Intelligent superabsorbent polymer composites based on chitosan-graft-polyacrylamide and carboxymethylcellulose

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Abstract ——A series of intelligent superabsorbent polymers composites based on Chitosan-graft-polyacrylamide and carboxymethylcellulose (CTS-g-PAAm/CMC) was prepared through free radical graft-copolymerization of acrylamide (AAm) onto chitosan backbone in aqueous medium using potassium persulfate and N,N'-methylenebisacrylamide as initiator and crosslinker, respectively. The formation of the grafted network was evidenced by Attenuated Total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Thermogravimetric Analysis (TGA). Scanning Electron Microscopy (SEM) has showed a typical porous structure. The composites were also partially hydrolyzed to achieve superabsorbents with ampholytic properties. The effect of CMC content on the swelling capacities of these superabsorbent composites was examined in doubly distilled water and various pH swelling media. The water absorbency was enhanced by adding CMC in the network, where the highest value was reached at 1 wt % of CMC. Also, their hydrolysis has not only greatly optimized their absorption capacity but also improved their swelling rate. These composites have displayed a pH-responsiveness, in where two maxima at pH 4 and 8 were clearly observed after hydrolysis. From TGA analysis, the addition of the CMC into the grafted CTS-g-PAAm has marginally affected its thermal stability. The antibacterial activity tests of these composites against S. Aureus and E. Coli have showed moderate inhibition of the bacteriocides growth.

I. INTRODUCTION

Superabsorbent polymers (SAPs) or hydrogels have three-dimensional network structure. They are not only able to absorb a large amount of water, but also the absorbed water is hardly removed under some pressure. The majority of them are responsive to environmental stimulants such as pH, ionic strength, solvent composition, electrical field and irradiation. This is the reason that these gels are occasionally referred to as responsive, stimuli-sensitive, and intelligent or smart [1,2]. SAPs were initially introduced into the agriculture and diaper industries, and then their applications were extended to other industries where an excellent water holding property was of prime importance [3-5]. However, the most of superabsorbents are based on synthetic polymers, such as acrylic acid and acrylamide, which are poor in biodegradability with potential for inherent environmental issues. So, introduction of biodegradable polymers is a convenient way to improve biodegradability of corresponding superabsorbent materials. In this context the polysaccharides constitute the most part of the natural-based superabsorbent polymers owing to their exceptional properties, i. e. biocompatibility, biodegradability, renewability and non-toxicity. Great attention has been directed toward superabsorbents being prepared through graft copolymerization of vinyl monomers onto natural polymer chains such as starch, cellulose and chitosan [6, 7]. The reactive NH_2 and OH groups of the chitosan are convenient for graft

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copolymerization of hydrophilic monomers such as acrylamide. Besides, many efforts have been made to improve swelling capacity as well as mechanical strength and toughness of hydrogels, several multicomponent composites networks, including biopolymers, as semi- or full interpenetrating polymer networks (IPN) has been designed [8].

In this paper, we prepared a series of superabsorbent composites based on chitosan-graft-polyacrylamide and carboxymethylcellulose, with the aim to elaborate superabsorbent materials having ampholytic properties, highly swelling capacity and improved biodegradability. The CMC is select owing to its hydrophilic character and polyelectrolytic nature. Also, we partially hydrolyzed the elaborated materials, and then we focused our study on the effects of CMC content and hydrolysis treatment on the swelling capacities of the networks. The structure and properties are investigated.

II. Expérimental section

II.1. Materials

Chitosan (CTS, 75 % degree of deacetylation, medium average molecular weight, viscosity 200-800 cps), Carboxymethylcellulose (CMC, DS 1.2, molecular weight Mw 25.10^4), Acrylamide (AAm), Potassium persulfate (KPS) and N,N'-methylenebisacrylamide (MBA), were used as received. Doubly distilled water was used for hydrogels preparation and swelling properties study. The polysaccharides structures used in this study are presented in Figure 1.
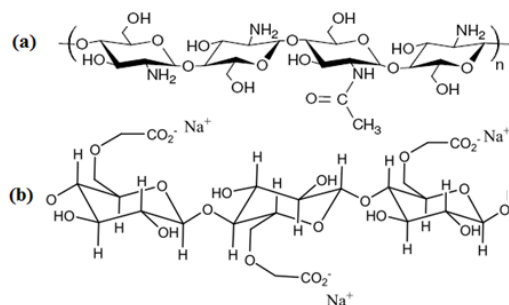

Figure 1: Structures of (a) chitosan and (b) carboxymethylcellulose.

