical grade.

Super absorbent composite synthesis: In a 1 L reactor equipped with mechanical stirrer (Heidolph RZR 2021, three blade propeller type), variable amounts of CMC (0.20-0.80 g) were added to 40 mL degassed distilled water. After complete dissolution of CMC, various amounts of kaolin powder (0.80-0.20 g) were added to the CMC solution and allowed to stir

for 10 min. Then, APS initiator (0.05-0.40 g, dissolved in 5 mL water) was added to the reaction mixture and the mixture was stirred for 10 min. Methylenebisacrylamide (0.05-0.25 g, dissolved in 5 mL water) and acrylic acid (1.0-5.0 g, completely neutralized with NaOH) were poured into the reactor. All of the reactions were carried out at 80 °C under an argon gas atmosphere. At the end of the propagation reaction, the gelly product was poured in ethanol (300 mL) and allowed to dewater for 24 h. Then, the product was filtered and washed with 100 mL ethanol. The filtered product was dried in an oven at 50 °C for 10 h. After grinding, the powdered super absorbent composite was stored away from moisture, heat and light.

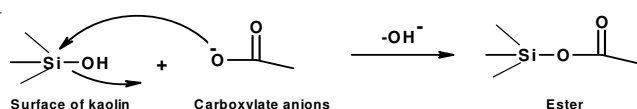
Swelling measurements: An accurately weighed sample (0.2 ± 0.001 g) of the powdered super absorbent with average particle sizes between 40-60 mesh (250-350 μm) was immersed in distilled water (200 mL) and allowed to soak for 3 h at room temperature. The equilibrium swelling (ES) capacity was measured twice at room temperature according to a conventional tea bag (*i.e.* a 100 mesh nylon screen) method and using the following formula:

$$\text{ES(g/g)} = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}} \quad (1)$$

RESULTS AND DISCUSSION

Synthesis and characterization: The super absorbent composite was prepared by graft copolymerization of acrylic acid onto CMC in the presence of a crosslinking agent and powdery kaolin. Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate anion-radicals that abstract hydrogen from -OH groups of CMC backbones. So, this persulfate-saccharide redox system results in active centers capable to radically initiate polymerization of acrylic acid led to a graft copolymer. Since a cross-linking agent, *e.g.* MBA, is presented in the system, the copolymer comprises a crosslinked structure.

For identification of the product, FTIR spectroscopy was used. Fig. 1a. represents the spectrum of the physical mixture of CMC and kaolin. In the layer silicate structure of kaolin, the hydroxyl groups show absorption bands at 3675-3628 cm^{-1} . The broad band at 3400-3200 cm^{-1} is due to stretching of -OH groups of the polysaccharide. In the spectrum of the composite (Fig. 1b.), two new absorption peaks at 1579 and 1722 cm^{-1} are appeared. The characteristic band at 1572 cm^{-1} is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another peak at 1410 cm^{-1} , which is related to the symmetric stretching mode of the carboxylate groups. The absorption band at 1722 cm^{-1} can be corresponding to the ester groups that can be formed during the graft polymerization reaction. The carboxylate groups of the grafted poly(acrylic acid) can be react with the -OH groups on the kaolin surface results in the ester formation. The reaction can be shown as follows:



Effect of methylenebisacrylamide concentration on swelling: Crosslinks is necessary to form a super absorbent in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. The effect of methylenebisacrylamide (MBA) concentration on the water absorbency of the composite was studied by varying the concentration of MBA from 0.005 to 0.035 mol/L (Fig. 2). As the concentration of MBA was increased, the water absorbency of the super absorbent composite was decreased. This is due to a decrease in the space between the copolymer chains as the crosslinker concentration is increased.

