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Factors on the preparation of carboxymethylcellulose hydrogel and its degradation behavior in soil

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Abstract

A hydrogel, with water content more than 97.0 wt%, was prepared through crosslinking sodium carboxymethylcellulose (Na-CMC) with $AlCl_3$, The effects of amount of crosslinker, water, Na-CMC and the reaction temperature on modulus and biodegradation of the hydrogel were investigated and optimized. At the same time, the factors of amount of antiseptic, nutriments and different soils on the biodegradation of the hydrogel were also discussed in detail. The results showed that the hydrogel had better biodegradation and strength when the mass ratio of crosslinker to Na-CMC was 0.13 at room temperature. The degradation rate of the hydrogel was enhanced by addition of nutrient element especially by addition of urea. The results of biodegradation in different soils showed sand soil is favorable to degradation of the hydrogel.

Keywords: Sodium carboxymethylcellulose (Na-CMC); Hydrogel; Biodegradation; Modulus

1. Introduction

Superabsorbents are widely attended to be a kind of water retention materials in agriculture and forestry. As the primary products of superabsorbents, the polyacrylates can not be widely used, because of their difficult degrade in soil (Stahl, Cameron, & Haselbach, 2000) and expensive cost. Na-CMC as an amylose with many hydroxy and carboxylic groups can absorb water and moisture, so the hydrogel made of it has many excellent properties, such as high water content, good biodegradation (Wach, Mitomo, Yoshii, & Kumo, 2001) and wide source for its low cost. Therefore, it can be widely applied in agriculture and forestry with a good foreground. Early at the end of 1980s, Na-CMC as the raw material, was prepared a product called 'moisture retention reagent' (Avera, 1989). The effect was remarkable when the product was applied in planting trees and grasses experiment. Later many hydrogels were synthesized with high water content via crosslinking Na-CMC with metal ion (Motofuji, Tamura, & Hanada, 1999; Ohno, 2000; Ohno, & Aoto, 2000). Several studies have been performed to prepare the hydrogle with Na-CMC (Liu, Peng, & Wu, 2002; Liu, Zhai, Li, Peng, & Wu, 2002), but little information about biodegradation of Na-CMC hydrogel in soil. In the present work, based on our former work (Nie & Liu, 2003; Nie, Liu, & Chen, 2004), a hydrogel has been made by the reaction between Na-CMC and $AlCl_3$ at room temperature, with high water content and good strength. As a moisture retention reagent, the way that the hydrogel supply water to plant is different from the conventional absorbents. It releases water by means of biodegradation. The microbes in soil decompose the net framework of the hydrogel, then the water embed in which is released slowly, so the usability of the hydrogel depend on the rate of biodegradation. Based on the importance of biodegradation behavior in soil, this study has investigated it in systematicaly. Due to the simple preparation and low cost, the hydrogel has a better foreground in planting trees and grasses.

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2. Experiment

2.1. Materials

Na-CMC was eatable grade and supplied from Huian Corporation (China) in the form of sodium salt (Molecular weight 3×10^5 and degree of substitute 0.93). Cellulase (C-0901) was supplied from Sigma Corporation (America). Other chemicals were of analytical grade.

2.2. Carboxylmethylcellulose hydrogel (CMCH) preparation

The reaction was conducted in a 2000 ml-beaker equipped with a mechanical stirrer. A proper amount of tap water was added in the beaker. Then a known weight of $AlCl_3$, using as a crosslinker, antiscorbutic acid ($C_6H_8O_6$) using as antiseptic substances and urea (or glucose) as a nutriment were subsequently added under violently stirring. After stirring for 5 min, Na-CMC (15 g) were slowly added. Stirred for another 5 min to have Na-CMC dissolved completely, a hydrogel with colorless, tasteless and full of small air bubbles was obtained. The content of water in the hydrogel was about 97.0%. Sealed it off with a plastic bottle to be used.

2.3. Modulus of CMCH measurement

The hydrogel was placed for 1 h before it was put into the modulus determination apparatus. The height of sample was noted down as L_0 when the load (W_0) was added, removed the load and left the hydrogel to revert for 3 min. Then increased the load to W_i, and noted down the height of the sample (L_i). Plotted a figure of W_i/A, namely stress (A was surface of sample container section acreage) versus $\Delta L_i/L_0$ namely deformation ($\Delta L_i = L_i - L_0$), the slope of the line was the modulus of the hydorgel.

