Preparation and Characterization of Sulfated CNF

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Outline

- ✓ Introduction
- ✓ Preparation of sulfated CNF
- ✓ Characters of sulfated CNF
- ✓ Application of sulfated CNF
- ✓ Summary

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About the anionic CNFs

- All or part of the surface hydroxyl groups are modified to the anionic groups.
- The force of electrostatic repulsion between anionic groups contributes greatly to the fibrillation, so the process consumes small amounts of energy.
- Until now, the below four kinds of anionic CNF have been reported.

- TEMPO-oxidized CNF
- Phosphorylated CNF
- Carboxymethylated CNF
- Succinate modified CNF

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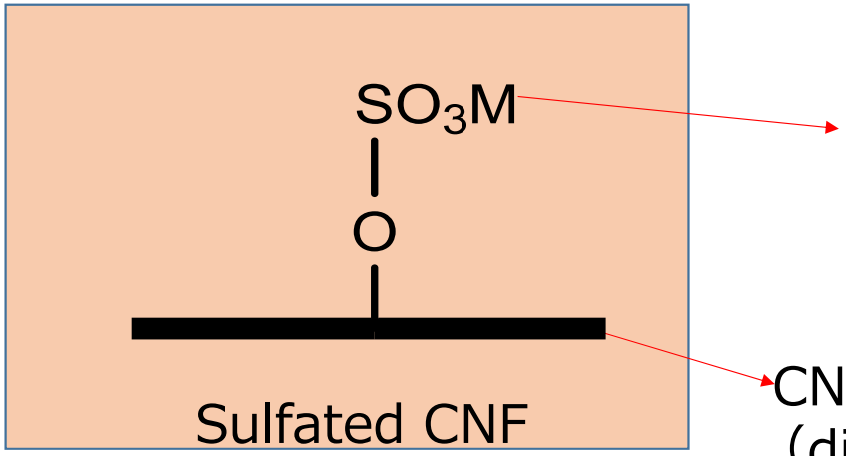
What is sulfated CNF?

- Sulfated CNF is one of the anionic CNFs, that we developed in 2017.
- Its surface hydroxyl groups are modified to sulfate esters , so it is significantly expected to be used as medicine and cosmetics like the natural saccharide sulfates.



M: Na, K, Ca, Al, amine, etc.

CNF
(diameter: 3-5nm; aspect ratio>100)

INTRODUCTION

Functions of saccharides sulfates

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- Natural saccharide sulfates have be found to have various biological activities, but they are very rare and expensive., and some of them have side effects.
- Synthesis of saccharide sulfates from cellulose can overcome the side effects and reduces the cost.

Stable 1. Natural saccharide sulfates*

Saccharide sulfate	source	Application
Chondroitin sulfate	Animal tissue	Anti-inflammatory agent
Dermatan sulfate	Animal tissue	Anticoagulant
Funoran	Red algae	Anti-cancer agent
Porphyran	Red algae	Immunostimulant
Fucoidan	Brown algae	Anticoagulant, ontraceptive

*Source: R. Takano, et al. Kagakutoseibutsu, Vol. 34, No. 9, 598-604 (1996)

Previous methods for sulfation

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Many methods have been developed for the sulfation of polysaccharides, but they have a number of disadvantages, such as, strict control of reaction temp., excessive degradation, difficulty in purification, or high cost, etc.

Previous methods

- concentrated sulfuric acid
- Chlorosulfonic acid/pyridine
- Sulfur trioxide/DMF
- Sulfuric acid/DCC/DMF

PREPARATION

A novel process for preparation of sulfated CNF

By using [sulfuric acid/carboxylic anhydride/DMSO] as the reaction medium, one is able to overcome the disadvantages of previous methods and keep the sulfation on the surface of CNF.

It is a gentle, safe and simple process.

Bleached kraft pulp/reaction medium

Stirring at r.t.

1-2hr

Sulfated pulp

Washing

Sulfated CNF
(d:3-5nm, aspect ratio>100)

Disperse sulfated pulp in water and mix it

PREPARATION

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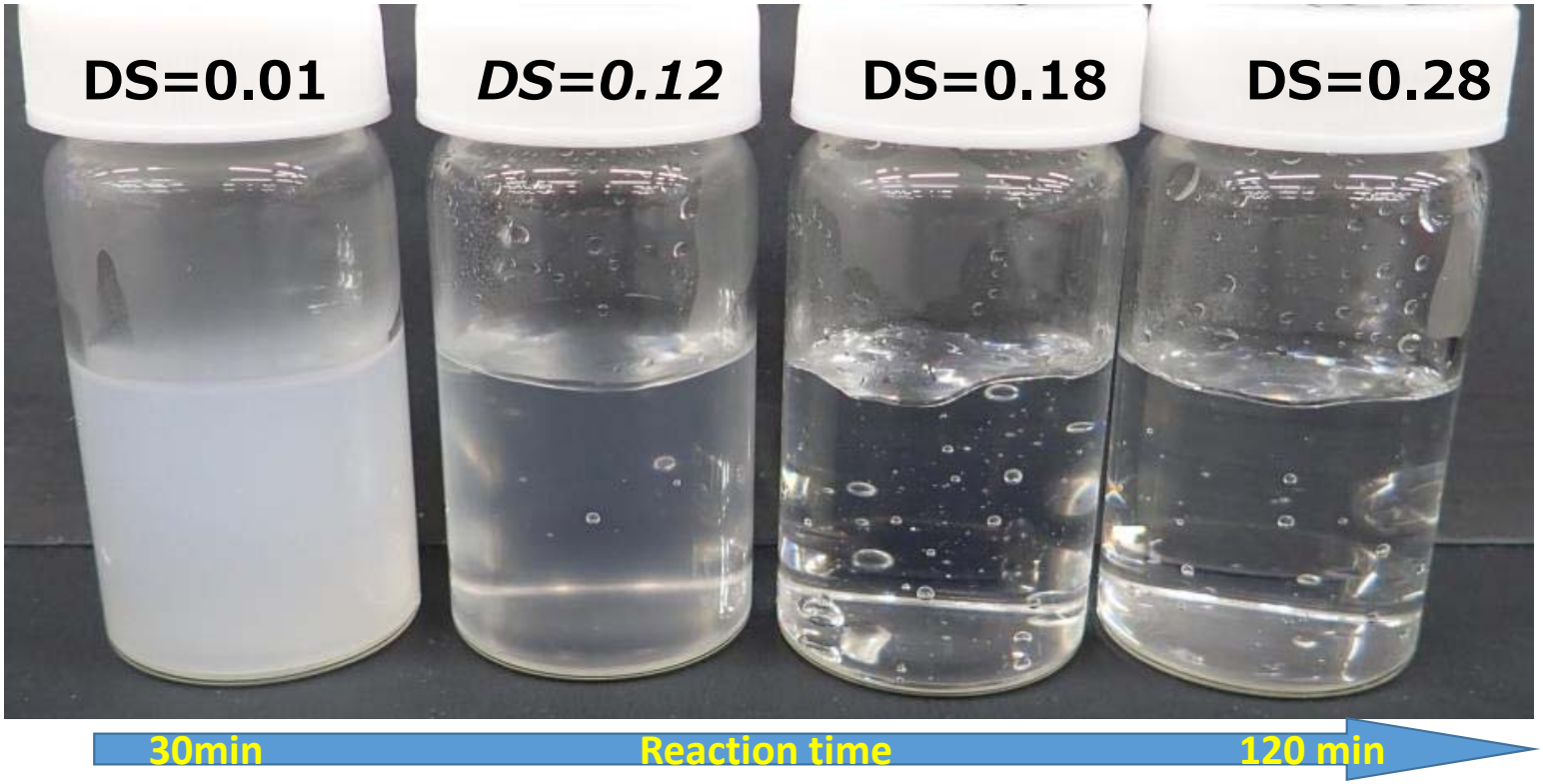
Water dispersion of sulfated CNF (0.3wt%)



