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Preparation and Characterization of CMC-Konjac Mannan Mixture Gel

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Carboxymethyl cellulose (CMC) forms a gel when mixed with acid as a result of replacement of sodium in carboxymethyl group with hydrogen; hydrogen bonds are formed among CMC molecules. CMC gel gets new property by mixing with konjac mannan (KM). KM is a water soluble glucomannan with high molar mass and has high viscosity in low concentration aqueous solution. The molar mass of KM is easily decreased by γ-irradiation. Novel CMC-KM mixture gel is made by two processes; (1) mixing CMC with KM solution, (2) immersing CMC-KM mixture paste in hydrochloric acid aqueous solution. Mechanical properties of CMC-KM mixture gel and CMC gel were measured by a material tester. CMC-KM mixture gel was more elastic than CMC gel when high molar mass KM was mixed with CMC. When low molar mass KM was mixed with CMC, properties of CMC-KM mixture gel were similar with those of CMC gel. It was because KM molecules are entangled with CMC molecules when high molar mass KM was used. Interaction of CMC and KM was elucidated by FT-IR.
Keyword: carboxymethyl cellulose, konjac mannan, gel, acid

1. INTRODUCTION

Carboxymethyl cellulose (CMC) is a water soluble polysaccharide having various application fields such as civil engineering, oil drilling, fish feed, food additives, pharmaceuticals, and textile printing. CMC forms a gel when mixed with acid as a result of replacement of sodium in carboxymethyl group with hydrogen. The replacement makes the solubility of CMC decrease, CMC molecules coagulate, and thus hydrogen bonds are formed among CMC molecules. [1]

If CMC can form mixture gel with other material in the presence of acid, the gel shows different properties with CMC gel.

We have carried out research work on Konjac mannan (KM) with different molar mass. [2, 3] KM has high molar mass and high viscosity in low concentration aqueous solution in nature. While KM with high molar mass forms gel under alkaline conditions, KM with lower molar mass does not form gel. Molar mass of KM will have a big effect on CMC-KM mixture gel. The molar mass of KM can be easily decreased by γ-irradiation.

The aims of this study are to examine mechanical properties of CMC-KM mixture gel and elucidate the effect of KM molar mass on characteristics of CMC-KM mixture gel.

2. EXPERIMENTAL

2.1 Materials

Carboxymethylcellulose (CMC) 1380 (sodium salt, DS=1.36, Daicel Chemical Industries, Ltd, Japan) was used all through the experiment. Konjac mannan (Akagi Odama, H18) was used for a part of the experiment. The chemicals used were reagent grade and used as received.

KM was irradiated with γ-rays at 1-30 kGy. Molar mass of each KM is shown in Table I. Molar mass was measured by SEC (Size Exclusion Chromatography, Shimadzu).

2.2 Preparation of CMC Gel

10 g of CMC was mixed with 90 g of water using a hybrid mixer ARE-250 (THINKY). 10% CMC paste was made into a sheet with the thickness of 1mm by pressing. The sheet of CMC paste was immersed in 0.5 M hydrochloric acid for 8 h, 16 h, 32 h and 64 h. Thus 10% CMC gel sheet was obtained.

2.3 Preparation of CMC-KM mixture gel

At first, 2 g of each KM was completely dissolved in 90 g water. CMC-KM mixture paste was prepared by mixing 8 g of CMC and 92 g of KM aqueous solution by the mixer and pressed to form sheet with the thickness of 1 mm. CMC-KM mixture gel was made by immersing CMC-KM mixture paste in 0.5 M hydrochloric acid. Immersion time was 8 h, 16 h, 32 h and 64 h.