2.4. Enzymatic degradation

Enzyme degradation was carried out using a cellulase enzyme in an acetic acid–NaOH buffer of pH 5.0 at 37 °C. A dried film of the gel (100 mg), with a thickness about 0.3 mm, was immersed in the enzyme solution for 96 h. Concentration of the enzyme in buffer solution was 0.1 mg ml^{-1}. At the same time, a blank test in the buffer solution without the enzyme using the same sample was carried out. After incubation, filtering through a silk sieve (aperture 0.076 mm) and washing with distilled water followed drying it at 80 °C to a constant weight. The results of enzymatic degradation was expressed as follow:

$$\text{percentage of degradation (DP)} = \frac{W_1 - W_2}{W_0} \times 100$$

where W_0, W_1 and W_2 denote, respectively, the weight of the films before degradation, the residual weight of the gel in the blank tests and enzymatic tests.

2.5. Biodegradation in soil

Another experiment was also carried out to investigate the biodegradation behavior of the hydrogel in different soils. The hydrogel was enclosed in a lidless plastic bottle, and the bottle was put in a pit, with a slope of 45° and it opening downwards, then buried with the soil. After a period of 3 months, the bottle was taken out and weighed. DP of the hydrogel was calculated using the following equation:

$$\%\ \mathrm{DP} = \frac{W_0 - W_1}{W_1} \times 100$$

where W_0 and W_1 were the wet weights of the hydrogel in the bottle before and after degradation.

3. Results and discussion

3.1. Optimization of CMCH preparation

Fig. 1 represents dependences of the modulus and DP of CMCH on amount of crosslinker. Fix the mass ratio of the antiseptic, urea and water to Na-CMC at 0.02, 0.06 and 50, respectively. The other conditions are the same as the ones in the preparation experiment. Changing crosslinker amount, we get the curves of crosslinker amount versus modulus and biodegradation of the CMCH. As shown in Fig. 1, the DP of CMCH decreases with the increasing of crosslinker amount. As we know, the more amount of crosslinker, the higher crosslinking density, the more net structures formed and the lower swelling ratio of

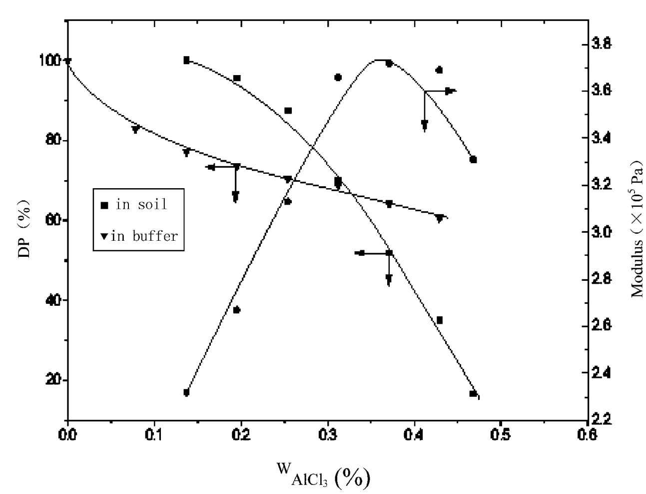

Fig. 1. Dependences of the modulus and biodegradation of CMCH on amount of crosslinker (15.0 g of CMC, 900 mg of urea (dextrose), 300 mg of antiscorbutic, 750 g of distilled water, changing $AlCl_3$ amount, reaction temperature = 25 °C).

the hydrogel. It's equal to form a density surface on the gel particles, which is effective to prevent the microorganisms or enzyme entering the hydrogel. So the degradation amount reduces. In addition, it is observed that the modulus of the CMCH increases at first, then decreases with the crosslinker amount increasing. It may be attributed to the number of the efficacious net chains per volume enhancing (Okay & Durmaz, 2002). Whereas when the mass ratio of the crosslinker to Na-CMC is more than 0.2, the elastic hydrogel may turn into soft one, and separate into two phases, solid and liquid, with a further increase of crosslingker amount. At this time, the hydrogel becomes rigid and loses its elasticity, the modulus falls down. So the suitable mass ratio of the crosslinker to Na-CMC is between 0.15 and 0.20 if modulus is the primary factor to be considered.