※DS was detected by Combustion-Ion chromatography

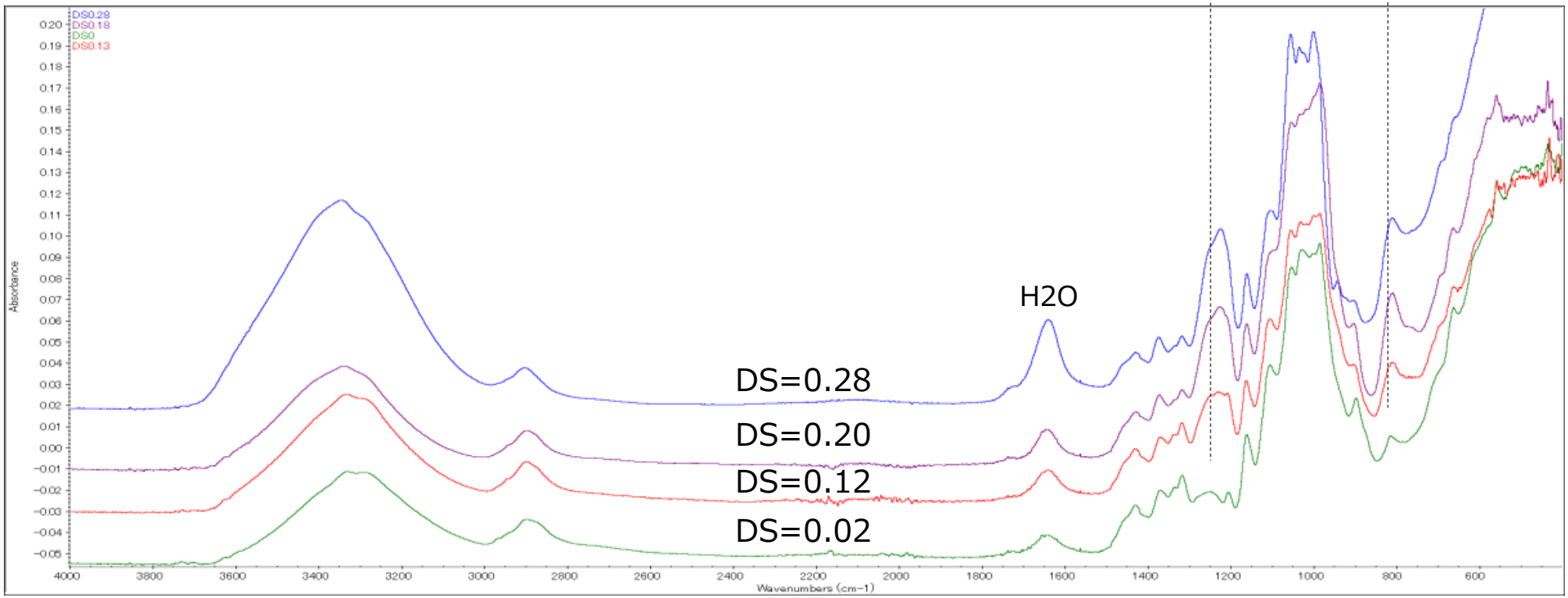
PREPARATION

IR spectra of sulfated CNF

Absorbance bands associated with the C-O-SO3 group:

Symmetrical C-O-S vibration

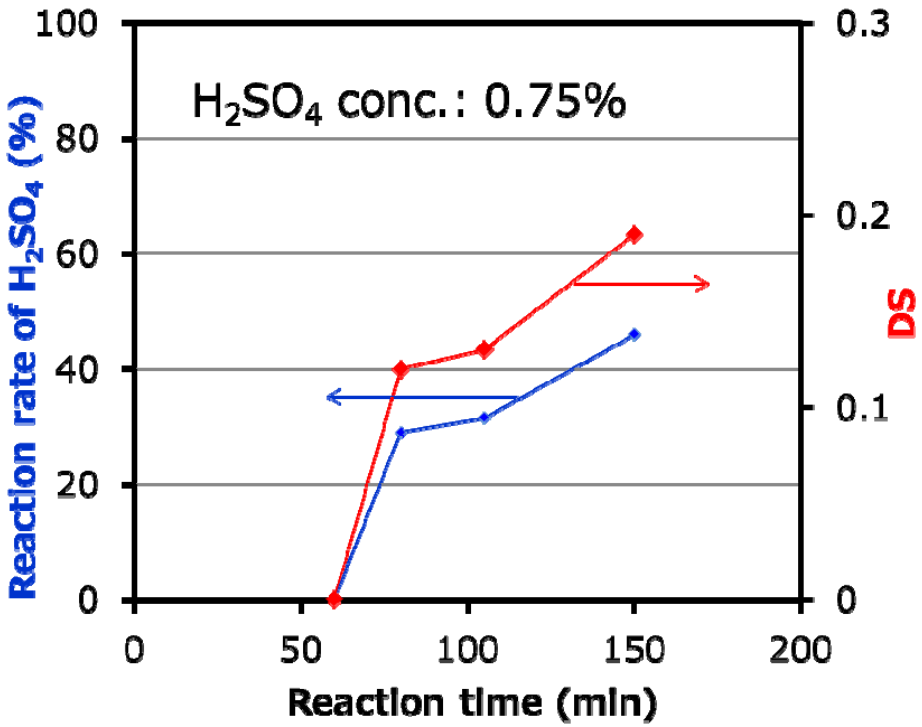
Asymmetrical S=O vibration

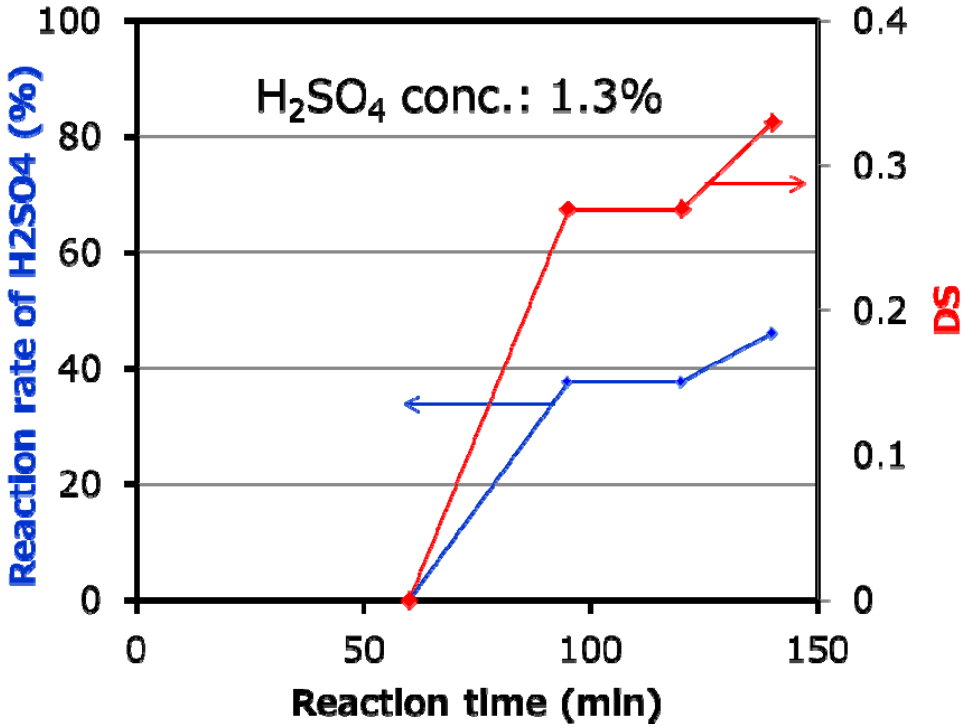


PREPARATION

DS of the sulfated CNF

- DS is affected by the concentration of sulfuric acid or reaction time.
- The reaction rate of sulfuric acid is about 50% when the reaction time is 150 min.





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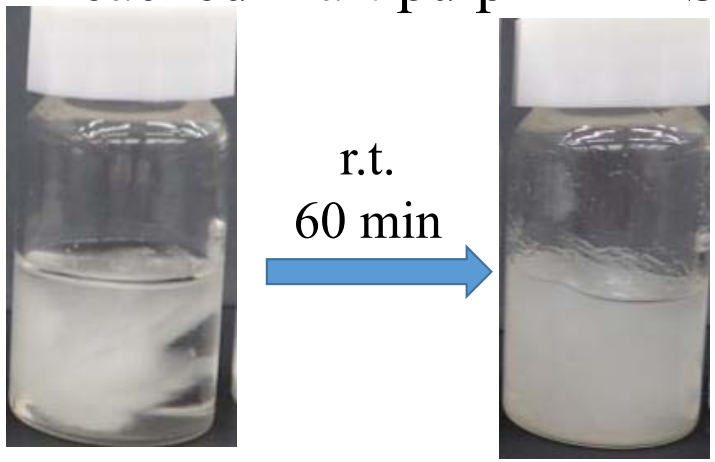
Why use DMSO as a reaction solvent?

Highly polar/aprotic/solvating cations

- A powerful solvent for penetrating and swelling cellulose.
- A valuable reaction solvent to accelerate the esterification reaction.
- Low toxicity

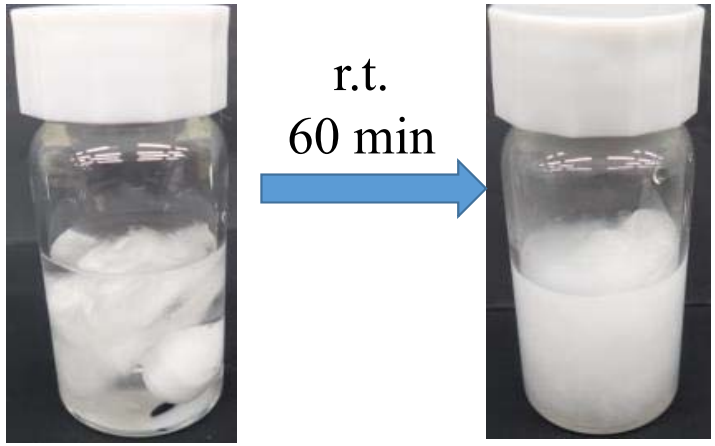
PREPARATION

✓ Bleached kraft pulp in DMSO



No free DMSO remained

✓ Bleached kraft pulp in water



A lot of water remained

CHARACTERS

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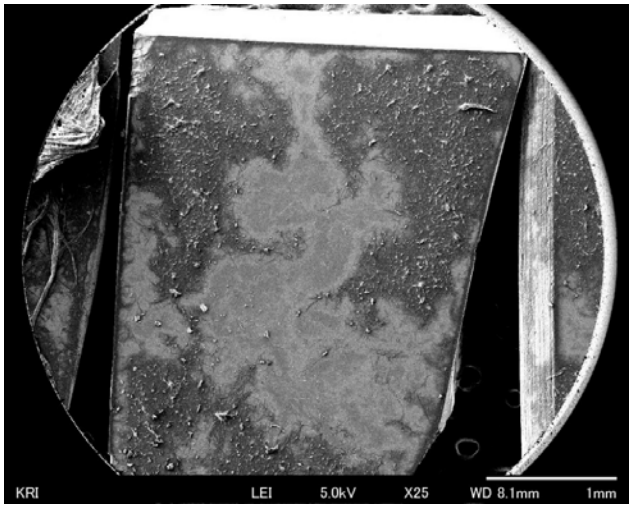
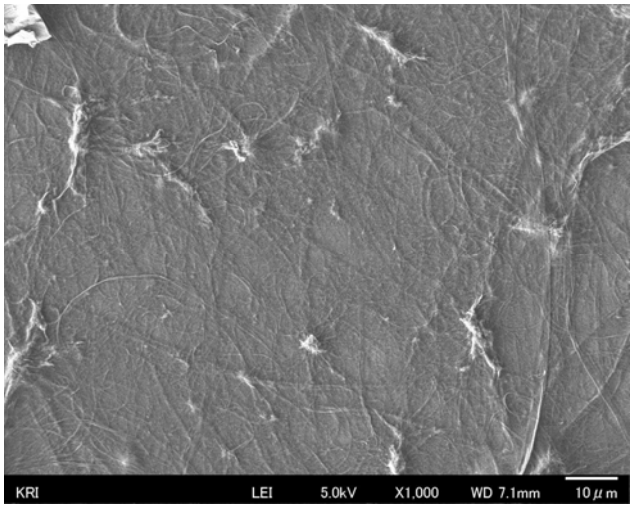
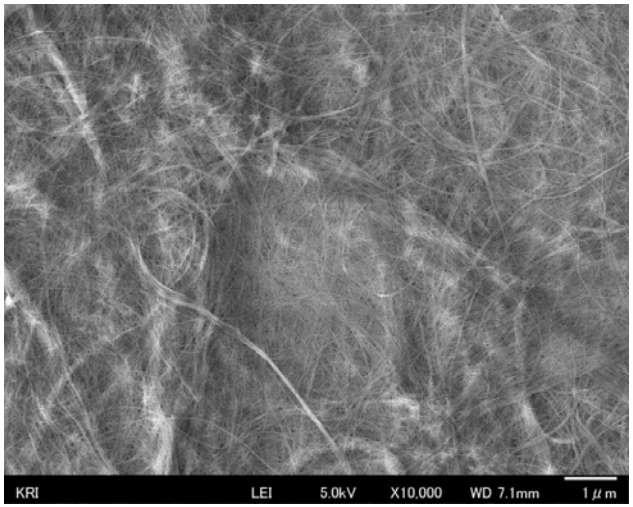
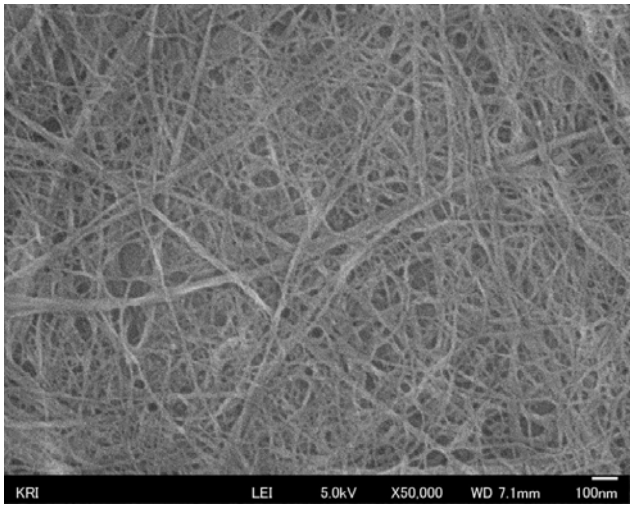
SEM image of the surface-sulfated CNF(DS=0.01)





