A study on synthesis and properties of SAPs based on carboxymethyl cellulose

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Abstract:

Carboxymethyl cellulose-graft-poly(acrylic acid-Sodium acrylate-acrylamide) SAPs have been prepared by the free-radical grafting solution polymerization of acrylic acid (AA) and acrylamide monomers (AM) onto carboxymethyl cellulose (CMC) in the presence of N,N′-methylenebisacrylamide as a crosslinker (MBA) and ammonium persulfate (APS) as an initiator. Various factors influencing the water absorbency of the polymer were studied. These include the weight ratio of APS, MBA, and CMC compared to the monomers. The optimal conditions were found as follows: 1% APS, 0.25% MBA, and 10% CMC (weight ratio to monomers). The maximum absorbencies for distilled water and 0.9 wt.% NaCl solution were 406 g/g and 69 g/g, respectively. The structure of the synthesized polymer was confirmed by Fourier Transform Infrared spectroscopy (FTIR). Additionally, the water absorption and water retention behavior of the polymer in soil were investigated. The results showed that this polymer could be employed as a suitable moisture-holding additive in soil for cultivation purposes.

Keywords: **absorbency, carboxymethyl cellulose, retention behaviour, SAP, water holding.**

Classification number: **2.2**

Introduction

Due to the water resource crisis, conserving water is essential for the sustainable development of agricultural production. Thus, there is an increasing urgent the need to use superabsorbent (SAP) in agriculture. After water absorption, SAP particles act as reservoirs near the root system that help to increase both the amount of water and the amount of time available for plants to grow [1-4]. However, because SAP is difficult to decompose, their use has negative impacts on the soil and the environment. For this reason, studying the manufacture of superabsorbent biodegradable polymers (BioSAP) is indispensable in order to trend to develop these products for use in the near future. BioSAP products can be synthesized from renewable materials such as cellulose, starch, chitin, natural resins, and so on. In particular, cellulose and their derivatives, such as CMC, are attracting much attention from researchers as they are the most abundant source of natural polymers and they are biocompatible and biodegradable. Many works devoted to grafting co-monomers such as acrylic acid, acrylamide and polyvinyl alcohol on cellulose derivatives have been carried out to form strongly absorbent polymer materials [5-8]. For example, Suo, et al. [5] synthesized highly water-absorbing carboxymethyl cellulose graft-poly(acrylic acid-co-acrylamide) by free-radical grafting solution polymerization in the presence of N,N'-methylenebisacrylamide as a crosslinker. The highest absorbency obtained was 920 g/g for distilled water, but the superabsorbent can retain 20.7% of the absorbency after heating for 10 h at 60ºC in an oven. Pairote, et al. [7] prepared a SAP based on graft copolymerization of sodium carboxymethyl cellulose and acrylic acid with maximum swelling capacities of 544.95 g/g in distilled water and 44.0 g/g in 0.9% w/v NaCl solution. Alam, et al. [8] reported a new cellulose/CMC hydrogel using epichlorohydrin (ECH) as a crosslinker that was able to absorb up to 725 g distilled water/g and 118 g saline water/g.

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However, cellulose-based superabsorbent materials reported to date are evaluated only by the absorbance and release capacity of water and a physiological salt solution in laboratory conditions. In many cases the absorbance and and release of water, as well as salt solutions and agricultural chemicals, in soil conditions have not yet been assessed. In addition, cellulose-based superabsorbent materials are easily broken due to weak gel stability under the pressure of the soil which greatly reduces the water holding capacity of the material. Specifically, the soil load causes a decrease in the water absorption capacity from 338.5 g/g to 19.3 g/g, and prolongs the swelling time [9]. Therefore, when making use of these materials in cultivation, the properties of the material do not reach what is reported in literature, for example, the mechanical durability and, the ability to absorb/release. In general, the material's properties sharply decrease under the pressure of ground conditions and the presence of salt minerals and fertilizer in the soil. Uncontrolled release of water is one of the main factors limiting their application in agriculture. Therefore, the target of this work is to determine the conditions for the synthesis of SAPs materials based on CMC with high water absorption while ensuring consistent gel stability. The BioSAP products are characterized by their properties and their ability to retain water in soil.

