CMC/Celite Superabsorbent Composites: Effect of Reaction Variables on Saline-absorbency under Load

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A series of superabsorbent composites were synthesized through graft copolymerization of acrylic acid (AA) onto carboxymethyl cellulose (CMC) in the presence of celite powder using N,N'-methylenebisacrylamide (MBA) as a cross-linking agent and ammonium persulphate (APS) as an initiator. The chemical structure and thermal properties of the composite hydrogels were characterized by FTIR spectroscopy and TGA methods, respectively. Morphology of the samples was examined by scanning electron microscopy (SEM). In free-state, the swelling conditions and hence the related data are not real, because in all their applications the swelling particles of superabsorbent must absorb aqueous solutions while they are under pressure. Therefore, the effect of the reaction variables (such as monomer and cross-linker concentrations and CMC/celite weight ratio) on the saline-absorbency under load (AUL) application was investigated. The AUL values were estimated using a simple AUL tester at two different pressures (0.3 and 0.9 psi). Surprisingly, the new synthesized composite samples exhibited about 86 g/g absorbency in 0.9% NaCl solution under 0.3 psi pressure. The AUL values considerably decreased with increasing the MBA concentration, 53.4 g/g (CMC/celite = 0.5/1.5 and P = 0.3 psi) vs. 42.4 g/g (CMC/celite = 0.5/1.5 and P = 0.3 psi). The ionic monomers increased saline-absorbency under load significantly and the effects of parameters such as monomer and cross-linker concentrations, and CMC/celite weight ratio were not considerably different from the free swelling. Therefore, this new synthesized composite may be considered as an excellent candidate for various industrial applications.

INTRODUCTION

Superabsorbents are lightly cross-linked hydrophilic polymers that can hold a large amount of water and/or biological fluids [1,2]. Since the early development of superabsorbent hydrogels [3] there has been considerable attention towards these promising materials. They were introduced to agriculture industry about thirty years ago to improve the water-holding capacity of sandy soils to promote the germination of seeds and plant growth [4-7].

Swelling under load is important for many industrial applications because hydrogels may be subjected to pressure in practical conditions [8,9]. However, the majority of the...
reported SAPs comprise only absorbency in free-state conditions. The values of this parameter are usually given in basic scientific literature [10]. Many efforts have been made to improve absorbency under load (AUL) and strength of the swollen gel [11,12] and several devices have been developed for quantitative determination of this parameter [8,13].

Higher production cost and low gel strength restrict application of natural-based SAPs, severely. To overcome these limitations, low cost inorganic compounds can be used. Minerals such as montmorillonite [14], hydrotalcite [15], smectite [16], vermiculite [17], laponite [18] bentonite [19], attapulgite [20], silica gel [21], sepiolite [22], and kaolin [23] have been widely used as fillers in superabsorbent composites. Furthermore, introduction of inorganic fillers to a polymer matrix increases its strength and stiffness.

Diatomaceous earth (known as diatomite, kieselgur or celite) is a naturally occurring siliceous sedimentary rock that is easily crumbled into a fine white powder. The typical chemical composition of the diatomaceous earth is comprised of 86% silicon, 5% sodium, 3% magnesium and 2% iron. Celite has several unique characteristics due to its lightness and porosity. It is an ideal filtering medium. In addition, it has other applications and can be used as water absorbent, filler and catalyst carrier [24,25].

Following our previous reports on SAPs [26-29], we have focused on the study of saline absorbency under load of CMC/celite-g-poly(sodium acrylate) superabsorbent composite samples. Optimization of synthetic conditions of CMC-g-poly(acrylic acid)/celite superabsorbent composite via Taguchi method has been reported earlier by our group [30].

In this work, the most important reaction variables such as monomer and cross-linker concentrations and CMC/celite weight ratio that affect the under load saline absorbency of the composite samples were investigated and a unique AUL value (86 g/g) was achieved under a definite set of conditions.