Table I Molar mass of γ-irradiated KM

Absorbed dose (kGy)	0	1	2	4	10	20	30
Molar mass (10^5g/mol	12.6	11.0	9.90	7.67	4.66	2.53	1.96

2.4 Mechanical Properties of Gel

Mechanical properties of gel was measured using a Compact Table-Top Universal Material Tester (EZ-Test, Shimadzu Co.). The gel sheets of CMC and CMC-KM mixture were cut into strips with the size of 50 mm × 10 mm. Young's modulus, elongation and breaking strength were measured. The samples were elongated at the seed of 5 cm/min.

2.5 FT-IR

Gels after drying were crashed into fine powder using a Freezer Mill (SPEX 6700).

FT-IR spectra of the gels were measured by Magna 560 + continuμm II (Nicolet, Thermo Fisher Scientific K.K.).

3. RESULTS AND DISCUSSIONS

3.1 Effect of Immersion Time in Hydrochloric Acid

All CMC dissolved in water without immersion in acid. CMC paste became insoluble in water after immersion in 0.5 M hydrochloric acid. The gel was soft and extensible.

It is known that sodium in CMC is replaced with hydrogen by immersing CMC in acid. The replacement makes the CMC solubility less and makes the distance among CMC molecules closer. Accordingly, hydrogen bonds are formed between CMC molecules, and thus gel is formed.

Young's modulus of CMC and CMC-KM (high molar mass) mixture gels immersed in acid are shown in Fig.1. Young's modulus increased slightly in CMC gel with immersion time, however, it showed maximum value for 16 h immersion and decreased after longer time immersion in CMC-KM mixture gel. CMC-KM mixture gel is more elastic than CMC gel. CMC gel is not strong, however, CMC-KM mixture gel is much stronger. The reason of the maximum strength for 16 h immersion is elucidated as follows: CMC molecules shrink moderately when immersed for 16 h, however, CMC and KM molecules distribute uniformly. But CMC molecules shrink more after 32 h and 64 h immersion, CMC and KM molecules separate, and they become weaker than those immersed for 16 h.

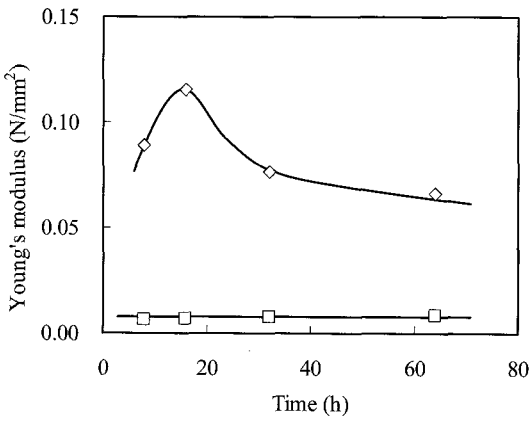

Fig.1. Young's modulus of CMC and CMC-KM mixture gels.
◊: CMC-KM mixture gel, □: CMC gel

Elongation of the CMC gels is shown in Fig. 2. together with that of CMC-KM mixture gel. Elongation of CMC gel was almost constant regardless of the immersion time. Elongation of CMC-KM mixture gel decreased with immersion time. By immersion in acid, the movement of CMC-KM is restricted and loose elasticity.

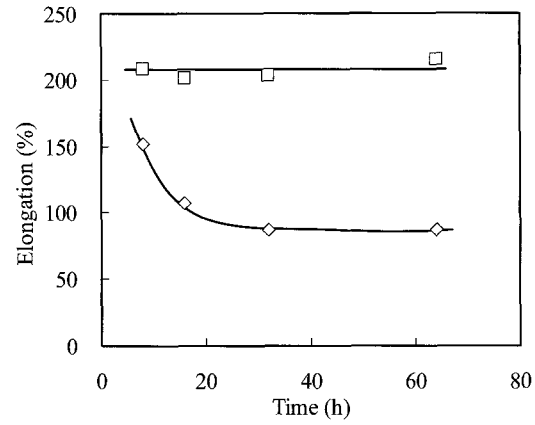

Fig.2. Elongation of CMC and CMC-KM mixture gels.
◊: CMC-KM mixture gel, □: CMC gel

Breaking strength is shown in Fig.3. Breaking strength increased with immersion time in CMC gel, however, it showed a maximum for 16 h immersion in CMC-KM mixture gel in the same way with Yung's modulus.