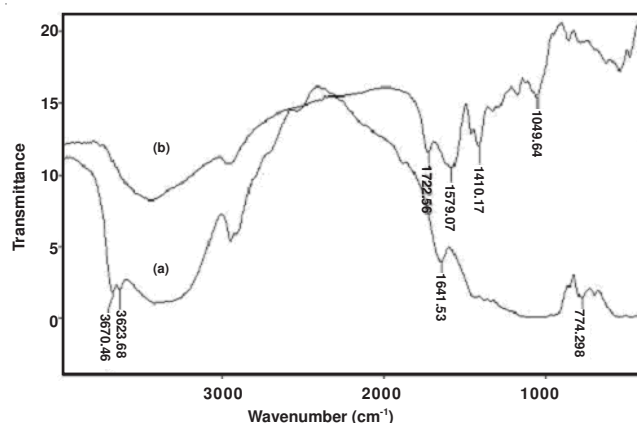


Fig. 1. FTIR spectra of the physical mixture of CMC and kaolin (a) and CMC-g-poly(sodium acrylate)/kaolin composite

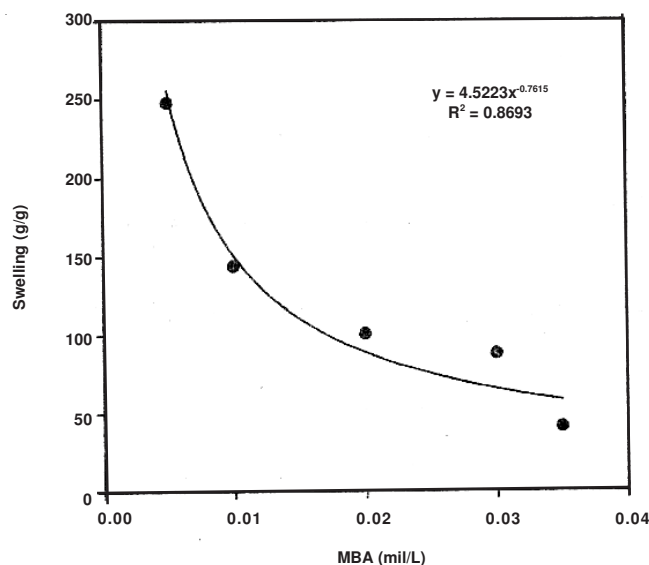


Fig. 2. Effect of the crosslinker concentration on water absorbency of the composite

Effect of the monomer concentration on swelling: Fig. 3 demonstrates the effect of the monomer concentration on swelling capacity of CMC-g-PAA composite. The absorbency is increased *versus* increasing the acrylic acid concentration from 0.50 to 1.00 mol/L and then, it is decreased with a further increase for acrylic acid. The initial increase in swelling values can be attributed to the higher the hydrophilicity of the hydrogel and the greater availability of acrylic acid molecules near the CMC macroradicals. The swelling-loss after the maximum may be attributed to (a) preferential homopolymerization over

graft copolymerization, (b) increase in viscosity of the medium, which restricts the movement of free radicals and monomer molecules and (c) the enhanced chance of chain transfer to monomer molecules.

Effect of ammonium persulfate concentration on swelling: The effect of the initiator ammonium persulfate (APS) concentration on the water absorbency of the super absorbent composite was also studied (Fig. 4). The increase of water absorbency with increasing initiator concentration up to 0.019 mol/L may be ascribed to the increase of the active sites on the backbone of the CMC arising from the attack of sulfate anion-radical. An additional reason, according to Flory¹⁴, is imperfection of the polymer networks obtained from high-initiator polymerization systems.