II.2. Preparation of the superabsorbent composites

Superabsorbent composites were prepared at various CMC content via graft-copolymerization and crosslinking in aqueous solution at 60 °C. The weight ratios of CTS, KPS and MBA with respect to AAm were kept constant. In typical procedure: 1g of CTS was dissolved in 30 mL 1% (v/v) acetic acid solution in three-neck flask, equipped with a reflux condenser, a funnel, a nitrogen line and a magnetic stirrer. After being purged with nitrogen, the flask was placed in water bath preset at 60 °C for 30 min. Then, 2 wt % of KPS was added and the resulting mixture was gently stirred for an additional 15 min to generate radicals. Following this, the CMC solution was added to aqueous mixed solution of AAm (5g) and MBA (1 wt %), and kept under stirring for 30 min. Subsequently, the mixture was introduced into the funnel under nitrogen flux, and then added to the flask. The solution was stirred vigorously for another 3 h. The resulting hydrogel was neutralized to pH 8 by adding 1N NaOH solution, washed repeatedly, dewatered with excess of methanol and then dried in an oven. The crosslinked PAAm (without CTS) was also prepared according to the same procedure. The partial hydrolysis of the obtained CTS-g-PAAm and its CMC composites were carried out in alkaline medium at 95 °C using 1N NaOH solution. The obtained product was neutralized by adding acetic acid solution, dewatered and then dried in an oven.

II.3. Characterizations

ATR-FTIR spectra were performed on Bio-Rad spectrometer model FTS-162. All samples were analyzed in solid state as small grains.

The surface morphology of samples was examined on JSM-6360LV Scanning Electron Microscope (JEOL,) after coating with gold film using an acceleration voltage of 10 kV.

Thermal stabilities of these superabsorbents were investigated using TGA analysis. The measurements were performed on a Q500 analyzer, TA instruments, at a heating rate of 10 °C/min, under nitrogen flux.

Swelling properties of CTS-g-PAAm network and its CMC composites were gravimetrically studied at room temperature: 0.1 g of each sample was immersed in swelling solvent and allowed to soak to reach swelling equilibrium. The swollen sample was separated from unabsorbed water by filtering through an 80-mesh stainless steel screen and drained for 30 min until no free water remained. The swelling equilibrium ratio (Qeq) was calculated as in equation (1), in where Wd and Ws are the sample's weights in dry and swollen states, respectively.

(1) $$Qeq \, (g/g) = \frac{W_S - W_d}{W_d}$$

Antibacterial activity of the hydrogels composites was tested against S. Aureus and E. Coli bacteria. This activity was evaluated by inhibition zone method. The bacteria were incubated overnight at 37 °C. Then individual colonies were isolated and suspended in 0.9 % NaCl solution to reach 10^6 CFU/mL. The inhibitory zone tests were performed in Müller Hinton Agar into Petri plates that were streaked with the bacterial suspension. All hydrogels were sterilized in an autoclave at 120 °C and swollen in diluted acetic acid solution. After 24 h, the samples were cut into disks, placed over the surface of the plates and then incubated at 37 °C for 24 h.

According to previous studies [9,10] together with the above results, the proposed mechanism for KPS-initiated graft-copolymerization of AAm onto CTS backbones in presence of MBA crosslinker as well as the interpenetration of linear CMC chains is outlined in Figure 3.

It is important to mention that the hydrolysis treatment of synthesized superabsorbents converts the carboxamide groups of PAAm to carboxylate ions (COO$^-$) following by the release of ammonia. Hence, the structure of the hydrolyzed hydrogels is composed of COONH$_2$, carboxylate COO$^-$ and NH$_2$ groups, resulting in hydrogels with ampholytic properties.

