Surface chemical modification of cellulose nanofiber (octanoylation)

(Laboratory of Active Bio-based Materials, RISH, Kyoto University)

Naoki Yoshida

Surface chemical modification has potentials for broadening application of cellulose nanofibers (CNF). For chemical modification, it is necessary to exchange solvent dispersing CNFs from water to polar aprotic solvent. In this case CNFs have not to be aggregated and water has to be removed completely. Conventional solvent exchange method (by centrifugation or freeze-dry) is not enough to attain these requirements. In the study reported here, the author developed new solvent exchange method for surface chemical modification of CNFs. By the method, CNFs were octanoylated to yield CNF derivatives with hydrophobic surface, and some octanoylated CNFs were dispersed in hexane.

Materials and methods

1) New solvent exchange method

CNFs were prepared from the wood flour of cryptomeria using a grinder (MKCA6-3, Masuko Sangyo Co., Ltd.). A mixture of 0.82 wt% CNF aqueous slurry 12.20 g (CNF's dry weight : 100 mg) and N-methylpyrrolidone (NMP) 60 mL was agitated well and heated at 150 °C under atmospheric pressure for 2 h until water was almost evaporated. In order to remove slightly remaining water, the CNF-NMP slurry was heated at 150 °C under reduced pressure (100 hPa) until about 10 mL NMP was collected. Thus, 0.2 % CNF-NMP slurry was prepared without water.

2) Octanoylation

After pyridine was added into 0.2 % CNF-NMP slurry, octanoyl chloride was added slowly and then the mixture was heated at 60 °C for 6 h. After the reaction mixture was poured onto ethanol, octanoylated CNF precipitated were washed with ethanol thoroughly by using vacuum-filtration.

The structure of octanoylated CNFs were confirmed by ATR-IR spectra and the degree of substitution (DS) was determined by back titration. Then, octanoylated CNFs were subjected to wide angle X-ray diffraction, SEM observation and solvent dispersibility test.

Results and discussion

Octanoylation of CNFs were confirmed by IR spectra and the author found that surface chemical modification of CNF efficiently proceeded by using new solvent exchange method. And, chemical modification proceeded on only the surface of CNFs in the less than DS 0.55 and into the inside of crystal in the more than DS 0.87 according to wide angle X-ray diffraction and SEM observation. Figure 2 shows dispersibility of octanoylated CNFs in water and hexane. According to an increase in the DS, CNFs weren't dispersed in water, whereas CNFs were dispersed in hexane. Thus, there is difference in solvent dispersibility by DS.

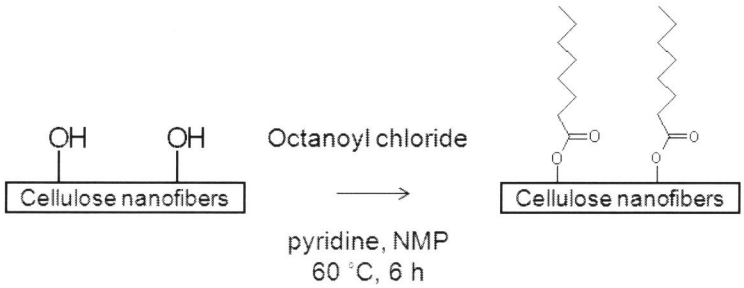

Figure1. Octanoylation of cellulose nanofiber

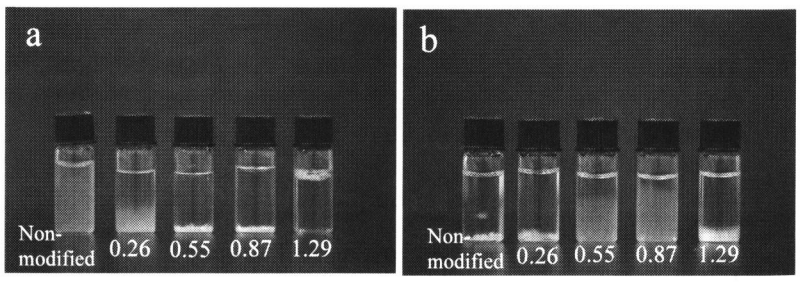

Figure 2. Dispersibilty of octanoylated CNF in water (a) and hexane (b).
Figures are the degree of substitution (DS).