Effects of CMC Molar Mass on Mechanical Properties of CMC-Acid Gel

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Carboxymethyl cellulose (CMC) with different molar mass was prepared by acid hydrolysis at 121°C. CMC thus prepared was mixed with citric acid aqueous solution to form CMC-acid gel. By replacing sodium existing as counter ion in carboxymethyl group with hydrogen, CMC molecules coagulate and hydrogen bonds are formed among CMC molecules. The CMC-acid gel prepared in that way was subjected to evaluation of gel fraction, water absorption and mechanical properties. Gel fraction was higher in CMC with higher molar mass than that in CMC with lower molar mass at short incubation time. However, there was no difference in gel fraction attributable to molar mass of CMC after long time incubation. CMC with higher molar mass crosslinked more easily than CMC with lower molar mass. The gel made of CMC with lower molar mass was softer and absorbed more amount of water than that with higher molar mass. All the results were elucidated by number of hydrogen bonds in CMC molecule. The gel made of higher molar mass CMC becomes stiff and brittle after long time incubation, however, the gel made of lower molar mass CMC keeps softness and strength longer.

Key words: CMC, molar mass, acid, gel, hydrogen bond

1. INTRODUCTION

Carboxymethyl cellulose (CMC) is a widely used water-soluble polymer derived from wood pulp. Because of its safe and environmentally friendly properties, its use extended after gelation by multivalent metal ions, crosslinking agents and radiation crosslinking. We found that CMC formed a gel (CMC-acid gel) by mixing with acid [1]. The mechanism of gel formation was elucidated as a replacement of sodium with hydrogen in carboxymethyl group existing as a counter ion. Commercial CMC is generally in the form of sodium salt owing to the production process. CMC in the form of sodium salt is easily soluble in water, however, it is not soluble in water once it is replaced with hydrogen. As the result, CMC molecules became close enough to form hydrogen bonds between the molecules and gel was formed in this way. The resultant gel is elastic, adherent and strong. Those characters were very specific as for

polysaccharide gels.

We have examined the properties of CMC-acid gel consisting of CMC and Konjac glucomannan (KM), in which KM with different molar mass was used. The mechanical properties depended on the molar mass of KM [2]. When KM with higher molar mass was used, the gel was more elastic than that prepared by using KM with lower molar mass.

We have reported a method to decrease molar mass of polysaccharides using acid hydrolysis at elevated temperature and pressure [3]. By the method, KM with varieties of molar masses was prepared without chemical structural changes. Applying the method, CMC was hydrolyzed with citric acid to prepare CMC with various molar masses.

As we have not examined the effects of molar mass of CMC on mechanical properties of the CMC-acid gel in the former report [2], the effects are examined in the present work to seek

application areas of CMC-acid gel.

2. EXPERIMENTAL

2.1 Materials

CMC 1380 having degree of substitution of 1.36 and viscosity of 1820 mPa·s (1% solution, 25°C), produced by Daicel Chemical Industries, Ltd., Japan, was used throughout the experiment. It was in the form of sodium salt owing to its preparation process. Citric acid was reagent grade and used as received.

2.2 Hydrolysis

CMC was mixed with 0.05 M citric acid solution at the concentration of 20%. For mixing, a hybrid defoaming mixer (AR-250, Thinky Cooperation, Japan) was used. After mixing, the mixture in paste was transferred into an autoclavable polypropylene bag. Autoclaving was performed at 121°C for 1–30 min using a table top autoclave (Pasolina IST-150, Chiyoda Seisakujo, Japan).

2.3 Molar mass measurement

Original and hydrolyzed CMC samples were dissolved in 50 mM aqueous NaNO₃ solution and filtered with 0.45 µm cellulose acetate membrane filters (Millipore), and molar mass of the CMC was measured by multiangle static light-scattering (MALS) system equipped with a size exclusion chromatography (SEC) column of GMPW_{XL} (Tosoh) as described in the former paper [3].

2.4 FT-IR measurement

FT-IR spectra of CMC before and after hydrolysis were measured by Magna 560 + Continuum MII (Nicolet, Thermo Fisher Scientific K.K.).

2.5 Gelation of CMC

Using the hybrid defoaming mixer, the autoclaved sample was mixed with citric acid solution. The final concentrations of CMC and 0.5 M citric acid were 10% and 90%, respectively.

The mixture was molded into a cylinder with a thickness of 10 mm and a diameter of 20 mm. The cylinders were kept at 30 or 50°C to be served for the measurement of mechanical properties.

2.6 Mechanical properties of CMC-acid gel

Mechanical properties of the gels were measured using a table-top universal tester (EZ-Test, Shimadzu Co.). The CMC-acid gel cylinders were pressed at 2 mm/min.