III.2. Morphological study by SEM analysis

One of the most important properties that must be considered is hydrogel morphology. SEM micrographs of CTS, CTS-g-PAAm and a typical of its composite containing 1 wt % of CMC were observed and are shown in Figure 4. CTS-g-PAAm network exhibits porous structure though no porosity is observed in CTS structure. These pores are convenient for the penetration of water and are the sites for interaction of external stimuli with the hydrophilicgroups of the network. The structure surface of the composite is visibly dissimilar from that of CTS-g-PAAm displays a smooth anddense surface Figure 4(c,d), whereas its CMC composite exhibited a comparatively loose and coarse surface and some pores and gaps can be observed, Figure 4(e,f). This observation revealed that the introduction of CMC improves
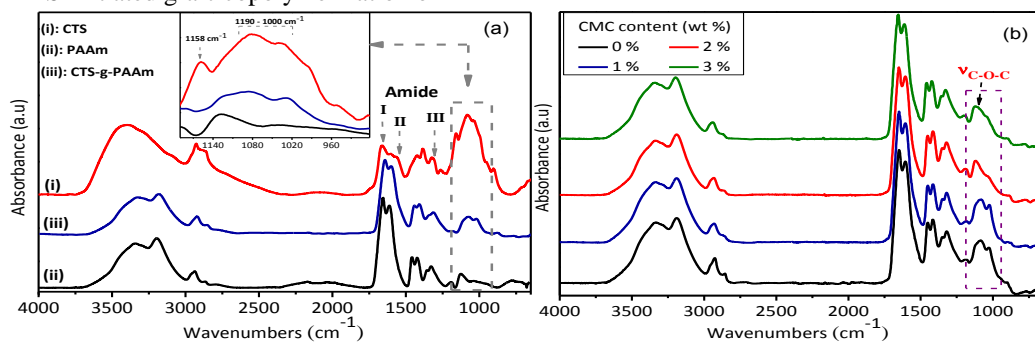

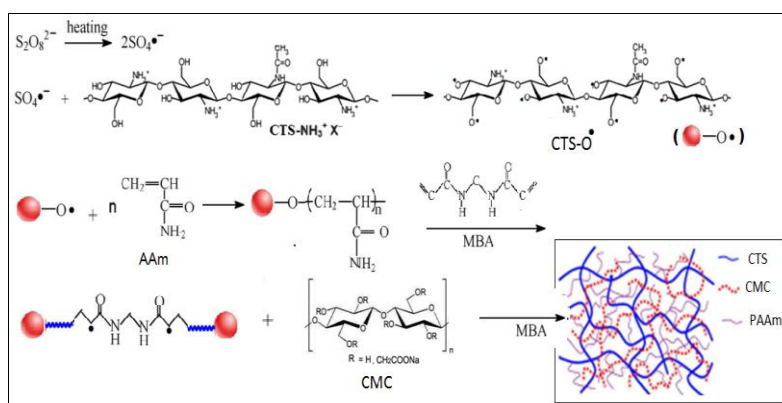**Figure 2:** ATR-FTIR spectra of (a) CTS, PAAm and CTS-g-PAAm and (b) CTS-g-PAAm/CMC.
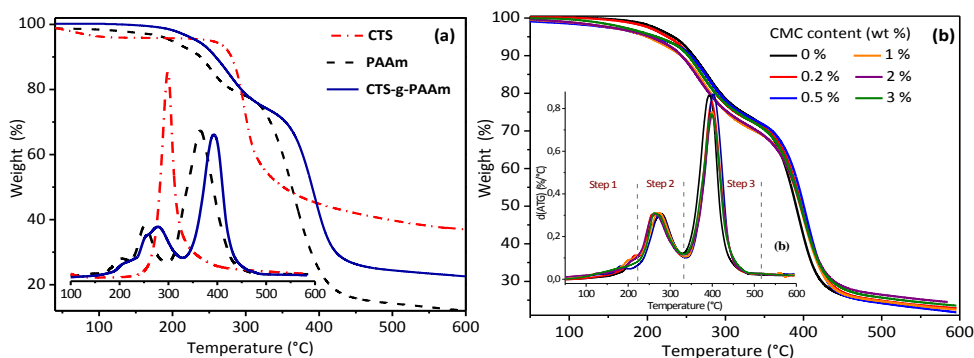
Figure 5: TGA and d(TG) curves of (a) CTS, PAAm hydrogel, the grafted network CTS-g-PAAm and (b) CTS-g-PAAm/CMC composites.

capacity of the network is subsequently decreased. Besides, the water absorbency of the hydrolyzed superabsorbents is remarkably higher than that of unhydrolyzed counterparts, regardless CMC content. This difference is obviously ascribed to the appearance of a polyelectrolytic nature in the grafted network after hydrolysis. Thus, additional anionic charges are formed into the network, which increase in the swelling capacity.
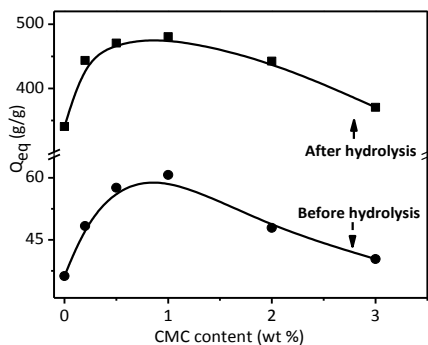

Figure 6: Effects of CMC content and hydrolysis on water absorbency of the grafted network CTS-g-PAAm and its composites in distilled water.