Fig. 2 shows the effects of amount of water on the modulus and DP of CMCH. The mass ratio of the crosslinker to the Na-CMC is 0.13, change amount of water, and the other conditions are the same as in Fig. 1. The DP of the CMCH in buffer solution continuously goes up with water amount increasing. It is well known that the swelling ratio goes up when amount of water increases. The surface area of the xerogel film with same mass enlarges, which enhances the possibility of enzymes attacking the substrates. So it avails to CMCH degradation in buffer solution. But in the soil, the rate of degradation goes up first and then falls down when water mass ratio is more than 98.0%. It is because that high water content hinders oxygen from transferring in the substrates (Xia, 1999) and forms an anaerobic environment that makes against microbes growing, so DP reduces. On the contrary, we may find out that the modulus of the hydrogel continuously decreases along with water amount increasing. It is considered that the water exists in the hydrogel as three states (Hatakeyama, Hatakeyama, & Nakamura, 1995), that is, bound water, nonfreezing water and free water. Quantity of the free water in the nets of the gel increases with the increasing of the total amount of water, as a result, the compressible volume of the gel increases, thus the modulus reduces.

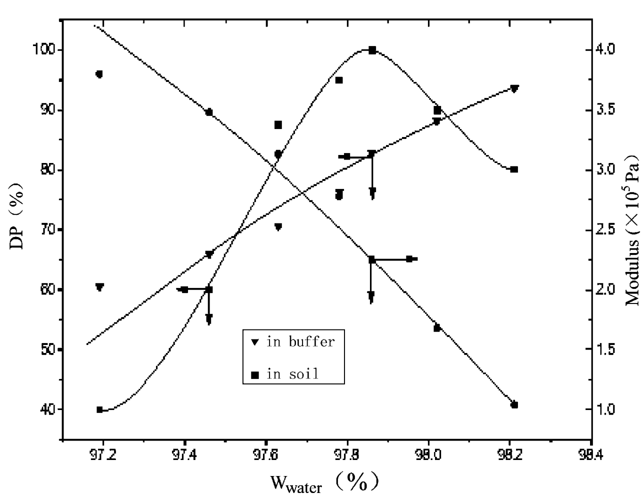

Fig. 2. Dependences of the modulus and biodegradation of CMCH on amount of water (2 g of $AlCl_3$, changing amount of water, other conditions same as in Fig. 1).

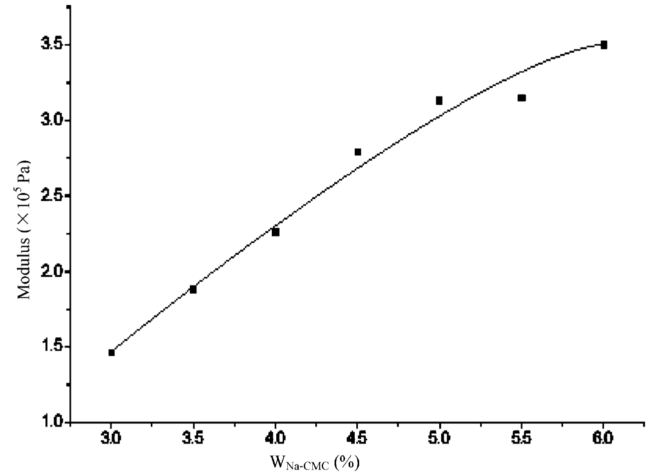

Fig. 3. Dependence of the modulus of CMCH on amount of CMC (2 g of $AlCl_3$, changing CMC amount, other conditions same as in Fig. 1).

Fix mass ratio of crosslinker to water at 2.7×10^{-3}, change Na-CMC amount, and the other conditions are the same as in Fig. 1. As shown in Fig. 3, the modulus of the hydrogel increases with the increasing of the amount of Na-CMC, it is due to that the content of solid ingredient increases with the amount of Na-CMC increasing. Moreover, the gel network structures, which formed by crosslinking Na-CMC with Al^{3+}, will become complex with the addition of Na-CMC.

In Fig. 4, the modulus of CMCH is plotted against reaction temperature. Fix the mass ratio of crosslinker to Na-CMC at 0.13, change the reaction temperature, and the other conditions are the same as in Fig. 1. The results indicate that the modulus of CMCH decreases with the temperature increasing. It should be born in mind that

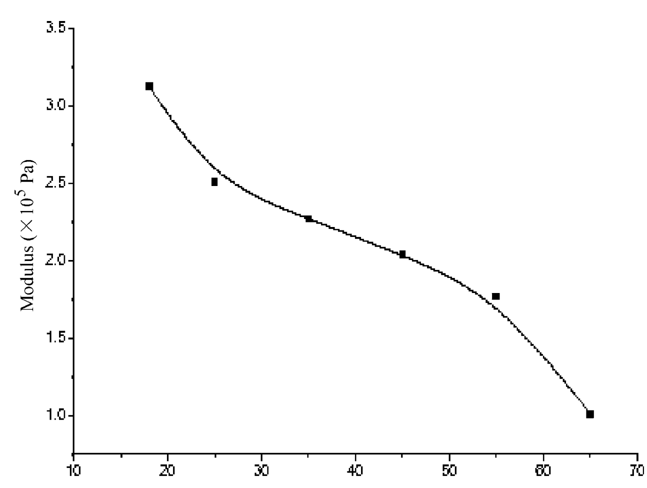

Fig. 4. Dependence of the modulus of CMCH on reaction temperature (2 g of $AlCl_3$, other conditions same as in Fig. 1).