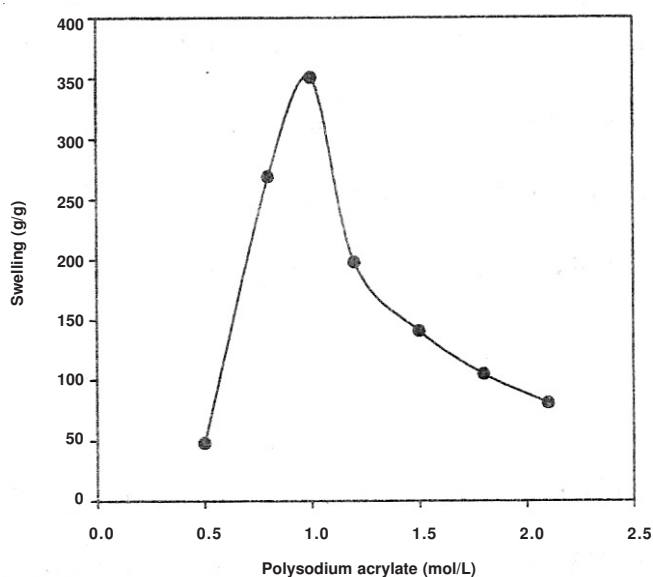


Fig. 3. Swelling dependency of the composite on the monomer concentration

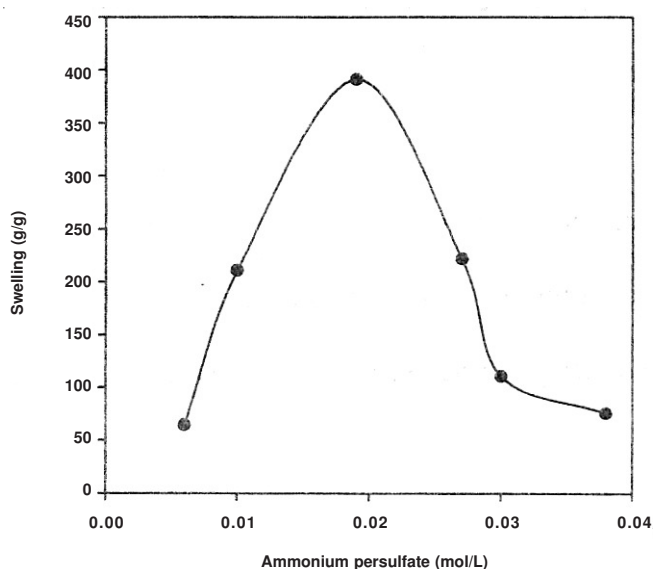


Fig. 4. Effect of initiator concentration on water absorbency of the composite

The decrease of water absorbency with initiator concentration beyond 0.019 mol/L may be due to (a) increased

number of produced radicals led to terminating step *via* bimolecular collision, (b) predominance of homopolymerization over grafting, (c) molecular weight loss of the synthetic part of the polymer network¹⁴ and (d) free radical degradation of CMC substrate.

Effect of kaolin amount on swelling: The effect of kaolin content on the water absorbency of the composite was also studied (Fig. 5). The kaolin/CMC weight ratio was varied from 0.3 to 2.5, while other reaction variables were constant. The effect of kaolin amount on water absorbency is similar to MBA influence on absorbency. The clay in the polymerization reaction may acts *via* two ways: (a) kaolin particles acts as a crosslinking agent (it means that carboxylate groups of sodium poly(acrylate) chains react with kaolin and (b) kaolin particles prevent the growing polymer chains through a chain transfer mechanism⁶.

