

## RECENT RESEARCH ACTIVITIES

**Preparation of tough hydrogels based on  $\beta$ -chitin nanofibers via NaOH treatment****(Laboratory of Active Bio-based Materials, RISH, Kyoto University)**

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Cellulose and chitin are some of the most abundant renewable polymers on earth. A key characteristic common to both is that they exist naturally in the form of highly crystalline nanofibers. They provide both rigid and flexible structural support in plant cell walls and in the exoskeletons of arthropods such as crustaceans and insects. Because of inferior mechanical properties such as low weight, very large surface-to-volume ratios and high aspect ratios, cellulose and chitin nanofibers have recently attracted significant interest for wide potential application in polymer reinforcement, flexible display, medical devices, separation membranes and many other areas.

The stable crystal structures in cellulose and chitin, however, prevent their molecules from dissolving in most common solvents. When hydrogels and aerogels are prepared from cellulose and chitin, for example, use of specific solvents such LiCl/DMSO and aqueous alkaline systems such as NaOH/urea (for cellulose), and calcium chloride dihydrate-saturated methanol and LiCl/NMP (for chitin) are essential. Not surprisingly, cellulose and chitin nanofibers do not dissolve in water. However, because the entanglement of their nanofibers creates a large hydrophilic surface area and high aspect ratios form a stable network in water, they are homogeneously dispersed. The result is very high viscosity, even with 1 wt% nanofiber. Their nanofibers appear to behave in water as if dissolved, maintaining good crystallinity.

In previous studies, we found that an aqueous suspension of cellulose nanofibers was easily transformed into stable and tough hydrogels through alkaline treatment<sup>1,2</sup>. The nanofiber hydrogels had two different kinds of cellulose crystal forms (cellulose I and cellulose II) in response to increasing concentrations of NaOH(aq) solutions, and both gels consisted of a highly porous and crystalline nano-network. In particular, the nanofiber gel with cellulose II demonstrated high tensile strength due to the continuous and strong nano-network formed by the interdigitation of nanofibers during the mercerization process in the crystal conversion from cellulose I to cellulose II. Based on these results, the present study applied the gel preparation to chitin nanofibers. Like cellulose, the crystal structure of  $\beta$ -chitin is converted to  $\alpha$ -chitin by NaOH(aq) treatment. We studied the gelation behavior of  $\beta$ -chitin nanofibers and investigate the physical and morphological properties of the hydrogels.

The crystal structure of chitin nanofibers (Figure 1), which were extracted from purified squid pen powder, was transformed from  $\beta$ -chitin to  $\alpha$ -chitin by NaOH(aq) treatment above 30 wt%. The crystal conversion involving the interdigitation among adjacent nanofibers caused the formation of stable hydrogels with a  $\alpha$ -chitin nanofiber network (Figure 2). The use of ethanol voided the dissolution during neutralization and enabled preparation of a highly crystalline hydrogel with high mechanical strength. It achieved a Young's modulus of 16.6 MPa, a tensile strength of 7 MPa and a strain at break of 52.2%, on average. Finally, we note that the shrinkage of the cellulose I and  $\beta$ -chitin nanofibers in aqueous NaOH solutions was caused by the release of residual stress due to the intracrystalline swelling in NaOH solutions.

**References**

- [1] Abe, K., Yano, H., "Formation of hydrogels from cellulose nanofibers", *Carbohydrate Polymers* 85, 733–737, 2011
- [2] Abe, K., Yano, H., "Cellulose nanofiber-based hydrogels with high mechanical strength" *Cellulose* 19, 1907–1912, 2012

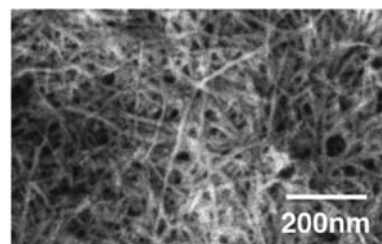
Figure 1. FE-SEM micrograph of  $\beta$ -chitin nanofibers.

Figure 2. Chitin nanofiber-based hydrogels prepared at 35 wt% NaOH.