Experimental

Materials

CMC with degree of substitution, DS=0.8-0.9, 99.0%, 40-60 mPa.s (1% solution, 25°C) (F04HC, Sunrose), amonium persulfate (APS) 99.9% (Merck), N,N-methylene bisacrylamide (MBA) 99.9% (BioBasic), acrylic acid (AA) 99.6% (Wako), acrylamide (AM) 99.9% (Merck), NaOH 99% (alytical grade from Xilong Chemical), NaCl 99.9% (Merck). Solvents: ethanol and methanol from Xilong Chemical.

Procedure of samples synthesis

CMC aqueous solution is put into a 4-neck flask with a mechanical stirrer, reflux condenser, N_2 gas pipe and thermometer. After neutralizing AA to 65% with NaOH, the solution was mixed with AM (mass ratio AA/AM=6), followed by an addition of MBA. The mixture was then poured into the CMC solution, stirred, and continuously aerated with N_2 for 30 min, then the temperature of the mixture was rised to 40°C before adding the APS solution dropwise. The reaction was carried out at 60°C for 2 h, then the product was chopped and,

washed with ethanol and soaked overnight in ethanol before drying for 8 h at 60°C. Raw BioSAP products come in a white opaque powder.

The control sample without CMC (denoted as SAP) was synthesized with the same procedure. The parameters of the samples are given in Table 1.

Table 1. The absorption of distilled water (S_{DW}) of SAP and BioSAP samples with synthetic conditions varies.

Samples	APS, wt.%	MBA, wt.%	CMC, wt.%	S_{DW}, g/g
M1	0.5	0.5	10	49
M2	1.0	0.5	10	193
M3	1.5	0.5	10	147
M4	2.0	0.5	10	141
M5	2.5	0.5	10	121
M6	1.0	0.10	10	311
M7	1.0	0.25	10	333
M8	1.0	0.50	10	193
M9	1.0	0.75	10	145
M10	1.0	1.00	10	110
M11	1,0	0.25	2	200
M12	1.0	0.25	5	220
M13	1.0	0.25	10	333
M14	1.0	0.25	20	259
M15	1.0	0.25	30	215
M16	1.0	0.25	40	210
SAP	1.0	0.25	0	285

Investigation methods

Fourier Transform Infrared spectroscopy (FTIR): the FTIR spectra were recorded on an FTIR-Affinity-1S-Simadzu by KBr disk fabrication technique, 32 scans were performed at 4 cm^{-1} resolution in the range of 600-4000 cm^{-1}.

Determination of gel fraction contents: the gel fraction contents were determined by the Soxhlet technique using acetone as a solvent for 8 h, according to the following formula:

$$G\ (\%) = \frac{m}{m_0}.100$$

where m_0 and m are the mass of samples before and after Soxhlet, respectively.

Determination of liquid absorption: the absorption capacity of the synthesized SAPs and BioSAPs were measured in distilled water, tap water and in saline 0.9 wt% of NaCl using the tea bag method. For the tea bag method, an accurately weighed powdered SAP sample (0.2 g) was placed into a tea bag (acrylic/polyester gauze with fine meshes) and the bag was immersed in an excess amount of water or of another solution (approximately 500 ml) in a standard laboratory (t=25±2°C, relative humidity RH=55±3%). The initial mass of the samples was determined on the analytical balance with 10^{-4} accuracy (m_o). After each designated period, the bag was removed from the solution, allowed to drain for 10 min and the bag was weighted (m_t). This process was repeated several times until the swelling equilibrium was reached (approximately 24 h), i.e. until the bag presented a constant weight.