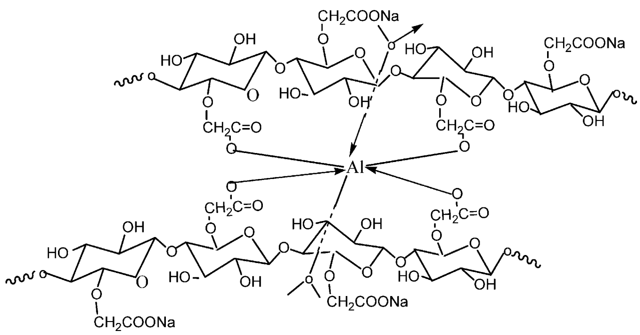

Fig. 5. CMCH framework (2 g of $AlCl_3$, other conditions same as in Fig. 1).

the hydrogel structure(shown as Fig. 5), formed through Al^{3+} crosslinking Na-CMC, is stable at low temperature and easily decomposes at high temperature. Additionally, it can be observed from the experiment that the hydrogel turns from elastic state to soft one when temperature rises. So the room temperature (25 °C) is suitable for the reaction.

3.2. Biodegradation of CMCH in soil

The hydrogel based on Na-CMC, a ramification of natural cellulose, can be decomposed by the microbes which exist in air and in water. Therefore, to ensure the stability of CMCH before using, antiseptic was added in the preparation of the hydrogel. Fix the mass ratio of crosslinker to Na-CMC at 0.13, change amount of antiseptic, and the other conditions are the same as in Fig. 1. The dependence of biodegradation of CMCH on amount of antiseptic (antiscorbutic, $C_6H_8O_6$) is shown in Fig. 6. The curve show that the rate of biodegradation of CMCH is decreasing with the antiseptic amount increasing. As we know antiseptic can disturb the function of enzyme in bacterium cell in some way to weaken the activities of enzyme. However, the stability during reservation is the basic requirement for

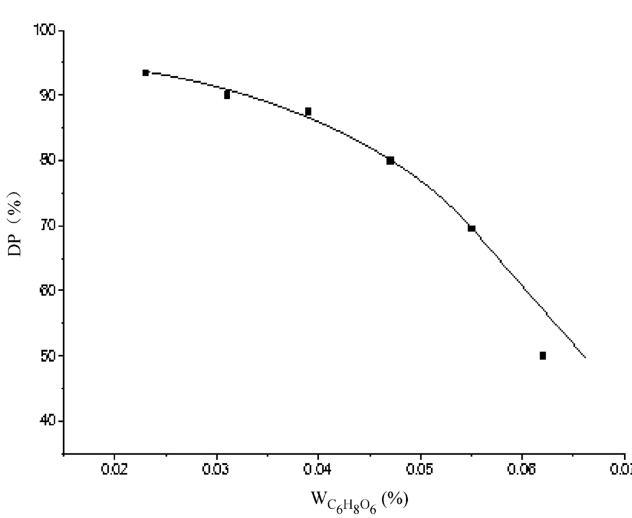

Fig. 6. Dependence of biodegradation of CMCH on amount of antiseptic (2 g of $AlCl_3$, changing antiscorbutic amount, other conditions same as in Fig. 1).

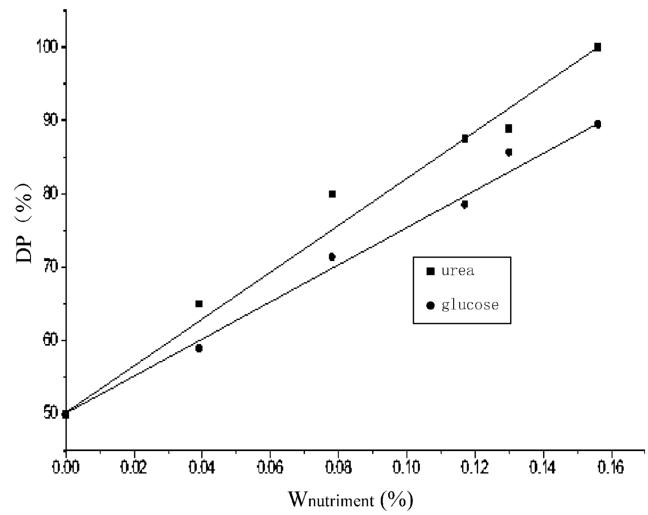

Fig. 7. Dependence of biodegradation of CMCH on amount of nutritive element (2 g of $AlCl_3$, changing urea (glucose) amount, other conditions same as in Fig. 1).

