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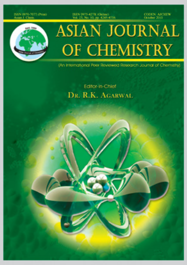

Synthesis of a Novel Hydrogel composite Based on CMC-*g*-poly(AA-*co*-IA)/Montmorrolonite

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In this work, A novel superabsorbent hydrogel composite based on carboxymethylcelloluse have been prepared *via* graft copolymerization of acrylamide and itaconic acid monomers in the presence of montmorolonite powder as a clay and methylenebisacrylamide as a crosslinking agent and ceric ammonium nitrate as an initiator. A mechanism for the superabsorbent hydrogel formation was also suggested. Hydrogel formation was confirmed by FTIR spectroscopy. Results from scanning electron microscopy observation also showed a porous structure with smooth surface morphology of the hydrogel. Furthermore, the water absorbency of hydrogels composite was measured in solutions with pH ranged 1 to 13.

Key Words: Carboxymethylcelloluse, Hydrogel, pH-Responsive, Composite.

INTRODUCTION

Highly swelling polymers, *i.e.* superabsorbent hydrogels, are hydrophilic, three dimensional networks that can absorb water in the amount from 10 % up to thousands of times their dry weight. They are widely used in various applications such as hygienic, foods, cosmetics and agriculture[1]. This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996[2-4]. Nowadays, the worldwide production of super absorbent polymers is more than one million tons in year. Hence, synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world[3-6].

The properties of the swelling medium (*e.g.* pH, ionic strength and the counter ion and its valency) affect the swelling characteristics[2,7]. The hydrogels sharply and reproducibly responding to the medium conditions are referred as to responsive, smart or intelligent. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs[8,9].

Although hydrogels made from synthetic polymers, such as polyacrylate, posses excellent water-absorbing properties, their toxicity and non-biodegradability might pose long-time environmental problems and limit their use in drug delivery systems and consumer products. Natural-based superabsorbent polymers polymers have attracted much attention in medical and pharmaceutical interests because of their non-toxicity, biocompatibility and biodegradability. The higher production cost and low gel strength of these superabsorbents, 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[10]. The interaction of mineral powders, reactive site of natural polymers and monomers result in a superabsorbent composite. Superabsorbent composites based on synthetic polymers[11,12] or natural polymers[7,8] have been reported.

In this work, we attempt to synthesize a new hydrogel composites based on carboxymethylcelloluse in the presence of montmorrolonite particles. The preparation of the biopolymer-based superabsorbent 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.

EXPERIMENTAL

The polysaccharide, carboxymethylcellulose (CMC, degree of substitution 0.52, from Condinson Co., Denmark) was of analytical grade and was used as received. Itaconic acid (IA, Merck), acrylic acid (from Merck) were used after vacuum distillation. Ceric ammonium nitrate (CAN, Merck), methylenebisacrylamide (from Fluka) and montmorolonite from Fluka, particle size < 5 μm) were used as received. All other chemicals were of analytical grade.

Synthesis of superabsorbent hydrogel composite: A weighed amount of carboxymethylcellulose (1.0 g) was dissolved in 50 mL of distilled water in a 100 mL two-necked flask equipped with magnetic stirrer, immersed into a thermostated water bath, preset at 65 ºC. An inert gas (argon) was gently bubbled into the reactor to remove the oxygen during the graft copolymerization reaction. After complete dissolution of carboxymethylcellulose, various amounts of montmorolonite powder (0.25-0.55 g) were added to the carboxymethylcellulose solution and allowed to stir (300 rpm) for 15 min. After complete dissolution of the polysaccharide to form a homogeneous solution, a definite amount of ceric ammonium nitrate solution (0.10-0.3 g in 5 mL H_2O-HNO_3) was added into the mixture and was allowed to stir for 15 min. Then certain amounts of acrylamide (0.40-3.50 g in 5 mL H_2O) and itaconic acid (0.40-3.50 g in 5 mL H_2O) and methylenebisacrylamide (0.04-0.15 g in 5 mL H_2O) were simultaneously added to the reaction mixture. All of the reactions were carried out at 65 ºC under an argon gas atmosphere and the reaction mixture was continuously stirred (300 rpm) for 1 h. 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 ºC for 10 h. After grinding, the powdered superabsorbent composite was stored away from moisture, heat and light[13].