The liquid absorption of the samples at each time is determined by the formula:

$$S\,(g/g) = \frac{m_t - m_0}{m_0}$$

where m_t and m_0 are the mass of samples absorbed at time t and the mass of the original dry samples, respectively. The final absorption of the samples was the average result of determinations.

Determination of water retention under laboratory conditions: samples after water saturation absorption were monitored for the release process at 50°C in an oven. After each designated period, the samples are weighed. Water retention of the samples is determined by the formula:

$$R(\%) = \frac{m_t}{m_0} x 100 \tag{1}$$

where m_t and m_o are the water mass of samples at time t and initial time, respectively. The experiment was conducted at 50°C and was repeated 3 times.

Determination of water retention in soil: two hundred grams of dried soil mixed with 1 g BioSAP was put into a perforated plastic container at the bottom. The sample was watered until the first drop of water appeared from the bottom of the box. The samples were weighed after each designated period of time. Two hundred grams of control soil sample was prepared with no BioSAP was also performed. The water retention in the soil was calculated using Eq. (1). The experiment was conducted at 25±2°C and was repeated 3 times.

Results and discussion

Study on synthesis conditions of BioSAP

Survey on content of APS catalyst: the samples are prepared with a varying amount of APS (from 0.5 to 2.5%) in the presence of 10% CMC and 0.5% MBA by mass.

From Table 1, when the content of APS increases, the distilled water absorption of BioSAP increases and reaches its largest value at 1%. As the contet of APS continues to increase, the water absorption decreases gradually. This can be explained by the additional free radicals created by increasing APS contents, which increasing the number of grafted hydrophilic polymers onto CMC and, results in increased water absorption [10]. However, when the APS content is too large, an excess amount of free radicals were created, resulting in a reaction that occures too quickly and, a sudden increase in the viscosity of the reaction system. The reaction, therefore quickly ended and hydrophilic polymer short chains were created. The reaction was incomplete, which reduced water absorption [10]. Thus, the optimal APS content was 1 wt.%.

Survey on content of MBA crosslinker: the samples were prepared with a varying amounts of MBA (from 0.1 to 1%) in the presence of 10% CMC and 1% APS by mass.

From Table 1, it can be clearly seen that the distilled water absorption of BioSAP decreases with increasing MBA contents from 0.25 to 1%. The increased MBA contents boosts the number of crosslinks leading to a decrease of three-dimensional network space in the material structure, thus decreasing the water absorption [10, 11]. However, the lower the MBA content, the BioSAP gel is observed to be weaker (low gel strength). This is due to the low MBA content, which weakens the gel structure making, it easier to deform and, unable to hold a large amount of water. Thus, the most suitable content of MBA was 0.25 wt.%.

Survey on content of CMC: the BioSAP samples were prepared with a varying amounts of CMC (from 2 to 40%) in the presence of 1% APS and 0.25% MBA by mass.

From Table 1, it can be seent that, increasing the CMC contents increases the distilled water absorption of BioSAP, which reaches a maximum at 10%. Then further increase