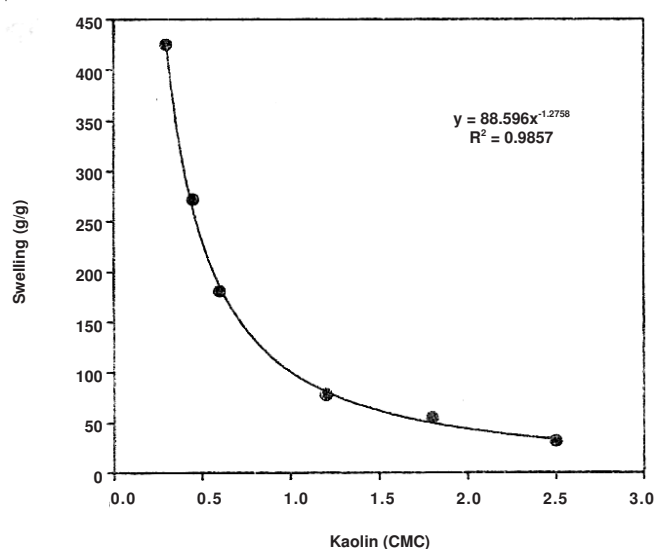


Fig. 5. Effect of kaolin/CMC weight ratio on swelling of the hydrogel composite

Effect of pH on swelling: A pH-dependent swelling behaviour was observed at 25 °C with changes in pH, as shown in Fig. 6. The swelling of the hydrogel composite is increased with increasing of the pH values from 1 to 8, while it is decreased at pHs ranged of 8-12. The pK_a of the poly(acrylic acid) is around 4.5. When pH is less than pK_a, the H⁺ ion strength will be high, which will effectively suppress the ionization of carboxylic acid groups. So, at acidic pHs, the gel is neutral and flexibility of the polymeric chain is rather low. Carboxylic acid groups within the polymeric network is ionized to the COO⁻ form and attract cations into the gel region to replace H⁺ ions, since the pH of the environmental solution rises above its pK_a value. This effectively increases the concentration of the free ions inside the composite. Therefore, because of the ionic swelling pressure increase, the composite tends to expand and thereby maximizes the repulsion between the ionized polycarboxylate groups.

Swelling behaviour in salt solutions: Changing of environmental ionic strength affects significantly the swelling capacity of super absorbents. Table-1 shows the effect of the various

salt solutions on the water absorbency of CMC-g-poly(sodium acrylate)/kaolin composite and a non-composite crosslinked CMC-g-poly(sodium acrylate) hydrogel. The decrease of the swelling capacity of the both hydrogels is due to the screening effect and a loss of the osmotic pressure difference between the hydrogels and the fluids. The super absorbents comprise carboxylate groups in their structures. In salt solutions, the perfect anion-anion repulsion of the carboxylate groups is prevented by the M^{n+} cations that shield the carboxylate groups, so the swelling capacity is decreased. In addition, the swelling of the super absorbents depends on the valency of the cations. Multivalent cations decrease drastically the swelling capacity. The decrease is attributed to the complexing ability of carboxylate groups inducing interchain complexes formation and consequent enhancing of the network crosslink density. The composite comprises carboxylate anions ($-COO^-$). The water absorbency of the composite in the presence of the Ca^{2+} and Al^{3+} cations is lower than that of NaCl solution. This phenomenon is arisen from ionic crosslinking of these cations with carboxylate anions that causes low water absorbency.

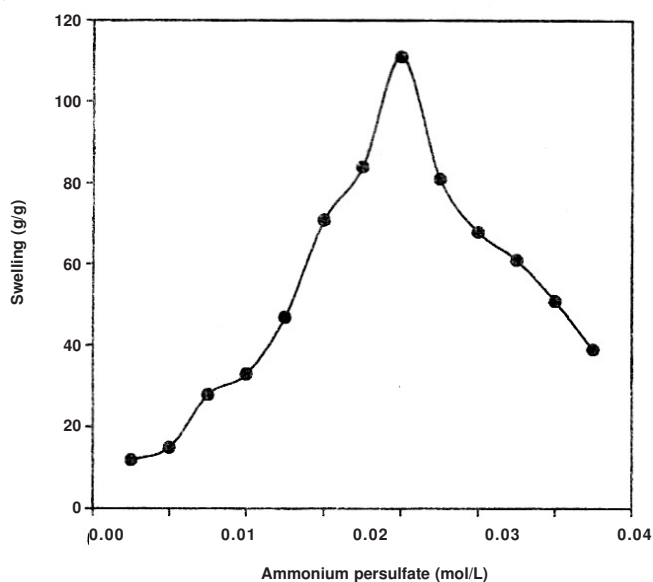


Fig. 6. pH-dependent swelling of the super absorbent composite

TABLE-1
A COMPARISON BETWEEN THE EQUILIBRIUM SWELLING CAPACITY OF THE CMC-g-PAANa/KAOLIN SUPER ABSORBENT COMPOSITE AND ITS COUNTERPART IN DISTILLED WATER AND VARIOUS SALT SOLUTIONS (0.15 M)

Swelling medium	Crosslinked CMC-g-PAA	Composite
	ES (g/g)	ES (g/g)
H ₂ O	322	392
NaCl	41	61
CaCl ₂	15	24
AlCl ₃	5	12

As arises from the results, the swelling of the composite, especially in salt solutions, is higher than that of its non-composite counterpart. The swelling improvement may be

attributed to attraction of the salt cations on the surface of kaolin in the composite hydrogel that results in lower screening effect in the composite comparing with the similar kaolin-free sample.

