Effect of KM Molar Mass on CMC-KM-Acid 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 having new properties can be formed by mixing CMC with other materials. Konjac glucomannan (KM) is a water-soluble glucomannan with high molar mass and has high viscosity in low concentration aqueous solution. Previous study showed that CMC-KM-acid gel was stronger than CMC-acid gel, however, the strength depended on the molar mass of KM. When KM with high molar mass was mixed with CMC and acid, the gel was uniform, however, turbid at first glance, showing that compatibility of CMC and KM with high molar mass was not so good. However, when KM with low molar mass was mixed with CMC and acid, the gel was uniform and transparent, showing good compatibility of CMC and KM. Molar mass of KM showing good compatibility was less than 300 kDa. Scanning electron micrographs taken under moist condition clearly showed uneven and even surfaces for gels made using high molar mass and low molar mass KM, respectively. The compatibility of CMC and KM affected the mechanical properties of the CMC-KM-acid gels.

Key words: carboxymethyl cellulose, konjac mannan, gel, acid, compatibility

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 a mixture gel with other material in the presence of acid, the gel shows different properties from CMC gel.

Konjac glucomannan (KM) has high molar mass and high viscosity in low concentration aqueous solution in nature. Traditional Japanese food “Kon-nyaku” is prepared by adding alkaline solution to the paste-like mixture of Konjac flour and water. While KM with high molar mass forms high quality “Kon-nyaku” gel under alkaline conditions, KM with lower molar mass does not give highly elastic gel.

The molar mass of KM can be easily decreased by acid hydrolysis at 121°C [2] and γ-irradiation [3, 4]. Previous study showed that CMC and KM gave a gel in the presence of acid. CMC-KM-acid gel was stronger than CMC-acid gel, however, the strength depended on the molar mass of KM [5]. In the present study, effects of molar mass on mechanical properties of CMC-KM-acid gel and compatibility of CMC and KM will be discussed.

2. EXPERIMENTAL

2.1. Materials

Carboxymethyl cellulose (CMC) 1380 (sodium salt, DS=1.36, Daicel Chemical Industries) was used all through the experiment. Konjac glucomannan (KM, Akagi Odama sp.) used was commercial konjac flour. Other chemicals used were reagent grade and used as received.

2.2 Hydrolysis of KM

KM was dissolved in citric acid aqueous solution, and pressurized at 0.247 MPa for 20 min using a pressure cooker. Concentrations of KM and citric acid were 3% and 0-50 mM, respectively. Thus, KM samples with various molar masses were prepared.

2.3 Molar mass measurement

Molar mass of KM sample was determined by a multiangle laser light-scattering (MALS) using MALS detector from DAWN DSP (Wyatt Technology) with a vertically polarized He-Ne laser operated at wavelength of 632.8 nm. The photometer was connected to a size exclusion chromatography (SEC) column of GMPWXL ( Tosoh) and a differential refractive index detector RI-71S (Shodex). The temperatures of the MALS flow cell and the column were controlled at 40°C.

The KM sample solution was filtered through a 0.45 μm cellulose acetate membrane filter (Sartorius). Scattered light intensities at scattering angle between 15° and 163° were measured. The angular dependence
of the scattering intensity was analyzed using Berry’s square-root plot to determine the radius of gyration ($R_g$) and molar mass at each position of the peak. 50 mM sodium nitrate aqueous solution was used as both solvent and eluant at 1 mL/min.

2.4 Preparation of CMC-acid gel

The 10% of CMC-acid paste was prepared by mixing 10 g of CMC with 90 g of 0.5 M citric acid using a hybrid mixer ARE-250 (THINKY). The CMC paste was made into a sheet with a thickness of 1 mm by pressing. The sheet was stored in an incubator at 30°C. Thus, CMC gel sheet was obtained. The storage time was from 7 days to 56 days.

2.5 Preparation of CMC-KM-acid gel

The hydrolyzed KM solution prepared as described in section 2.2 was mixed with citric acid solution using the hybrid mixer. Then, CMC was added to the solution and mixed using the mixer. The final concentrations of CMC, KM and 0.5 M citric acid in CMC-KM-acid paste were 9%, 1% and 90%, respectively. The paste was pressed to make a sheet with a thickness of 1 mm and the sheet was stored in the incubator at 30°C.

2.6 Gel fraction and water absorption

Gel is defined as an insoluble part after immersing the CMC-KM-acid paste in water. Gel fraction means weight % of gel compared to the combined initial weights of CMC and KM. Water absorption is defined as weight of water absorbed by 1 g gel.

2.7 Mechanical property measurement

Mechanical properties of the gel (strictly speaking, it is not gel, however expressed as gel hereafter) were measured using a compact table-top universal material tester (EZ-Test, Shimadzu). The sheets of CMC-acid gel and CMC-KM-acid gel were cut into strips with a size of 60 mm × 10 mm. Elongation and breaking strength by tensile test were measured. The samples were elongated at the speed of 5 cm/min.

2.8 Scanning electron microscopic observation

CMC-acid gel and CMC-KM-acid gel were observed by a scanning electron microscope (Quanta200 FEG, FEI Company). Observations were carried out under wet and dry conditions. Accelerating voltage was 10 kV in both conditions. Pressure was 5.4–5.7 Torr and humidity was 100% in wet condition, however, pressure was 0.10–2.0 Torr and humidity was 2–30% in dry condition.