2.7 Gel fraction and water absorption

After weighing the cylinders, they were immersed in purified water for 2 days to remove uncrosslinked CMC (soluble CMC) and acid. Then the samples were dried and weighed. The gel fraction and amount of water absorbed by the gel were defined as follows:

$$\text{Gel fraction (\%)} = 100 \times W_g/W_i$$

where W_i and W_g are the weights of initial dry CMC, and insoluble part after immersing in water, respectively.

$$\text{Water absorbed by gel} = (W_s - W_g)/W_g$$

where W_s is the weight of swollen hydrogel.

3. RESULTS AND DISCUSSION

3.1 Effects of hydrolysis on molar mass and chemical structure of CMC

Molar mass of CMC hydrolyzed by 50 mM citric acid at 121°C decreased with increase of autoclaving time as shown in Fig. 1.

The hydrolysis did not cause any big change in CMC as shown in Fig. 2. Carboxylmethyl group around 1620 cm⁻¹ was the same in both CMC before and after hydrolysis with 50 mM citric acid at 121°C.

3.2 Gel fraction

The hydrolyzed CMC and 0.5 M citric acid were mixed to prepare CMC-acid gel. Gel fraction was plotted against molar mass as shown in Fig. 3 and clearly showed that CMC with higher molar mass was crosslinked more easily than CMC with lower molar mass. The gel fraction increased with incubation time.

Fig. 1 Relation between autoclaving time and molar mass of CMC hydrolyzed by 50mM citric acid at 121°C.

CMC-acid gel incubated at 50°C gave higher gel fraction than that incubated at 30°C at the initial stage of gelation, namely on the 4th day of incubation. Incubation at higher temperature causes quicker hydrogen bond formation among CMC molecules.

3.3 Water absorption by gel

Water absorbed by gel increased with decrease of molar mass of CMC, and decreased with incubation time as shown in Fig. 4. Incubation at 50°C decreased water absorption because of the progress of hydrogen bonds formation among CMC molecules.

3.4 Mechanical properties of gel

Compression modulus of CMC-acid gel is shown in Fig. 5. Compression modulus decreased with decrease of molar mass meaning that gel became

softer. The high value in compression modulus using CMC with smaller molar mass less than 500,000 Da reflects hard sample stage of the universal tester.

All gels incubated at 30°C were not broken after applying a load of 4.8 N/mm². Gels with less gel fraction (~80%) enlarged and did not recover the initial thickness after compression, however, the gels with higher gel fraction (80% ~) recovered the thickness after compression as shown in Fig. 6. Elastic and strong gels were formed.

Some of the gels incubated at 50°C broke after incubation as shown in Fig. 7. At 50°C, gelation proceeds rapidly compared to that at 30°C. Hydrogen bonds are formed among CMC molecules and the gels become brittle, however, gels made of smaller molar mass CMC keep elasticity longer.

Fig. 2. FT-IR spectra of CMC before (a) and after (b) hydrolysis by 50 mM citric acid for 10 min at 121°C.

Fig. 3 Relation between molar mass of CMC and gel fraction. Gels were kept; ○: 4 days at 30°C, △: 7 days at 30°C, ◇: 10 days at 30°C, □: 14 days at 30°C, ●: 4 days at 50°C.

Fig. 4 Relation between molar mass of CMC and water absorption by gel. Notations are the same with those shown in Fig. 3.

Fig. 5 Relation between molar mass of CMC and compression modulus. Notations are the same with those shown in Fig. 3.

Fig. 6 CMC-acid gel under compression test.

(A): before compression
(B): under compression
(C): immediately after compression
(D): after removing load for 3h

Fig. 7 Relation between molar mass of CMC and breaking strength. Gels were kept; ●: 4 days at 50°C, ▲: 7 days at 50°C, ◆: 10 days at 50°C, ■: 14 days at 50°C.

3.5 Schematic model of CMC-acid gel

CMC-acid gel composed of higher molar mass CMC has more crosslinking point in one CMC molecule than that composed of lower molar mass CMC, as shown in Fig. 8. With the increase of incubation time and rise of the incubation temperature, the number of hydrogen bonds in CMC molecule increases and CMC-acid gel becomes stiff and fragile after incubation. When CMC with low molar mass was used for gel formation, hydrogen bonds formation proceeds gradually and gradually, keeping the CMC-acid gel elastic and strong for a long time.

4. Summary

CMC-acid gels with different mechanical properties were prepared by using CMC with different molar mass. As CMC is an environmentally friendly polymer, applications of CMC-acid gels to some fields which require considerable strength and elasticity are suggested.

Fig. 8 Simplified schematic model of CMC-acid gel.

A and C: CMC with high molar mass, B and D: CMC with low molar mass. A and B: Initial stage of gelation, C and D: Latter stage of gelation. Solid and dotted lines show CMC molecule and hydrogen bond, respectively.

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