d>10nm





CHARACTERS

SEM image of the surface-sulfated CNF(DS=0.28)

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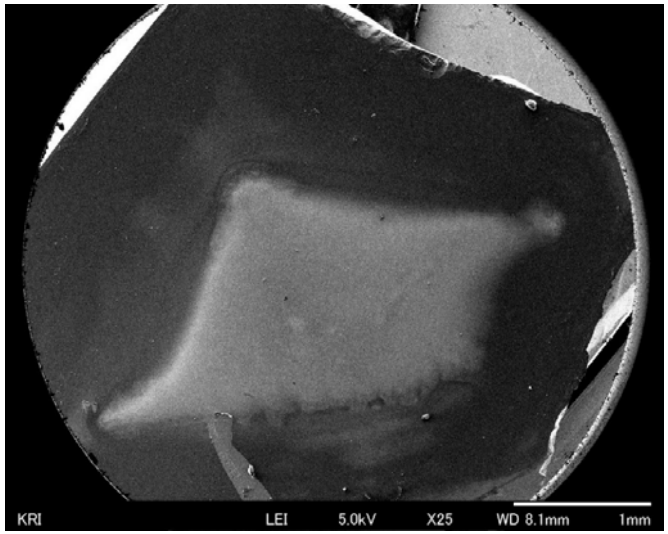