CMCH, so the amount of antiseptic should be as little as possible in order to ensure the stability of CMCH before using.

The hydrogel with antiseptic can not be decomposed entirely during the anticipation time, so adding some nutriment is necessary to accelerate the rate of biodegradation. Fig. 7 represents dependence of biodegradation of CMCH on amount of nutritive element. Fix the mass ratio of crosslinker to Na-CMC at 0.13, change amount of nutriment, and the other conditions are the same as Fig. 1. As is shown in Fig. 7, after adding nutriment, especially urea, the rate of CMCH biodegradation is obviously accelerated. The degradation of organic substance in soil is affected by the ratio of carbon to nitrogen in environment as well as by its own property. In a certain range, the rate of degradation is proportional to the increasing of the nitrogen concentration. But it is well known that nitrogen, a necessary nutriment to microbes, is generally deficient in soil, which restraints the activities of the microbes. So adding urea can increase the biodegradation rate of CMCH. The result is well consistent with the report (Maťková & Kunc, 1988). In addition, it must be born in mind that most of microbes grow up slowly when cellulose is the only source of carbon. Glucoses that can be easily assimilated by microbes are added, which provides nutriment of carbon to microbes. Then the microbes propagate quickly, the degradation rate of CMCH increases too.

Fig. 8 illustrates biodegradation rates of CMCH in different soils. It is shown in Fig. 8 that the degradation rates in different soils are different. Say, the rate is fast in sand soil, slow in damp soil, slower in clay soil. The abilities of holding water and aerating air are both different in different soils because of their different sizes of soil particles. There really exist lots of viscous particles and holes in clay soil, but most of the holes are held by liquids, which make

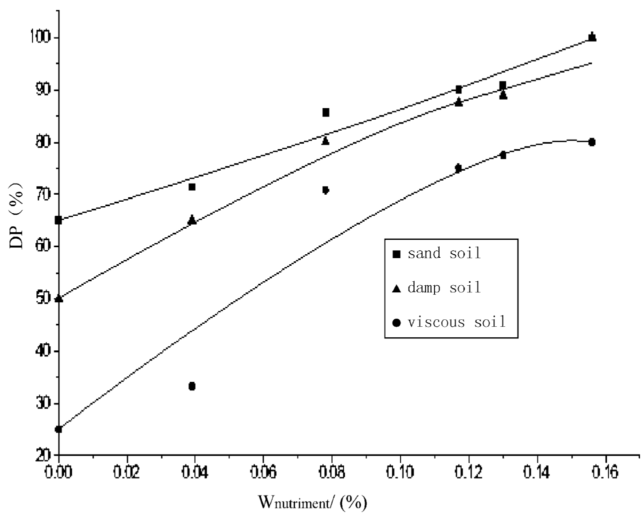

Fig. 8. Biodegradation of CMCH in different soils (2 g of $AlCl_3$, changing urea (glucose) amount, other conditions same as in Fig. 1).

against aerating air and result in the biodegradation of hydrogel to be weak. The holes in sand soil are bigger than that of clay soil, which are in favor of aerating oxygen and enhancing the activities of microbes. So the degradation rate of hydrogel increases (Lin, 1981). The damp soil is obviously viscous and moist, moreover, most of the free water is released with the hydrogel decomposed, all the active factors can restrict the supplying of oxygen to the microbes, then an anaerobic condition forms around the hydrogel. So the degradation rate of the hydrogel decreases.

4. Conclusions

Na-CMC hydrogel can be prepared by Na-CMC crosslinked with Al^{3+}. Its modulus can reach 3.13×10^5 Pa, when the amount of crosslinker, water, antiseptic and urea are, respectively, 0.26, 97.6, 0.039 and 0.117% of the whole reactant mass at room temperature. Antiseptic addition as a stability cannot contribute to the degradation in soil, but adding nutriment can accelerate the rate of degradation. Modulating their proper amount will not only ensure the stability before using but also adjust its degradation rate in using. The biodegradation rates of the hydrogel are different in different soils, and in sand soil the percentage of degradation is more than 50% during three months, so we believe it will have a better foreground in agriculture and forestry.

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