EXPERIMENTAL

Materials
Carboxymethyl cellulose sodium salt (CMC, DS = 0.52, \( M_w =100,000 \), Fluka, Switzerland) was used as received. \( N,N'\)-Methylenebisacrylamide (MBA, Merck, Germany), ammonium persulphate (APS, Fluka, Switzerland), acrylamide (Aam, Merck, Germany), and acrylic acid (AA, Merck, Germany) of analytical grades were used without further purification. Double distilled water was used for the hydrogel preparation and swelling determinations.

Instrumental Analysis
FTIR Spectra of the samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FTIR, (Quebec, Canada) spectrophotometer. Morphology of the dried gels was studied by scanning electron microscope (SEM). Dried superabsorbent powder was coated with a thin layer of gold and imaged in a SEM instrument (Philips, XL30, Eindhoven, Netherlands). The dynamic weight loss tests were conducted on a 2050 thermo-gravimetric analyzer (TGA) (TA Instruments, New Castle, NJ, USA). All tests were performed at a heating rate of 20°C/min under nitrogen atmosphere.

Preparation of Composites
A mixture of carboxymethyl cellulose (0.5-1.5 g) and celite (0.5-1.5 g) was dispersed in 50 mL double distilled water at 40°C. The aqueous solution of dispersed mixture was then added into a three-necked reactor equipped with a mechanical stirrer (300 rpm, three-blade propeller type, Heidolph RZR 2021, Germany). The reactor was immersed in a thermostated water bath pre-set at 75°C. Then, given amounts of the monomer (2.5-3.5 g), initiator (0.15 g APS dissolved in 5 mL H2O), and MBA (0.06-0.25 g dissolved in 5 mL H2O) were added simultaneously to the reaction mixture. After the completion of the reaction (30 min), to neutralize 100% of the acrylic groups, 50 mL of aqueous solution of NaOH (0.037-0.051 mol) was added to reactor. The final gel was poured into an excess non-solvent ethanol (200 mL) and remained for 12 h for dewatering. To proceed further, ethanol was decanted and the product was cut into small pieces. To remove the soluble content, the hydrogel was dispersed in double distilled water to swell for 48 h. After filtration, the extracted gel was dewatered by non-solvent ethanol and dried in an oven (50°C, 24 h). After grinding, the
powdered superabsorbent hydrogel was stored away from moisture, heat and light.

**Swelling Measurements**

Accurate weighed sample (0.1 ± 0.0001 g) of the powdered superabsorbent with average particle size of 40-60 mesh (250-400 μm) was immersed in 200 mL distilled water for 1 h. The equilibrium swelling (ES) capacity was measured twice at room temperature by "tea bag" method using the following formula:

\[
ES(g / g) = \frac{W_2 - W_1}{W_1}
\]

where \( W_1 \) and \( W_2 \) are the weights of dry and swollen gel, respectively.

**Absorbency Under Load (AUL)**

A macro-porous sintered glass filter plate (porosity \# 0, \( d = 80 \) mm, and \( h = 7 \) mm) was placed in a Petri dish (\( d = 118 \) mm and \( h = 12 \) mm) and a weighed dried hydrogel sample (0.5 ± 0.01 g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid weight (Teflon, \( d = 60 \) mm of variable height) which could slip freely in a glass cylinder (\( d = 60 \) mm and \( h = 50 \) mm) was used to apply the desired load (applied pressure 0.3 and 0.9 psi) to the dry hydrogel sample particles. Then, a 0.9% saline solution (NaCl) was added to the Petri dish so that the liquid level was equal to the height of the sintered glass filter. The whole set was covered to prevent surface evaporation and probable change in the saline concentration. After 1 h, the swollen particles were weighed again, and the AUL

![Scheme I. Proposed mechanism pathway for the synthesis of CMC/celite-g-poly(sodium acrylate) superabsorbent composite.](image-url)
was calculated according to eqn (1) [8].