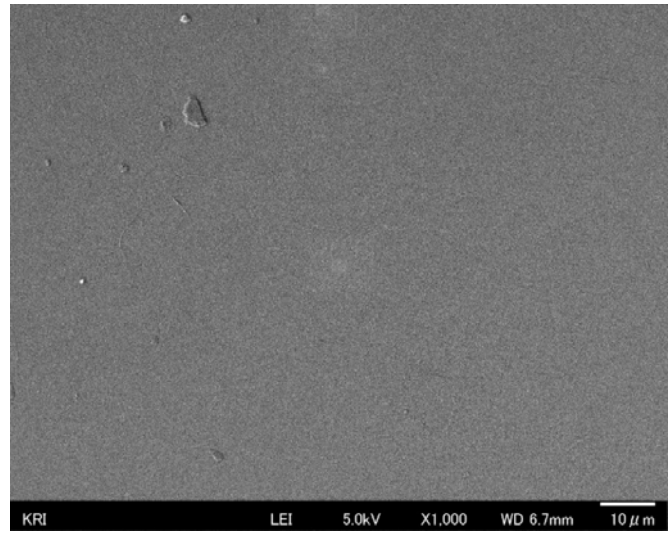

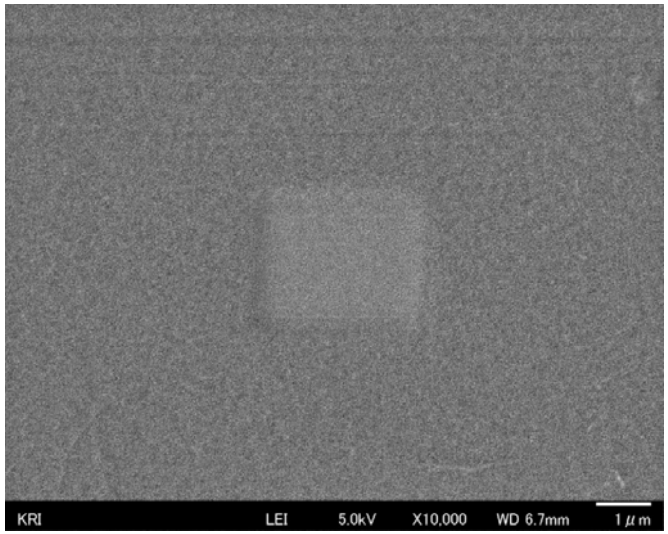

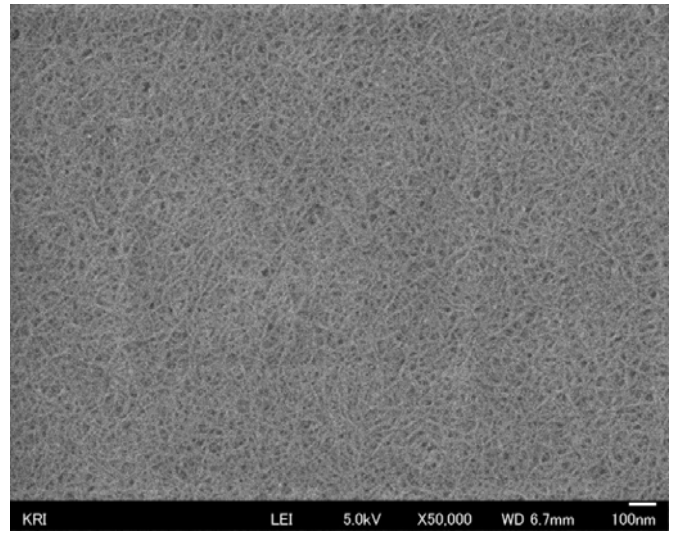

CHARACTERS

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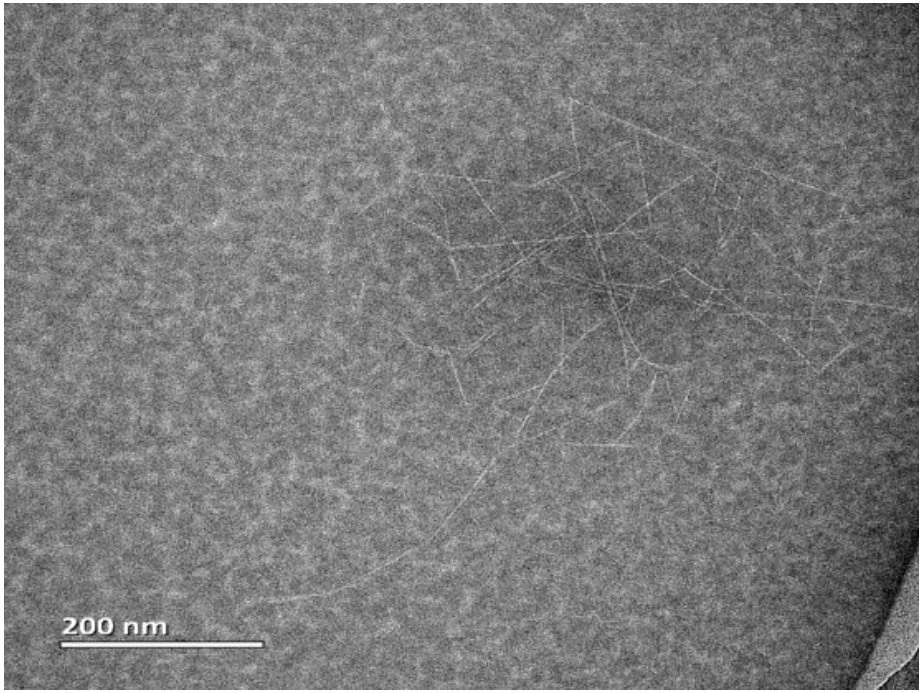
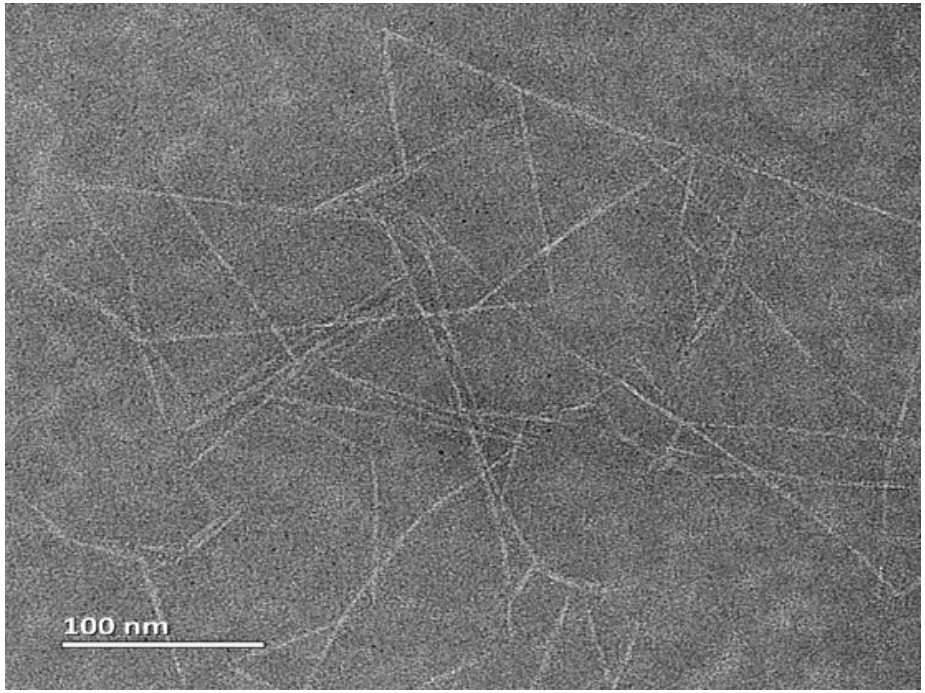
TEM image of the surface-sulfated CNF (DS: 0.28)