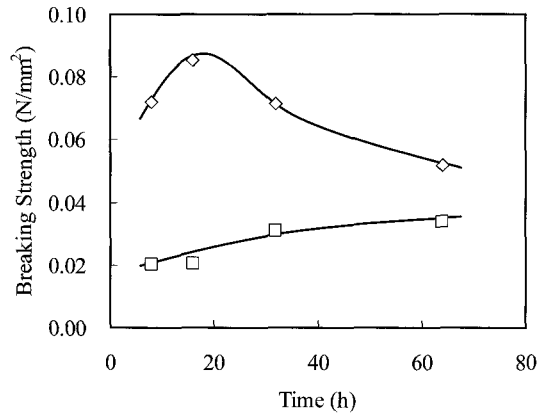

Fig.3. Breaking strength of CMC and CMC-KM mixture gels.
◊: CMC-KM mixture gel, □: CMC gel

3.2 FT-IR Spectra

FT-IR spectra of CMC and CMC gel are shown in Fig. 4. CMC before immersing in hydrochloric acid had COO^- group around 1600 cm^{-1}. But CMC immersed in hydrochloric acid changed from COO^- group to COOH group around 1730 cm^{-1}. We can understand that sodium carboxylate turned to carboxyl group.

FT-IR spectra of CMC-KM gel are shown in Fig. 5. Difference between CMC gel and CMC-KM gel was hardly observed. They were almost the same.

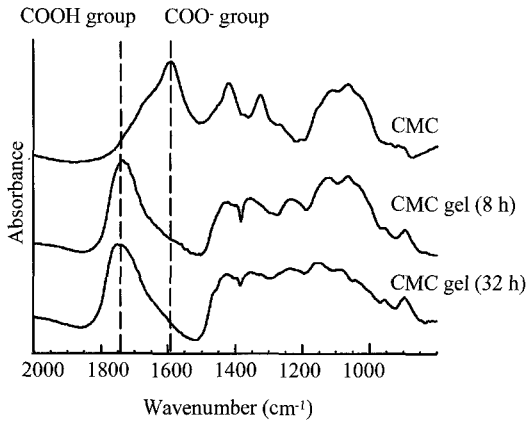

Fig.4. FT-IR of CMC gel.

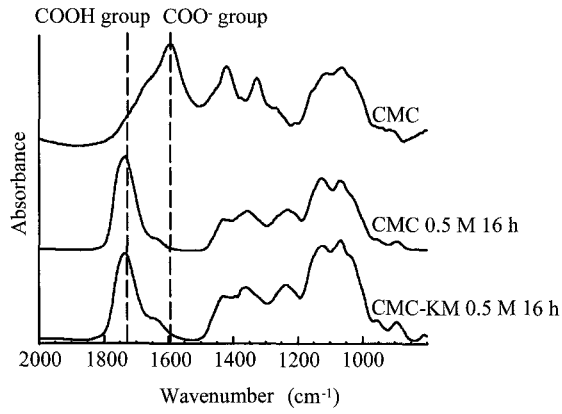

Fig.5. FT-IR of CMC-KM mixture gel and CMC gel.

3.3 Influence of Molar Mass of KM on Gel

Molar mass of KM decreased by γ-irradiation. Mechanical properties of CMC-KM mixture gel were greatly depended on molar mass as shown in Figs. 6-8.

Young's modulus of CMC-KM mixture gel is shown in Fig.6. CMC-KM mixture gel was more elastic than CMC gel when molar mass of KM was higher than 1,000,000. But young's modulus of CMC-KM mixture gel was almost the same with that of CMC gel when molar mass of KM was lower than 500,000.