Figure 7 displays the pH-sensitivity of the superabsorbents before and after hydrolysis of CTS-g-PAAm and a typical composite containing 1 wt % of CMC together with their hydrolyzed analogues. The swelling of unhydrolyzed hydrogels are higher in acid

medium than in basic one with a maximum at pH 4. It is well known that the swelling of PAAm hydrogel is insensitive to pH value because there are no ionizable groups in its structure. This result is obviously related to CTS as well as to the added CMC. In the case of CTS-g-PAAm, the swelling in acidic medium is controlled mainly by the protonated amino groups of the CTS. The electrostatic repulsions NH_3^+-NH_3^+ enhance the osmotic pressure inside the network and thus the swelling is increases. However, in basic region, the NH_3^+ ions of CTS change back to NH_2 groups and thus the swelling decreases.

In the other hand, the composites contain both NH_2 and COO- groups and different interacting species are form depending on pH medium. In acidic pHs ≤ 4, the swelling is promoted mainly by NH_3^+ species because most of carboxylate ions are protonated (COOH). In basic medium, another maximum of low intensity at pH ~ 8 is also observed since the presence of the COO- groups of CMC exert mutual electrostatic repulsions that cause an increase in swelling.

In the case of hydrolyzed superabsorbents, the two maxima at pH 4 and 8 are clearly noticed. Similar type of results has also been reported by other workers in studies of hydrogels [11,12].

III.5 Antibacterial activity
The results of inhibitory zone tests of CMC, grafted network CTS-g-PAAm and its composites CTS-g-PAAm/CMC swollen acetic acid solution are depicted in Figure 8.
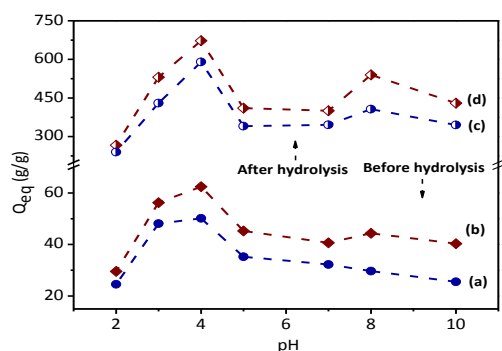
Figure 7: pH-sensitivity of CTS-g-PAAm superabsorbent (a,b) its composite with 1 wt % of CMC (c,d) before and after hydrolysis, respectively.

Figure 8: Photographs of antibacterial tests against *S. aureus* (a) and *E. coli* (b)bacteria of samples with CMC content (wt %): (1) 100%, (2) 0%, (3) 1%, (4) 2%, (5) 3%.

It appears that the antibacterial action of all samples is better against S. aureus than E. coli. Indeed, the structure of the cell wall of E. coli (Gram-negative strain) has another outside pepetidoglycan layer that is mainly constructed from tightly packed lipopolysaccharide molecules, resulting in the effective resistive barrier against foreign compounds attack [13].

The antibacterial activity of CTS observed in acidic medium can originates from its polycationic structure. Indeed, the positively charged chitosan-NH_3^+ can bind to anionic groups on cell surface and form polyelectrolyte complexes with the bacterial surface compounds thereby disrupt the normal functions of the membrane, e.g. by suppress its biosynthesis, promoting the leakage of intracellular components. Additionally, the moderate activity can be attributed likely to no solubility of the tested hydrogels that reduced the antimicrobial capacity.

IV.Conclusions

Intelligent superabsorbent composites were prepared via graft copolymerization of AAm onto CTS backbones in presence of polyelectrolyte CMC. The grafted network exhibits a porous structure and a more stable thermal degradation than its compounds. Besides, the partially hydrolyzed composites have shown similar swelling trend than the unhydrolyzed counterparts and the highest pH-sensitivity owing to the ionic repulsion forces
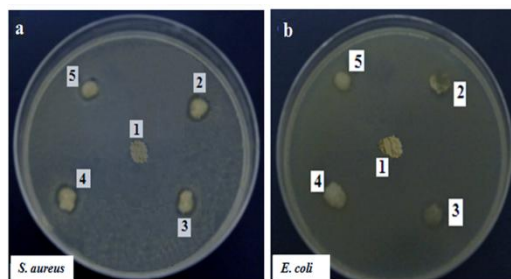
between the charged groups of the network. Also, CTS-g-PAAm/CMC superabsorbent composites have shown moderate antibacterial activity and lower sensitivity against E. coli compared to S. aureus. These materials would be useful in antibacterial applications such as in hygienic products and bio-related uses. This study will be extended to the study of their mechanical properties and biodegradability.

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