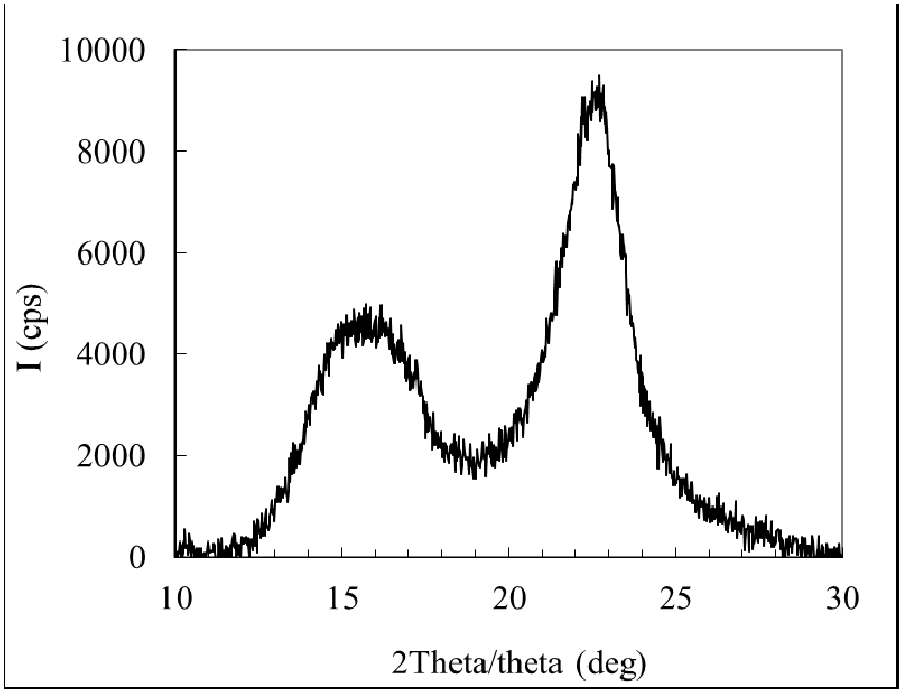
d=4nm

CHARACTERS

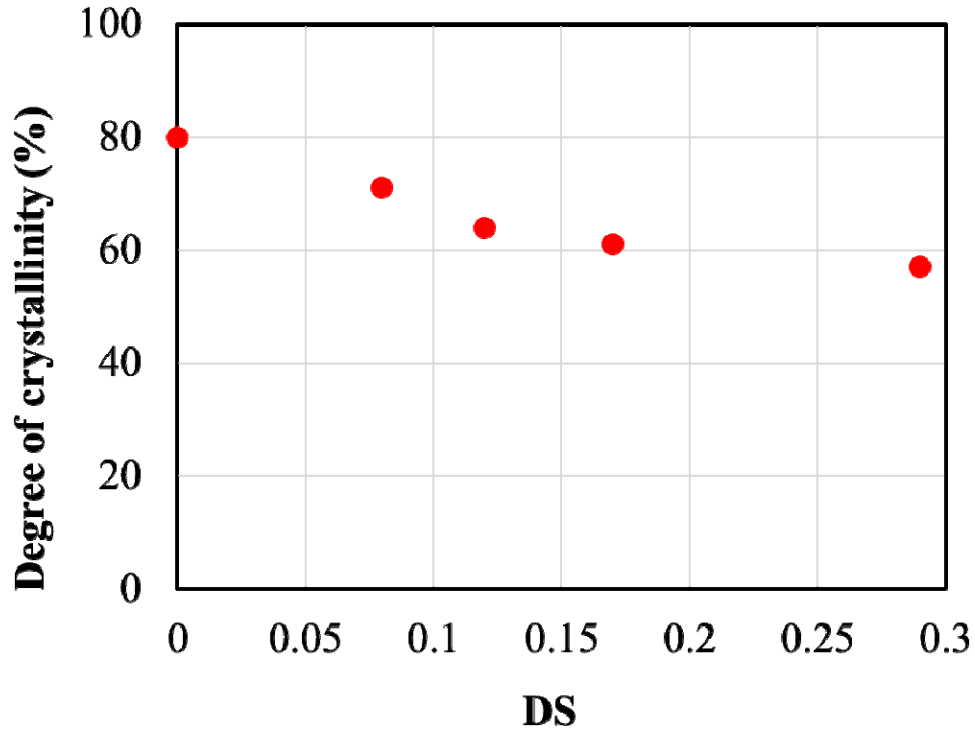
Crystallinity of sulfated CNF

Crystal structure: cellulose Iβ

XRD patterns of sulfated CNF(DS=0.12)



Relationship between the crystallinity and DS



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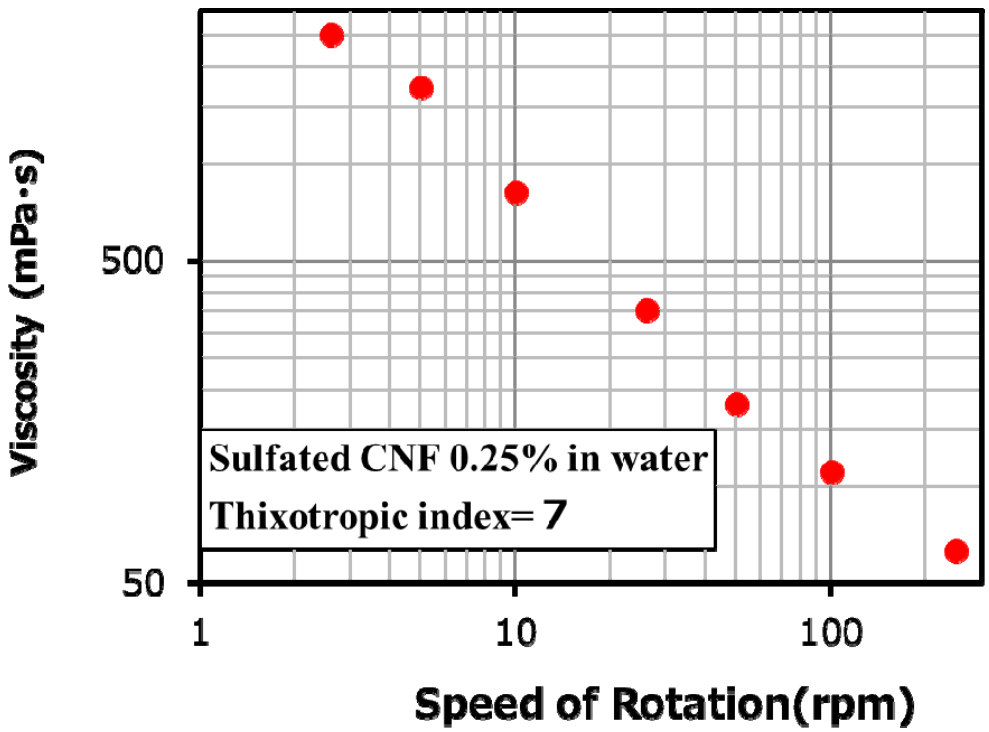
Rheological properties of sulfated CNF (DS=0.28)

- High viscosity and thixotropy
- High water-holding property

0.25% sulfated CNF in water



Relation between the viscosity of surface-sulfated CNF dispersion and the rotation speed

CHARACTERS

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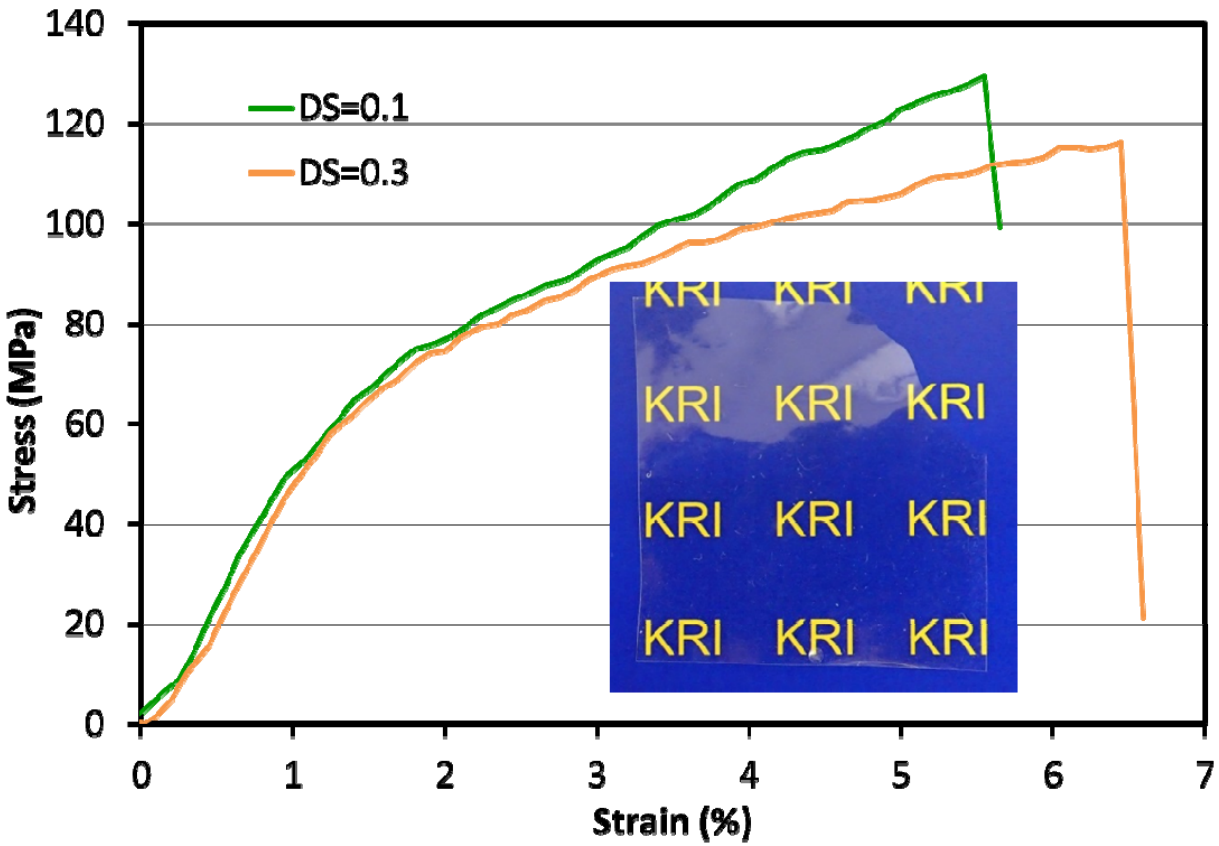
Sulfated CNF film and its characters