RESULTS AND DISCUSSION

Synthesis and Characterization

The superabsorbent composite was prepared by graft copolymerization of acrylic acid onto CMC as a natural polymeric backbone in presence of a cross-linking agent and celite powder. APS was used as an initiator. The sulphate anion radical that is produced from thermal decomposition of APS, abstracts hydrogen from the hydroxyl groups of the polysaccharide to form corresponding macro-radicals. These macro-radicals initiate polymerization of the monomers which lead to a graft copolymer. Since a cross-linking agent is introduced into the system the copolymer has a cross-linked structure. When acrylic acid is used as a monomer, there is a possibility of reaction taking place between the acrylic acid monomer and hydroxyl group of the celite surface (Scheme I).

Infrared Spectroscopy Analysis

Fourier transform infrared spectroscopy was used to identify the product. The FTIR spectra of the initial substrates and composites are depicted in Figures 1 and 2. Spectrum a in Figure 1 represents the spectrum of the celite. The bands at 1088 cm\(^{-1}\) could be attributed to the stretching of the siloxane group (-Si-O-Si-) which was confirmed by the -Si-O-Si-bending vibration at 478 cm\(^{-1}\). The band at 793 cm\(^{-1}\) was attributed to the Si-OH vibration mode [21]. In the spectrum b of the Figure 1, two strong peaks are observed at 1615 cm\(^{-1}\) and 1415 cm\(^{-1}\) due to the asymmetrical and symmetrical stretching modes of the -COO- groups.

Figure 2 shows the FTIR spectra of the physical mixture of the reactants (spectrum a) and CMC/celite-g-poly(sodium acrylate) composite (spectrum b). A new absorption peak, appeared at 1673 cm\(^{-1}\) may be attributed to the reaction between acrylic acid monomers and hydroxyl groups on celite.

Thermal Properties

Thermogravimetric analysis of CMC, CMC-g-poly (sodium acrylate) hydrogel, and CMC/celite-g-poly (sodium acrylate) composite are presented in Figure 3. Improvement in thermal stability of the superabsorbent composite may be concluded from its thermal analysis curve in Figure 3 and the data summarized in Table 1. According to this table, the values related to the composite such as \(T_{10}\) (246.9°C) and char yield at 700°C (44%) are higher than both celite-free hydrogel (\(T_{10} = 228.9°C\) and \(Y = 35.5\%\)) and the CMC (\(T_{10} = 191.2°C\) and \(Y = 36.1\%)\) samples. The celite particles in the network may act as heat barriers therefore, enhance the overall thermal stability of the synthesized composite.
Figure 2. FTIR Spectra of: (a) physical mixture of CMC/celite/poly(sodium acrylate) and (b) CMC/celite-g-poly(sodium acrylate) composite.

Figure 3. TGA Curves of: (a) CMC, (b) celite-free CMC-g-poly(sodium acrylate) superabsorbent hydrogel (CMC = 1.5 g, MBA = 0.06 g, and AA = 2.5 g), and (c) CMC/celite-g-poly(sodium acrylate) composite (CMC/celite = 1.5/0.5, MBA = 0.06 g, and AA = 2.5 g) at heating rate 20°C/min and N₂ purge.

Table 1. Thermal properties of the CMC, celite-free CMC-g-poly( AA-Na) superabsorbent hydrogel (CMC = 1.5 g, MBA = 0.06 g, and AA = 2.5 g), and CMC-g-poly( AA-Na)/celite composite (CMC/celite = 1.5/0.5, MBA = 0.06 g, and AA = 2.5 g) at heating rate 20°C/min under N₂ purge.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature (°C) at weight loss</th>
<th>( \gamma^a ) (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMC-g-poly(sodium acrylate)</td>
<td>104.0</td>
<td>191.2</td>
</tr>
<tr>
<td>CMC/celite-g-poly(sodium acrylate)</td>
<td>158.2</td>
<td>228.9</td>
</tr>
<tr>
<td>CMC/celite-g-poly(sodium acrylate)</td>
<td>187.7</td>
<td>246.9</td>
</tr>
</tbody>
</table>

(a) Char yield at 700°C under N₂ purge.