of CMC contents causes the water absorption to decrease gradually. This result can be due to CMC molecules contain many hydrophilic groups such as   -OH and -COO⁻ along the chain length. In addition, CMC chain acts as a framework for grafting polyacrylic acid, polyacrylate and polyacrylamide chains [12], so, the increase of CMC content was increased availability of grafting sites leading to better swelling capacity of the hydrogel. Thus, upon increasing the content of CMC, more space in the material is created and the number of hydrophilic functional groups increases, which leads to an increase in water absorption of materials. Specifically, at CMC 10% wt., the presence of CMC in the material structure significantly increases the water absorption of poly(acrylic acid-co-acrylamide) from 285 up to 333 g/g. This could be due to CMC molecules act as a backbone to make graft copolymers, increase hydgrogel strength, by this helping them retain the structure during the absorbing process to enhance the water absorption ability. So, this result indicated that at this most suitable CMC content seems to provide an interesting compromise between the absorbency and a stable gel structure. However, when furthur increasing the amount of CMC decreases both the water absorption capacity and stable gel. This decreasing could be due to the CMC loading is too high, the CMC acts as a filler that reduces the empty space in the BioSAP for water storage. This result is consistent with previous work reported in the literature [5]. Additionally, the higher of the CMC contents, the BioSAP gel is observed to be weaker (low gel strength) and materials becomes more sticky. In this study, attempts were made to synthesize SAP with CMC contents higher than 40%, but the obtained material dissolved in water when swelling studies were carried out for longer than 48 h. This suggests that, at too high CMC content, there is not enough cross linking density and the formed network is too loose and does not have enough strength to hold water molecules inside the structure. It is known in the literature that CMC increases biodegradability [3, 4], so, depending on the material's requirements for water absorption and self-degradation time, the CMC content can be selected anywhere 10 to 40%. In this work, the main purpose of introduction CMC into superabsorbent is to increase the water absorption while ensuring consistent gel stability, thus, 10% CMC is the most suitable content. This BioSAP material was characterized in terms of chemcial structure and gel fraction content. Its adsorption-desorption behavior in solutions was also studied. Finally, this BioSAP was tested on the water holding capacity in the soil.

The effect of CMC on liquid adsorption-desorption behavior of SAP materials

From Table 1, we can see that the presence of CMC in the material structure significantly increases the water absorption, from 285 up to 333 g/g. The increase in water absorption of the material can be explained by the fact that CMC molecules contain many hydrophilic groups such as -OH and -COO⁻ along the chain length. At the same time, CMC molecules act as a backbone to make graft copolymers and, increase hydrogel strength by helping them retain their structure during the absorbing process, which enhances the water absorption ability. In addition, the participation of CMC molecules in copolymer macromolecules also increases pore size, leading to an enhanced water absorption capacity of the material [8, 12, 13].

Notably, the presence of CMC significantly increased the absorption capacity of 0.9% NaCl solution in the BioSAP material from 51 up to 69 g/g. These results are shown in Fig. 1. Thus, CMC has increased the 0.9% NaCl solution absorption in SAP materials. It is noteworthy that the obtained product had a significantly higher absorption of 0.9% NaCl solution than other published studies [5-9]. Good water absorption is an important property to the application of this material in the agricultural sector as it helps to increase water absorption in the soil environment.
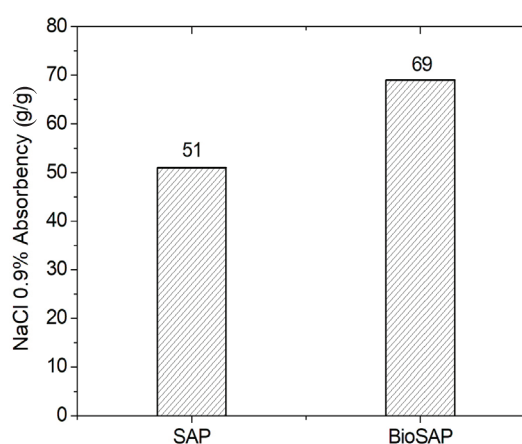

Fig. 1. Absorption of salt solution NaCl 0.9% of BioSAP containing 10% CMC and of SAP.

In this study, the effect of CMC on the desorption behavior of SAP materials is also investigated. The result is shown in Fig. 2.
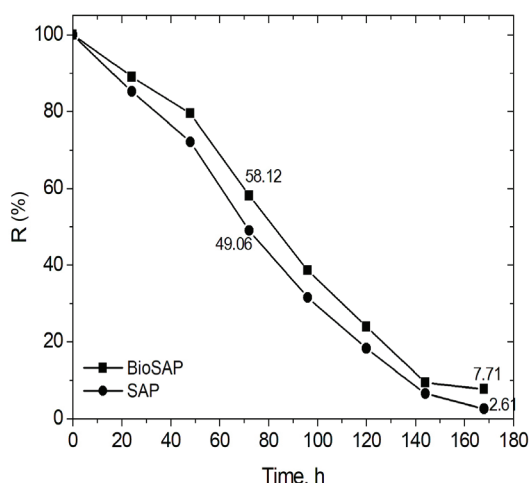
Fig. 2. Water retention of BioSAP and SAP at 50ºC.