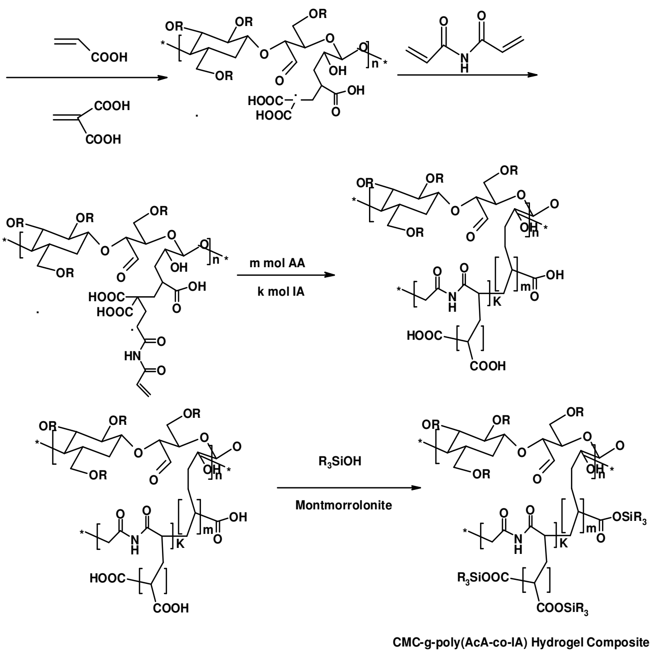
Swelling measurements: Hydrogel (0.2 g) were immersed in 250 mL solution with various pH values (pH 1-13) at 37 ºC to reach swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering through a 100-mesh screen under gravity for 0.5 h without blotting the samples. The equilibrium swelling (ES) capacity in buffer solution was calculated according to the following equation:

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

Fourier transform infrared (FTIR) spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature. The surface morphology of the gel was examined using scanning electron microscopy (SEM). After Soxhlet extraction with methanol for 24 h and drying in an oven, hydrogel composite powder was coated with a thin layer of gold and imaged in a SEM instrument (Leo, 1455 VP).

RESULTS AND DISCUSSION

Synthesis of hydrogels composite: The mixture of monomers, acrylic acid and itaconic acid, was simultaneously grafted onto carboxymethylcellulose backbones in a homogeneous medium using ceric ammonium nitrate as a radical initiator and methylenebisacrylamide as a crosslinking agent. The mechanism of co polymerization of acrylic acid and itaconic acid onto carboxymethylcellulose in the presence of methylenebisacryl-amide and powder montmorrolonite is shown in **Scheme-I**. In the first step, the thermally dissociating initiator, *i.e.* ceric ammonium nitrate, is decomposed under heating (65 ºC) and then pair redox ce^{3+}-ce^{4+} disconnect C-C bond from the carboxymethylcellulose backbones to form corresponding macroinitiators. These macroradicals initiate grafting of acrylic acid and itaconic acid onto carboxymethylcellulose backbones leading to a graft copolymer. Since a crosslinking agent, *e.g.* methylenebisacrylamide and powder montmorolonite are presented in the system, the copolymer comprises a crosslinked structure, so that a three dimensional network was obtained.



