Effect of Calcium Phosphate Precursor Salt on Gelation Temperature of Methylcellulose

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***Abstract*—The effect of methylcellulose (MC) concentration and calcium phosphate precursor salt concentration on the gelation of MC solution was studied by rheometer and attenuated total reflectance infrared (ATR-IR) spectroscopy. It was found that thermally induced gelation of MC was dependent on the concentration of MC and water hydration abilities of precursor salt for inorganic nanoparticle. At the constant concentration of MC, the gelation temperature was lowered with increasing salt concentration. This behavior had a similar tendency with MC concentration. From these results, the gelation temperature of MC could be simply controlled by changing the concentration of precursor salt or MC.**

Keywords-component; Hydrogel; methylcellulose; calcium phosphate; gelation temperature

I. INTRODUCTION

Stimuli responsive hydrogels exhibit a sol-gel transition in response to small changes in temperature, pH, light, electric field, and magnetic fields. These hydrogels have potential applications in biology and medicine fields, including drug delivery system, biochemical sensor and bio-engineering. Among these hydrogels, thermo-responsive hydrogels have been extensively investigated due to their simple application and low adverse effects on tissues, compared to other stimuli. In particular, the thermo-responsive properties make them potential candidates for drug delivery and tissue engineering. The common feature of thermo-responsive hydrogels is that they exhibit a sol-gel phase transition at certain temperature, and two types of thermal behavior are observed. One is lower critical solution temperature (LCST) and the other is upper critical solution temperature (UCST). Below the LCST, the polymers are soluble, and above the LCST, they form the gel mainly due to hydrophobic interaction. In contrast, polymer solutions with UCST form the gel upon cooling below the UCST. In general, the hydrogel with LCST than the UCST is often useful in biomedical fields.

Methylcellulose (MC) is one of cellulose derivatives with a certain degree of substitution of methyl groups, and is widely used in personal care products, foods and pharmaceutical applications. MC is well known to have LCST behavior due to their substituents. The thermal transition of MC solution is closely associated with concentration, heating rate and degree of substitution. Furthermore, thermo-responsive hydrogelation is also affected by salt. A salt, such as NaCl, has a greater affinity for water than MC, resulting in the removal of water from the hydrated polymer and thus a lowering of its sol–gel transition temperature due to an enhancement of the hydrophobic association of MC molecular chains. The gelation temperature of MC solution significantly decreases with increasing of the salt concentration. According to the Hofmeister, the effect of salt in reducing the gelation temperature becomes significant with increase in magnitude of anion. Then, the ability of salts to “salt out” or “salt in” effect is well classified in Hofmeister series.

In this study, the effect of MC concentration and precursor salt for inorganic nanoparticles on the gelation temperature of MC solution was investigated. Also, functional nanoparticles were *in situ* synthesized in MC hydrogel using two kinds of precursor salts, and the influence of nanoparticle and residue ion on MC gelation was examined.

II. EXPERIMENTAL

A. Materials

Methylcellulose (MC, 15 mPa • s viscosity, 28-29% methoxy content) was provided by SAMSUNG FINE CHEMICALS. Calcium chloride (CaCl2, KANTO CHEMICAL CO.) and sodium phosphate dibasic (Na2HPO4, SIGMA-ALDRICH) were used by calcium phosphate precursor salts for functional nanoparticles.

B. Methods

MC solutions were prepared by dissolving a specified weight of MC powder and salt in water. The solutions were vigorously agitated until the aggregates of powder were visually dispersed. And then, solutions were stirred for 24 h using magnetic stirrer to allow complete dissolution and hydration of MC.

III. RESULTS AND DISCUSSION

A. Effects of MC Concentration on Thermo-Reversible Gelation

The gelation behavior and temperature of MC (4, 6, 8, 10, 12 wt %) solutions was measured by using rheometer and attenuated total reflectance infrared (ATR-IR) spectroscopy. In these experiments, we observed that MC solutions formed gel at specific temperature and its temperature lowered with increasing MC concentration. Gelation temperature of MC (4, 6, 8, 10, 12 wt %) solution also decreased 37.38℃ to 22.39℃ with the concentration of polymer. Similar results were observed in the ATR-IR.

B. *Effects of Precursor Salt Concentration on Thermo-Reversible Gelation*

When a salt is added into a MC solution, the thermodynamic properties during gelation will be changed. Two types of the salts have different effect on the gelation temperature of MC. In this experiment, Na2HPO4 caused the sol-gel transition of MC at lower temperatures then CaCl2. The gelation temperature of 8 wt% MC solution with Na2HPO4 (0, 0.025, 0.05, 0.1 M) decreased 29.4℃ to 19.46℃ along with the salt concentration. Whereas, gelation temperature of 8 wt% MC solution with CaCl2 (0, 0.1, 0.3, 0.5 M) decreased 29.4℃ to 17.42℃ with the salt concentration. Similar results were observed in the ATR-IR.

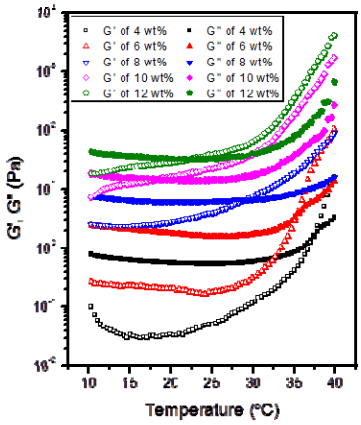

FIGURE I.GELATION BEHAVIOR OF MC (4, 6, 8, 10, 12 wt %)

IV. CONCLUSION

In this work, we investigated the effect of MC concentration and inorganic nanoparticle precursor salt concentration on the gelation temperature of MC solution. Also, we synthesized nanoparticles in MC hydrogel using two kinds of inorganic nanoparticle precursor salts and also examined the influence of nanoparticle and residue ion on MC hydrogel

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