It can be seen that the presence of CMC reduces the rate of water release of the materials, which implies that CMC increases the water holding capacity. For example, after 72 h at 50°C, the polymer sample containing CMC (BioSAP) held up to 58% of the water absorbed while the sample without CMC (SAP) held only 49%. This may be explained by the presence of a large number of hydrophilic groups such as -OH and -COO⁻ along the molecular backbone of CMC chains, which form hydrogen bonds with water molecules and reduce the probability of water release in material. Thus, the addition of CMC increases the absorption of water and 0.9% NaCl solution, while also increasing the water holding capacity of these SAP materials.

Characterization of BioSAP

The properties of the BioSAP synthesized in the presence of 1% APS, 0.25% MBA and 10% CMC by weight are studied.

Gel fraction contents: the refinement of raw products has been carried out by the Soxhlet technique, which removes impurities such as water-soluble homopolymers, oligomers, residual monomers, catalysts, and others. The gel fraction of the products reached 98.5%. The saturated absorption of distilled water (S_{DW}), tap water (S_{TW}), and 0.9% NaCl solution (S_{NaCl}) of the raw and refined products are given in Table 2.

Table 2. Saturated absorption of BioSAP samples.

Samples	S_{DW}, g/g	S_{TW}, g/g	S_{NaCl}, g/g
Raw BioSAP	333	163	59
Refined BioSAP	406	295	69

The results of Table 2 showed that the refined BioSAP samples have a significantly higher absorption for all the media tested. Therefore, refinement of the products after synthesis is very important. The absorption of tap water and 0.9% NaCl solution is significantly lower than that of distilled water, proving that the presence of metal ions has a great influence on the water absorption capacity of the BioSAP materials.

FTIR Spectrum: the FTIR spectra of the SAP and BioSAP samples are shown in Fig. 3.
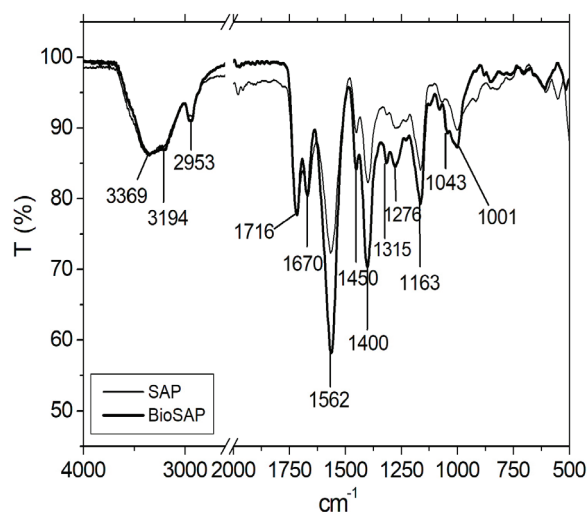

Fig. 3. FTIR spectrum of SAP and BioSAP samples.

As can be seen, from the FTIR spectra of the BioSAP, peaks appearing at 3369 cm⁻¹ and 3194 cm⁻¹ are typical for the valence vibrations of the O-H and N-H bonds, respectively, and the peak at 2953 cm⁻¹ represents the valence vibrations of C-H bonds. The appearance of peaks at 1716 cm⁻¹, and 1670 cm⁻¹ characterize the vibrations of the C=O bonds of acids and amides, respectively. In particular, the peak at 1562 cm⁻¹ is typical for a sodium carboxylate salt [5-7]. The peaks at 1400 cm⁻¹, 1315 cm⁻¹, and 1276 cm⁻¹ characterize the vibrations of the C-N, C-H, and C-C bonds, respectively. The increase in peak intensity of BioSAP compared to SAP at 1562 cm⁻¹, 1163 cm⁻¹, and 1001 cm⁻¹ in the FTIR spectrum is due to the appearance of the C=O bonds of carboxylmethyl groups, and the C-O-C bonding bridge between the glucoside rings and CH-β-glycoside of CMC [12, 13]. Thus, analysis of FTIR spectrum demonstrate the presence of CMC in the structure of BioSAP.