3. RESULTS AND DISCUSSIONS

3.1 Molar mass distribution of hydrolyzed KM

Original KM has high molar mass and narrow molar mass distribution ($M_w/M_n=1.04$, where $M_w$ and $M_n$ stand for weight and number average molar mass, respectively). KM was hydrolyzed by citric acid under pressurization. As shown in Fig. 1, molar mass decreased and molar mass distribution of hydrolyzed KM broadened with increase of acid concentration. The decrease of molar mass is caused by the main chain scission of KM inducted by the hydrolysis.

3.2 Effects of acid concentration on molar mass and weight average $R_g$ of hydrolyzed KM

Effects of acid concentration on molar mass and weight average radius of gyration ($R_g$) of hydrolyzed KM are shown in Fig. 2. The values of molar mass and $R_g$ of 0 mM KM were 961 kDa and 96.8 nm, respectively. Molar mass of hydrolyzed KM decreased and weight average $R_g$ of hydrolyzed KM decreased with increase of acid concentration. It means weight average $R_g$ relates to molar mass of KM.

3.3 Appearance of CMC-KM-acid gel

CMC-KM-acid gels made of CMC and KM with the molar mass of more than 506 kDa and less than 247 kDa are turbid and transparent in appearance, respectively, as shown in Fig. 3. The compatibility of CMC and KM depends on molar mass of KM.
3.4 Gel fraction of CMC-KM-acid gel

Gel fraction of CMC-KM-acid gel is shown in Fig. 4. Gel fraction increased with decrease of KM molar mass. As the gel fraction for CMC-KM-acid gel exceeded 90% when lower molar mass KM was used, not only CMC but also KM were involved in gel formation. However, hydrogen bond formation among CMC and KM molecules is not certain yet. KM might be entrapped among CMC molecules in a way not being able to dissolve in water, without forming hydrogen bonds between CMC and KM. In gels made using higher molar mass KM, whether KM is included in the gel or not is not clear yet, because gel fraction is less than 90%. However, the difference of gels after immersion in water infers that KM is included in the CMC-KM-acid gel; gels made of high molar mass KM are turbid, while gels made of low molar mass are transparent.

3.5 Water absorption of CMC-KM-acid gel

Water absorption of CMC-KM-acid gel is shown in Fig. 5. Water absorption increased with decrease of KM molar mass and decreased with increase of storage time. As the hydrogen bonds formation among CMC molecules proceeds gradually at 30°C [6], gelation in CMC-KM-acid gel is expected to proceed gradually. Number of hydrogen bonds increases during storage and water absorption decreases with storage time.

3.6 Mechanical properties of CMC-KM-acid gel

Elongation of CMC-KM-acid gel is shown in Fig. 6. Elongation of CMC-KM-acid gel changed depending on molar mass of KM and storage time. Gels made of KM with lower molar mass elongated more than those made of KM with higher molar mass. There is a big gap in elongation between the molar masses of KM, 500 kDa and 300 kDa. With storage time, difference in elongation owing to molar mass of KM became less, elongation of CMC-KM-acid gel was almost constant regardless of the molar mass of KM and close to elongation of CMC-acid gel.

Breaking strength of CMC-KM-acid gel measured by elongation test showed different phenomena with elongation (Fig. 7). For short time storage, breaking strength was almost constant and close to that of CMC-acid gel. Then the difference in breaking strength of CMC-KM-acid gel owing to the molar mass became clearer. The biggest change was observed between the molar mass of 500 kDa and 300 kDa.

Molar mass of KM gave a big influence on mechanical properties of CMC-KM-acid gels. Gels made of KM with higher molar mass than 500 kDa were different from those made of KM with lower molar mass than 300 kDa.

3.7 Scanning electron microscopic observation of gels

Scanning electron micrographs (SEMs) of gels in wet condition are shown in Fig. 8. SEMs seemed uniform in CMC-acid gel and CMC-KM-acid gel made using low molar mass KM. However, SEM had unevenness in CMC-KM-acid gel made using KM with higher molar mass. The compatibility of CMC and KM observed by naked eyes was confirmed by SEM observation.

SEMs measured under dry condition are shown in Fig. 9. SEM of CMC-acid gel was uniform, however, SEMs of CMC-KM-acid gels had creases. The creases became distinct in gels placed in dry conditions longer. It means water evaporation from CMC and KM differs. Water binds more firmly to KM with higher molar mass and evaporates more gradually, while water binds loosely to CMC. The difference in water evaporation behavior between KM and CMC causes the creases when gel was placed in dry condition.
3.8 Schematic model of CMC-KM-acid gel

From the results mentioned above, a schematic model for CMC-KM-acid gel is proposed as shown in Fig. 10. Original KM molecules are too big in size to make uniform network with CMC in CMC-KM-acid gel. KM with lower molar mass can be entrapped in CMC network and behaves as a part of CMC network. That is the reason of good compatibility of CMC and KM with low molar mass. The boundary of KM molar mass to have good compatibility with CMC seemed to be around 300 kDa.

4. CONCLUSIONS

CMC-KM-acid gels were prepared by mixing hydrolyzed KM with CMC and mechanical properties of the gels were examined.
1) Mechanical properties of CMC-KM-acid gel and compatibility of CMC and KM is dependent on molar mass of KM.
2) CMC-KM-acid gel mixed with high molar mass KM is stiff, however, gel mixed with low molar mass KM is elastic.
3) Compatibility of CMC and KM in CMC-KM-acid gel depends on molar mass of KM. The boundary KM molar mass to have good compatibility is around 300 kDa.

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