Gelation mechanism of freeze-crosslinked cellulose nanofiber gels with high compressive strength

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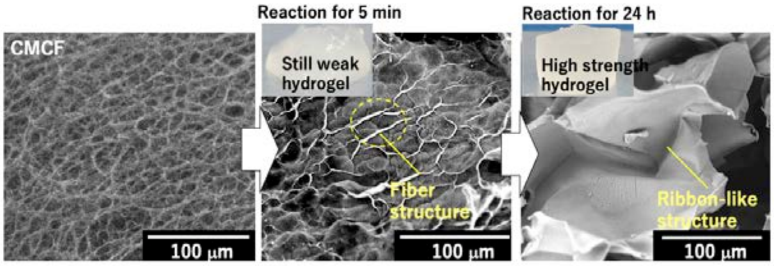
Cellulose nanofibers (CNFs) derived from natural polymers and their applications are promising raw materials, especially for medical and environmental applications. Developments of gelation methods of cellulose nanofibers, which are eco-friendly, non-toxic, and easily, are required for these applications. Recently, we developed a freeze crosslinking method to obtain a physically crosslinked hydrogel with high compressive strength and high compressive recoverability from carboxymethyl cellulose nanofiber (CMCF) and citric acid (CA)[1)]. The freeze crosslinked CMCF hydrogel was formed by adding an aqueous CA solution to a frozen CMCF sol and then thawing the sol. Without the freeze crosslinking method, the CMCF sol and CA complex produced hydrogels, which easily collapsed under compressive stress. The compressive strength of the freeze crosslinked CMCF hydrogel was approximately 200,000 times higher than that of the non-freeze crosslinked CMCF hydrogel. The result indicates that freezing is an important procedure to create a high strength hydrogel.

In this study, we investigated the gelation mechanism of the freeze crosslinked CMCF hydrogel by SEM observations, IR spectroscopy, and XRD methods using CMCF-CA mixtures during the gelation process. The samples were prepared by adding an aqueous CA solution to a frozen CMCF sol and then thawing the sol for 5 to 1440 min. The reaction between CMCF and CA was stopped by immersing the sample in a large amount~~s~~ of distilled water. From the SEM images of the samples, it was observed that CMCF bound to each other to form a larger ribbon-like structure with the reaction time. The IR spectra and XRD results also showed that the microscopic structure of CMCF changed due to the reaction with CA. We also demonstrated that the freeze crosslinked CMCF hydrogels are formed using other organic acids such as malic acid, ascorbic acid, succinic acid, and maleic acid. The results showed that the reaction between frozen CMCF sol and an organic acid solution created a ribbon-like structure that contributes to the high strength of the CMCF hydrogels.



1) Y. Sekine *et al.* , *ACS Appl. Polym. Mater.* **2020**, *2(12)*, 5842.