Scanning Electron Microscopy
Morphology of the composite was studied using scanning electron microscopy (SEM). Figure 4a indicates the SEM image of the superabsorbent hydrogel. This image confirms the higher structural porosity for the superabsorbent hydrogel compared to superabsorbent composite. Figure 4b shows the scanning electron microscopy of the CMC/celite-g-poly(sodium acrylate) composite with a porous structure as well. Moreover, no phase separation is observed in the micrograph (Figure 4b). This morphology reaffirms the homogeneity of our synthesized superabsorbent hydrogels as a real composite.

Effect of Reaction Variables on AUL Values
Load-free absorbency is a parameter usually given in the basic scientific literature and absorbency under load (AUL) values are often reported in the technical data sheets and patent articles. AUL values are of
great importance in various industrial applications such as irrigation systems in agriculture. Thus, the study of this parameter is of great interest from industrial point of view. In the current study, we determined AUL values by using a simple AUL tester at various applied pressures (0.3, 0.6 and 0.9 psi).

As it is seen from Table 2, the load-free absorbency values increase with decreasing the amount of celite incorporated into the composite structure. The celite particle may act as follows: (a) preventing the growth of polymer chains by chain transfer mechanism [31], (b) acting as cross-linkers [32], and (c) strengthening the swollen gels. Similar behaviour was reported in the case of other inorganic clays [21]. Swollen gels strengthen at higher concentrations of celite and therefore it increases the AUL value. Meanwhile, the AUL values also increase at lower concentration of celite because of high free-swelling values.

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Table 2. Load-free and AUL values of CMC/celite-g-poly(acrylamide) and CMC/celite-g-poly(sodium acrylate) composite.

<table>
<thead>
<tr>
<th>MBA</th>
<th>AAm*</th>
<th>CMC/celite-g-poly(acrylamide) composite</th>
<th>CMC/celite-g-poly(sodium acrylate) composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.06</td>
<td>2.5</td>
<td>46.4</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>3.5</td>
<td>38.5</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>2.5</td>
<td>24.5</td>
</tr>
<tr>
<td>MBA</td>
<td>AA</td>
<td>CMC/celite-g-poly(sodium acrylate) composite</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.06</td>
<td>2.5</td>
<td>490</td>
</tr>
<tr>
<td>5</td>
<td>0.06</td>
<td>3.5</td>
<td>214</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>2.5</td>
<td>184</td>
</tr>
</tbody>
</table>

(*) AAm has been used in the similar unreported work. (a) Load-free swelling capacity in distilled water in terms of g/g. (b) Absorbency in 0.9% NaCl solution under load in terms of g/g.
centration and water absorbency values was also investigated. According to the basic knowledge of SAP hydrogels [23,24], the water absorbency of a hydrogel increases initially with increased monomer concentration, though it decreases later. In the present study, two different concentrations of the monomer were used (Table 2). While at lower concentration of monomer, swelling capacity is increased, at higher concentration, however, both swelling capacity in free-state and under load are decreased at constant CMC/celite weight ratio. This is probably due to: (a) preference for homopolymerization over graft copolymerization, (b) an increase in the viscosity of the medium which hinders the movement of free radicals and monomer molecules, and (c) possible chain transfer to monomer molecules. Moreover, CMC/celite-g-poly(acrylamide) composite gives lower water absorbency values in comparison with CMC/celite-g-poly(AA-Na) under the same reaction conditions, which may be attributed to the presence of ionic groups in the latter composite. According to Tables 2 and 3, hydrogels with ionic structures have high load-free swelling capacity and high AUL values.