Conclusion

A novel super absorbent composite based on carboxymethylcellulose was prepared by graft copolymerization of sodium acrylate in presence of a crosslinking agent. The resultant super absorbent composite had a large degree of water absorbency. The study of FTIR spectra shows that in the composite spectrum a new absorption band at 1722 cm^{-1} was appeared that attributed to the ester formation from replacement of hydroxyl groups of kaolin with grafted carboxylate anions onto polysaccharide backbones. The optimum reaction conditions was achieved at methylenebisacrylamide 0.005 mol/L , initial acrylic acid 1.0 mol/L , ammonium persulfate 0.019 mol/L and kaolin/carboxymethylcellulose weight ratio 0.03 . The effect of the kaolin amount and methylenebisacrylamide concentration showed that with increasing of these parameters, the water absorbency of the super absorbent composite are decreased. The swelling of hydrogels in solutions with various pHs exhibited a high sensitivity to pH. Also swelling measurement of the synthesized composites in different salt solutions showed appreciable swelling capacity, especially in NaCl solution.

Overall, we reported a crosslinking polymerization to achieve super absorbing composite materials with lower cost and lower salt-sensitivity. The hydrogel composites will most probably possess higher biodegradability (due to the carboxymethylcellulose part) and higher swollen gel strength (due to the inorganic parts). The latter properties are of the subjects under consideration in our laboratory.

REFERENCES

1. F.L. Buchholz and A.T. Graham, *Modern Super absorbent Polymer Technology*, Wiley, New York (1997).
2. L.B. Peppas and R.S. Harland, *Absorbent Polymer Technology*; Elsevier, Amsterdam (1990).
3. R. Po and J. Macromol, *Sci.-Rev. Macromol. Chem. Phys.*, **34**, 607 (1994).
4. N.A. Peppas and A.G. Mikes, *Hydrogels in Medicine and Pharmacy*; CRC Press, Boca Raton, Florida, Vol. 1 (1986).
5. J. Kosti, in ed.: E. Mathiowitz, *Encyclopedia of Controlled Drug Delivery*, Wiley, New York, p. 445 (1999).
6. M. Sadeghi and H. Hosseinzadeh, *Asian J. Chem.*, **22**, 6734 (2010).
7. D.W. Lim, H.S. Whang and K.J. Yoon, *J. Appl. Polym. Sci.*, **79**, 1423 (2001).
8. H. Hosseinzadeh, A. Pourjavadi, M.J. Zohouriaan-Mehr and G.R. Mahdavinia, *J. Bioact. Compat. Polym.*, **20**, 475 (2005).
9. H.K. Stulzer, L. Lacerda, M.P. Tagliari, M.A.S. Silva, V.T. Favere and M.C.M. Laranjeira, *Carbohydr. Polym.*, **73**, 490 (2008).
10. J. Lin, J. Wu, Z. Yang and M. Pu, *Macromol. Rapid Commun.*, **22**, 422 (2001).
11. J. Lin, J. Wu, Z. Yang and M. Pu, *Polym. Polym. Composit.*, **9**, 469 (2001).
12. J. Wu, J. Lin, M. Zhou and C. Wei, *Macromol. Rapid Commun.*, **21**, 1032 (2000).
13. J. Wu, Y. Wei, J. Lin and S. Lin, *Polymer*, **44**, 6513 (2003).
14. P.J. Flory, *Principles of Polymer Chemistry*; Ithaca, Cornell University Press, New York (1953).