Scheme-I: General reaction mechanism for graft copolymerization of acrylic acid, itaconic acid onto CMC backbone in the presence of ceric (IV) ion and montmorrolonite

FTIR spectroscopy: Fig. 1 shows the IR spectroscopy of carboxymethylcellulose and carboxymethylcellulose-*g*-Poly(AcA-*co*-IA) hydrogel composite. The broad band at 3600-3100 cm^{-1} is due to stretching of -OH groups of carboxymethylcellulose. The IR spectrum of the hydrogel composite, carboxymethylcellulose-*g*-Poly(AcA-*co*-IA) (Fig. 1b) shows three new characteristic absorption bands at 1707, 1542 and 1402 cm^{-1} verifying the formation of graft copolymer product. These peaks attributed to carbonyl stretching of the carboxylic acid groups and symmetric and asymmetric stretching modes of carboxylate anions, respectively[14,15]. Combination of absorption of the carboxylate and alcoholic O-H stretching bands is appeared in the wide range of 3600-2550 cm^{-1}.

The absorption band at 1707, 411 and 548 cm^{-1} can be corresponding to stretching and bending of the ester groups that can be formed during the graft polymerization reaction. The carboxylate groups of the grafted poly(acrylic acid and itaconic acid) can be react with the -OH groups on the montmorrolonite surface. The replacement of -OH groups in the surface of montmorrolonite by carboxylate anions results in the ester formation.

Morphology of hydrogels composite: The morphology of the crosslinked hydrogel composite was observed by scanning electron microscope. Although the water inside the hydrogel was sublimed to make cavities, the structure of the composite was preserved. The SEM image is shown in Fig. 2. The structure of the hydrogel is very porous and it could help to form a high-water-content hydrogel, as is generally shown in other hydrogels[16].

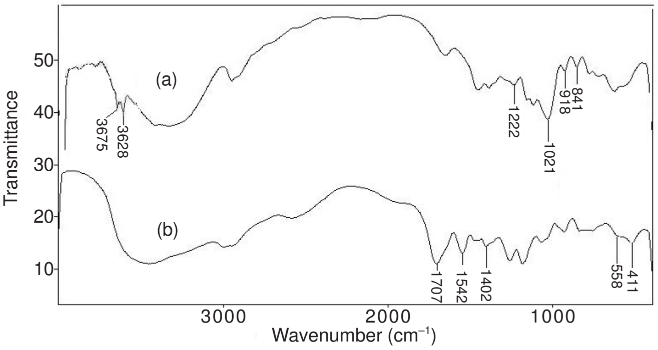


Fig. 1. FTIR spectra of (a) pure CMC and (b) CMC-*g*-poly(AA-*co*-IA)/ montmorrolonite hydrogel composite