The effect of cross-linker concentration on the swelling capacity was investigated. According to our previous works, high values of absorbency are obtained at lower concentrations of cross-linker in load-free absorbency. This can be fully explained by the following equation [33]:

$$q_m = \left( \frac{i/n_v S^*}{v_e/V_0} \right)^{5/3} + \left( \frac{1/2 - \chi}{v_1} \right) / v_1$$

(2)

where, $q_m$, $(i/n_v)$, $S^*$, and $(v_e/V_0)$ are swelling ratio, concentration of the fixed charge of unswollen networks, ionic strength of the swollen solution, and the cross-linking density which refers to the number of effectively cross-linked chains in unit volume, respectively. The expression $(1/2-\chi_1)v_1$ stands for the network-medium affinity. As it is obvious from eqn (2), the swelling ratio ($q_m$) increases with decreasing the cross-linking density ($v_e/V_0$). In fact, higher cross-linker concentration led to the higher cross-linking density and decreased the space between the copolymer chains. As a consequence, the highly cross-linked structure which cannot expand results in low load-free absorbency.

However, AUL value is strongly related to the degree of the cross-linking of the hydrogel. While higher cross-linker concentration would strengthen the swollen gels, it may lead to increased AUL values and lower absorbency with the same mechanism as given above. As a result, AUL values considerably decrease from 53.4 g/g (entry 4: CMC/celite = 0.5/1.5 and $P = 0.3$ psi) to 42.4 g/g (entry 6: CMC/celite = 0.5/1.5 and $P = 0.3$ psi) with increased MBA concentration.

Table 3 compares the AUL values of some superabsorbent hydrogels and superabsorbent hydrogel composites. The data indicate that, AUL values not only depend on gel strength but also can be affected by high SAP free swelling capacity and intrinsic properties of SAP materials. Indeed, high values of AUL may be attributed to a hydrogel with high mechanical strength or a superabsorbent hydrogel with high value of load-free absorbency.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Free swelling</th>
<th>AUL (0.3 psi)</th>
<th>AUL (0.9 psi)</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC/silica gel-g-poly(AA-co-AMPS)</td>
<td>4000</td>
<td>44</td>
<td>40</td>
<td>[21]</td>
</tr>
<tr>
<td>Salep-g-poly (sodium acrylate)</td>
<td>3050</td>
<td>75</td>
<td>73</td>
<td>[26]</td>
</tr>
<tr>
<td>Salep-g-polyacrylamide (gamma)</td>
<td>586</td>
<td>52</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td>Alginate/kaolin-g-poly (sodium acrylate)</td>
<td>307</td>
<td>24</td>
<td>20</td>
<td>[23]</td>
</tr>
<tr>
<td>Alginate/carrageenan-g-polyacrylamide</td>
<td>210</td>
<td>42</td>
<td>39</td>
<td>[29]</td>
</tr>
<tr>
<td>Salep-g-polyacrylamide (classic)</td>
<td>150</td>
<td>36</td>
<td>-</td>
<td>[28]</td>
</tr>
<tr>
<td>Taguchi optimized CMC/celite-g-poly(sodium acrylate)</td>
<td>310</td>
<td>38</td>
<td>-</td>
<td>[30]</td>
</tr>
<tr>
<td>CMC/celite-g-poly(sodium acrylate)</td>
<td>1325</td>
<td>86</td>
<td>72</td>
<td>Current work</td>
</tr>
</tbody>
</table>

Table 3. Comparative values of AUL reported in literature.
CONCLUSION

A series of superabsorbent composites containing natural polymer (CMC) and inorganic filler (celite) were prepared by graft copolymerization of poly(sodium acrylate) onto CMC in the presence of a cross-linking agent. The synthesized composites were characterized by FTIR, SEM, and thermogravimetric analysis. The AUL values were also determined in 0.9% saline solution. Therefore, the effect of reaction variables on saline-absorbency under load was studied. The resultant composite, CMC/celite-g-poly(sodium acrylate), possesses large degrees of water absorbency (about 86 and 72 g/g, respectively) under 0.3 and 0.9 psi in 0.9% NaCl solution. The results show that ionic monomers increase the saline-absorbency under load condition significantly. The effects of other parameters such as monomer and cross-linker concentrations, and CMC/celite weight ratio compared to the free swelling are not very significant. However, the synthesis of a superabsorbent with high AUL value is still challengeable.

REFERENCES

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