Tensile strength 130MPa, modulus 6GPa, transparence 93%



S-S curves of the sulfated CNF film

CHARACTERS

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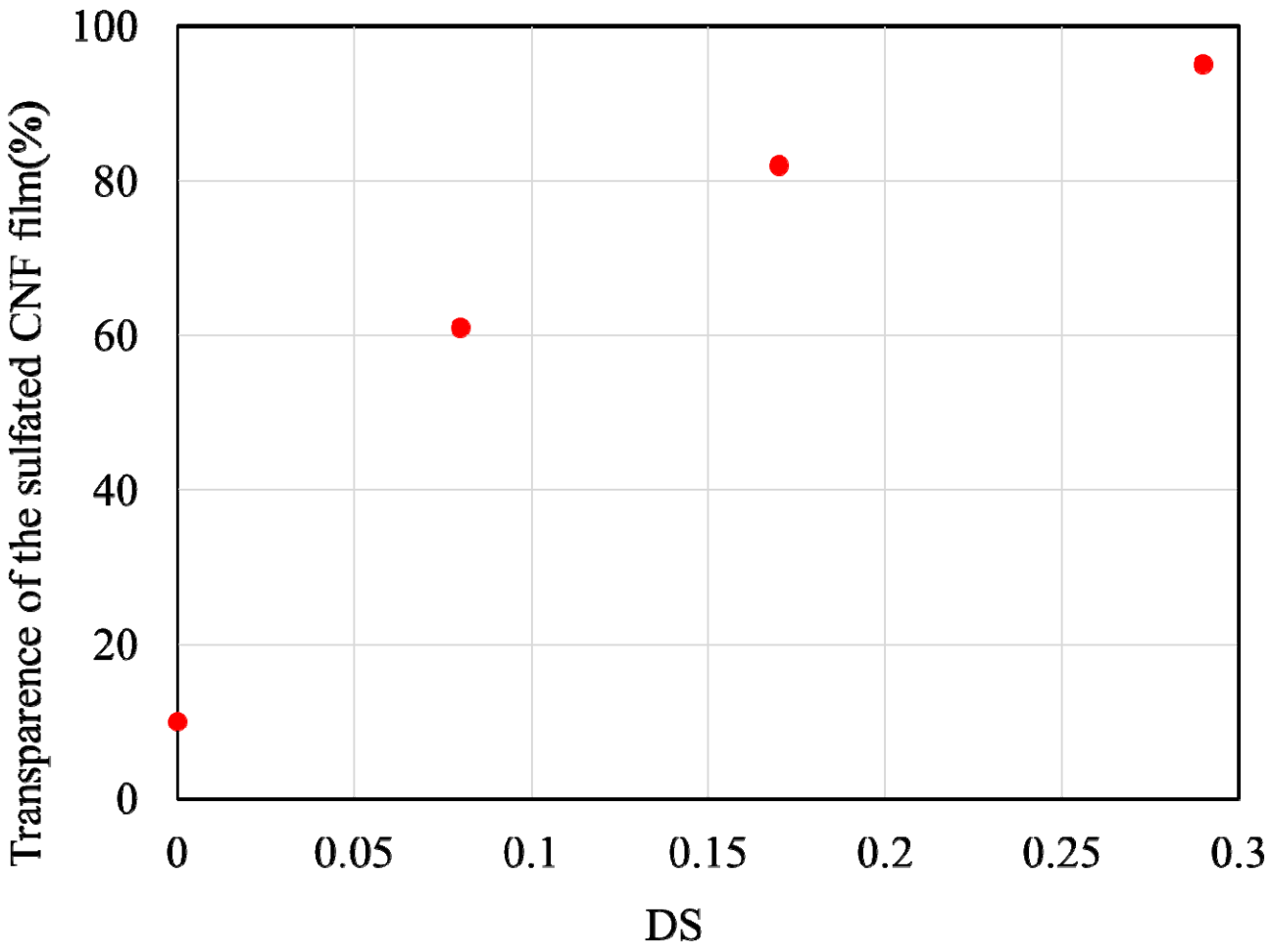
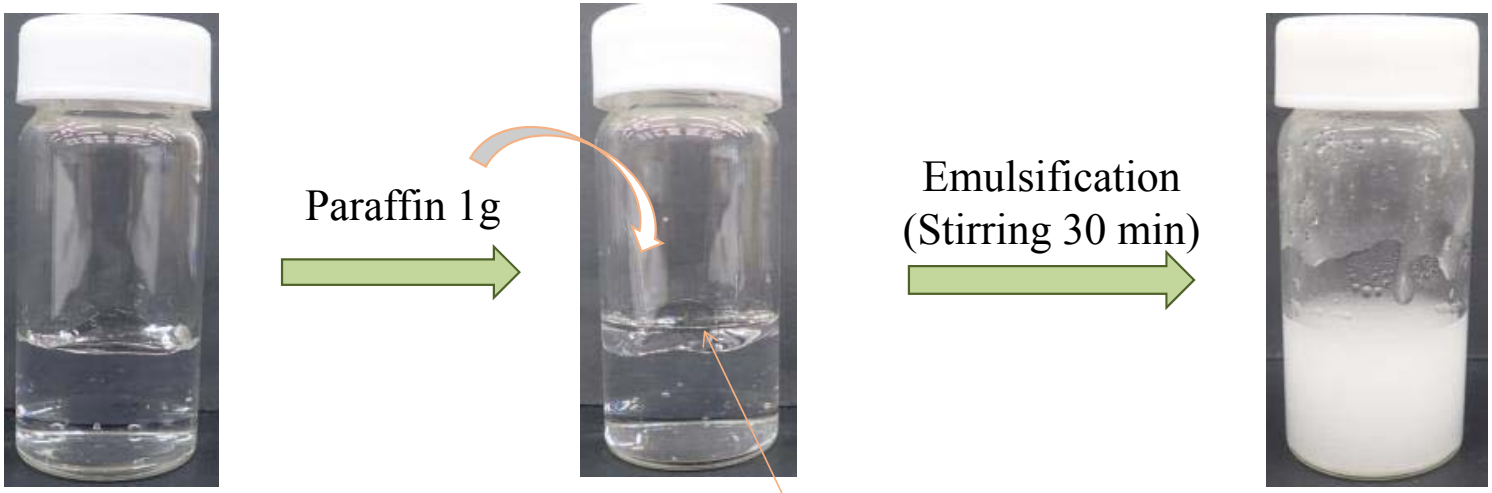
Effect of DS on the transparence of sulfated CNF films