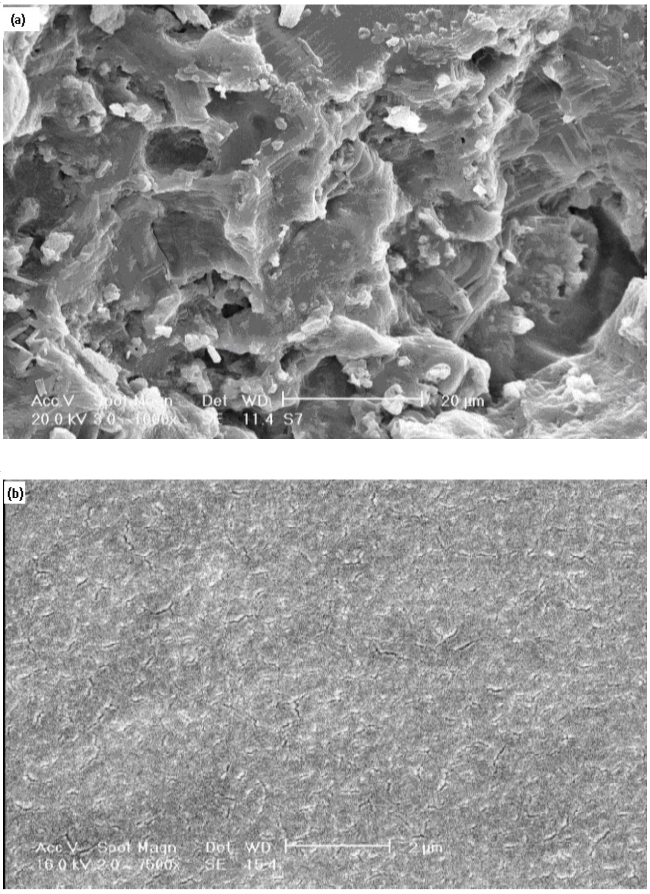


Fig. 2. SEM photograph of the pure CMC (a) and CMC-*g*-poly(AA-*co*-IA)/montmorrolonite hydrogel composite

Effect of pH on equilibrium swelling: Fig. 3 represents pH dependence of the equilibrium swelling for H-CMC-*g*-Poly(AcA-*co*-NaAI) hydrogel composites at ambient temperature (37 ºC). The equilibrium swelling (ultimate absorbency) of the hydrogels were studied at various pHs ranged from 1 to 13. No additional ions (through buffer solution) were added to medium for setting pH because absorbency of a superabsorbent is strongly affected by ionic strength. In addition, it has been reported that the swelling properties of polybasic gels are influenced by buffer composition (composition and pKa). Therefore, stock NaOH (pH 13) and HCl (pH 1) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

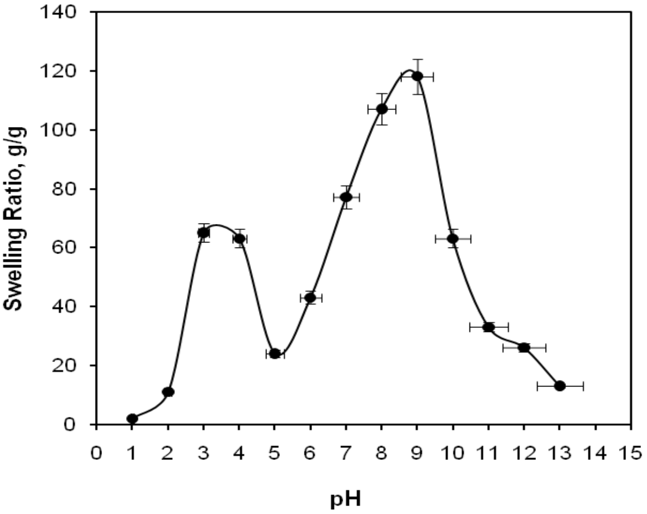


Fig. 3. pH-Dependent swelling of the superabsorbent composite (containing 10 wt % CMC and 4 wt % montmorrolonite)

The effective pKa for carboxylic acid groups is *ca.* 4.6. In Fig. 3, the dependence of the equilibrium swelling of the H-CMC-*g*-Poly(AcA-*co*-NaAI) hydrogel composite is characterized by a curve with two maximum at pHs 3 and 9. The remarkable swelling changes are due to the presence of different interacting species depending on pH of the swelling medium. The structure of carboxymethylcellulose and Poly(AcA-*co*-NaAI) are ionizable. So, maximum swelling (118 g/g) was obtained at pH 9. Because, 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 (5-9), 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[15].

Conclusion

The superabsorbent hydrogel composite, CMC-*g*-poly(AA-*co*-IA)/montmorrolonite, was synthesized by graft copolymerization of acrylic acid and itaconic acid onto carboxymethylcellulose, in a homogeneous medium and in the presence of montmorolonite powder as a clay and methylenebisacrylamide (MBA) as a crosslinking agent. The swelling of the hydrogels exhibited a high sensitivity to pH in 3 and 9. The maximum water absorbency in solution with pH = 9 (118 g/g) was achieved. The study of FTIR spectra also 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 montmorolonite with grafted carboxylate anions onto polysaccharide backbones. This hydrogel composite network intelligently responding to pH may be considered as an excellent candidate to design novel drug delivery systems.

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