Elongation of CMC gels is compared to that of CMC-KM mixture gel as shown in Fig.7. Elongation decreased gradually with decrease of molar mass from high to middle molar masses, and then increased with decrease of molar mass.

Breaking strength of CMC-KM mixture gel was compared with that of CMC gel as shown in Fig.8. Breaking strength of CMC-KM mixture gel was bigger than that of CMC gel. It showed almost the same tendency with their young's modulus.

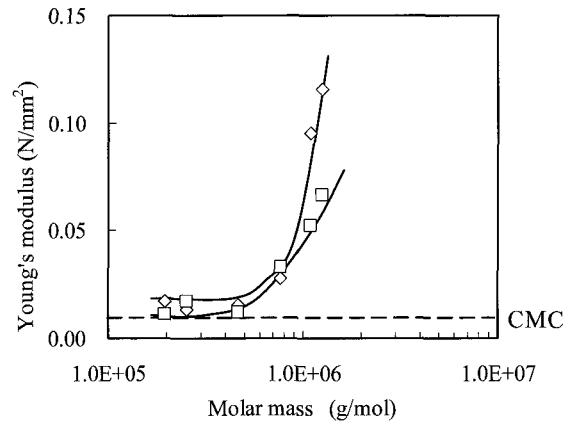

Fig.6. Young's modulus of CMC-KM mixture gel prepared using KM with different molar mass.
◊: Immersion time 16 h, □: Immersion time 64 h

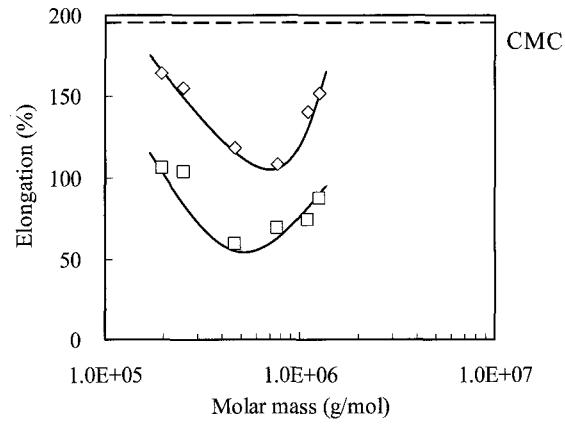

Fig.7. Elongation of CMC-KM mixture gel prepared using KM with different molar mass.
◊: Immersion time 8 h, □: Immersion time 64 h

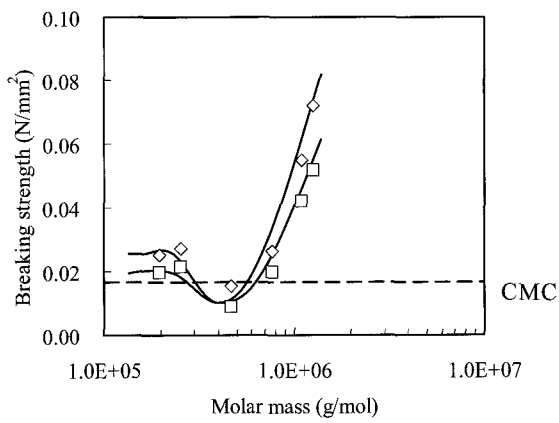

Fig.8. Breaking strength of CMC-KM mixture gel prepared using KM with different molar mass.
◊: Immersion time 8 h, □: Immersion time 64 h

CMC-KM mixture gel was more elastic when mixed with high molar mass KM. But it was not more elastic than high molar mass KM when low molar mass KM was used. These results are thought that CMC-KM mixture gel become tougher when KM molecules were entangled with CMC molecules; KM with high molar mass can be entangled with CMC. But KM with low molar mass cannot be entangled with CMC. CMC-KM mixture gel behaves like CMC gel when low molar mass KM was used. KM with low molar mass seems to have little interaction with CMC.

References

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