Test on the water holding capacity of BioSAP in soil

To assess the water holding capacity of BioSAP in soil, water retention and slow release tests were conducted and, the results are shown in Table 3 and Fig. 4.

It can be seen from Table 3 that the volume of water retained in the soil samples containing BioSAP is almost 3 times greater than that held in soil samples without BioSAP.

Table 3. Water retention of soil samples with and without BioSAP.

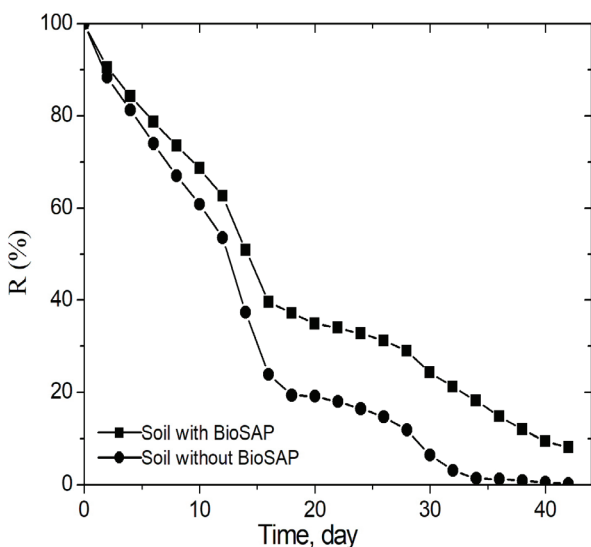| Samples	m_{BioSAP},g	m_{soil},g	m_{water},g
Soil with BioSAP	1.0	200±0.1	105±4.6
Soil without BioSAP	0.0	200±0.1	36±2.6

Fig. 4. Water retention in soil with and without 0.5% BioSAP by mass.

As can be seen from Fig. 4, soil samples containing 0.5% BioSAP have a significantly higher ability of water retention than the soil samples without BioSAP. Over the first 6 days, the amount of water decreased sharply and, then decreased gradually. After 10 days, samples with BioSAP could still hold 41.6% of water, while samples without BioSAP could only hold 23.8%. After 28 days, the water in the soil sample without BioSAP had completely evaporated, while the soil sample with BioSAP still retained nearly 20%. This proves that BioSAP improved the soil's ability to hold and release water slowly. Notably, the water retention and slow release capacity of our BioSAP products are significantly higher than that of other published studies [2, 3, 9].

Conclusions

- The effect of the content of catalyst, crosslinker and CMC on the water absorption capacity of SAP and BioSAP was examined. The results showed that the materials reached maximum absorption under the reaction conditions of 1% APS, 0.25% MBA, and 10% CMC by weight. The ratio of AA/AM=6 (AA was neutralized up to 65% by NaOH solution). The absorption of the product with distilled water and 0.9% NaCl solution was found to be 406 and 69 (g/g), respectively.

- The presence of CMC significantly increased not only water absorption, but also the water retention of the SAP materials, and in particular, significantly increased the absorption of 0.9% NaCl solution.

- Using 0.5% soil volume of BioSAP as a soil moisturizer significant increase in water retention and the ability to slowly release water from the soil was found. Therefore, SAP materials containing CMC have specific improved properties which help to increase water absorption in the soil environment and gives these BioSAP materials promising applications for agriculture.

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