APPLICATIONS

Use as surfactants

Using sulfated CNF to prepare a stable O/W emulsion, which is highly stable and its pH is about 7.



sulfated CNF disperse (0.2%)
(10g)

O/W emulsion
(Stable over years)

APPLICATIONS

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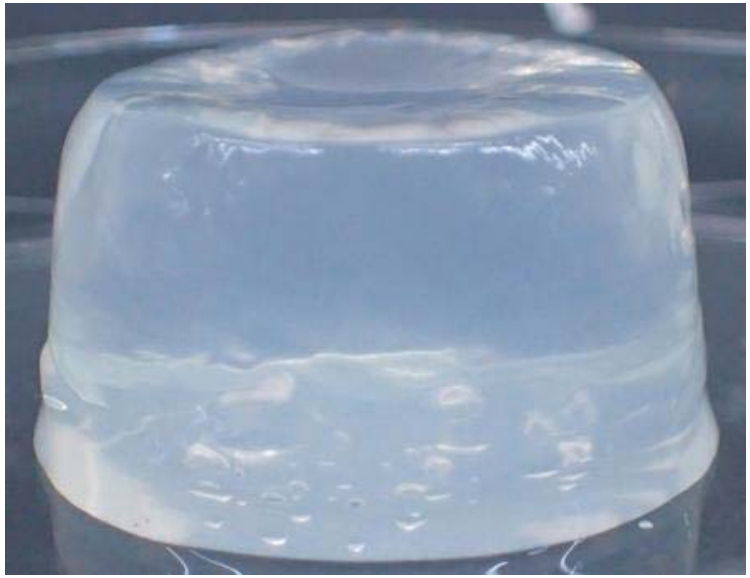
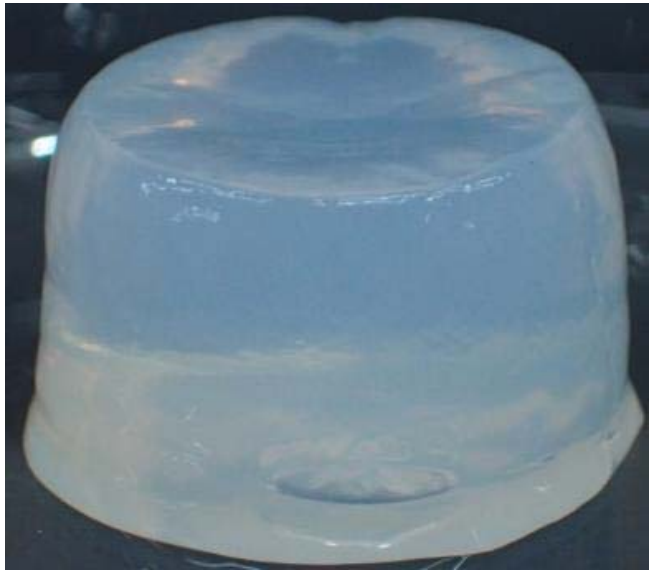
Hydrogel of sulfated CNF/chitosan blend

- Antibacterial and antiviral hydrogel
- A water adsorption rate of about 300 times



Sulfated CNF/chitosan composite
Water-holding: 300 times



SiO_2/sulfated CNF/chitosan composite
Water-holding: 150 times

APPLICATIONS

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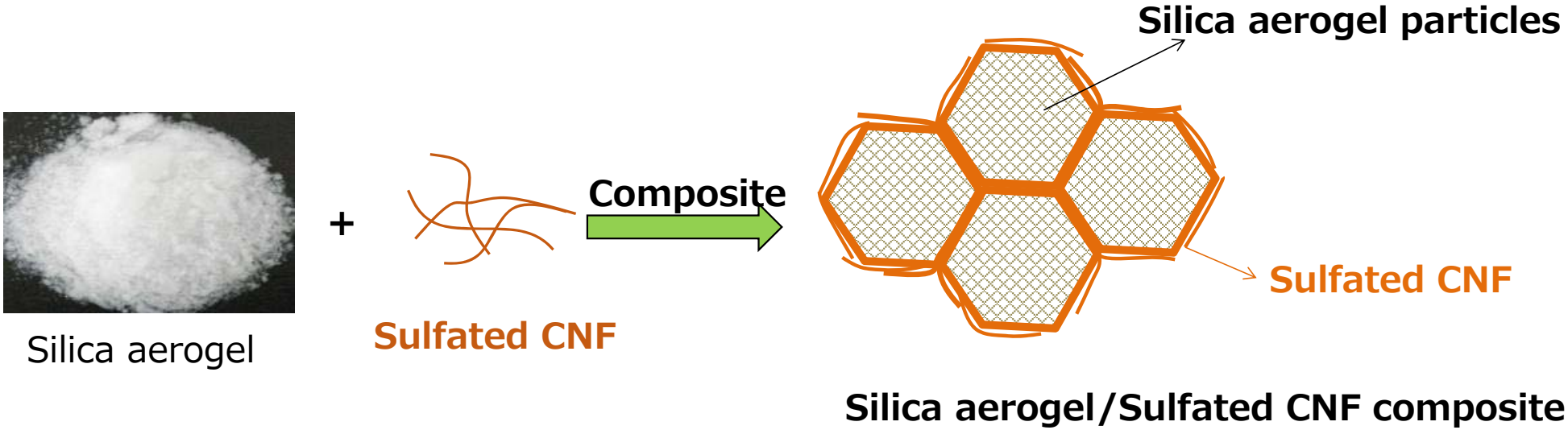
Silica aerogel/sulfated CNF composite: heat-insulator

- ✓ Sulfated CNF: the continuous phase
- ✓ Silica aerogel: the dispersed phase



APPLICATIONS

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Preparation process and properties of silica aerogel/sulfated CNF composite

Sulfated CNF

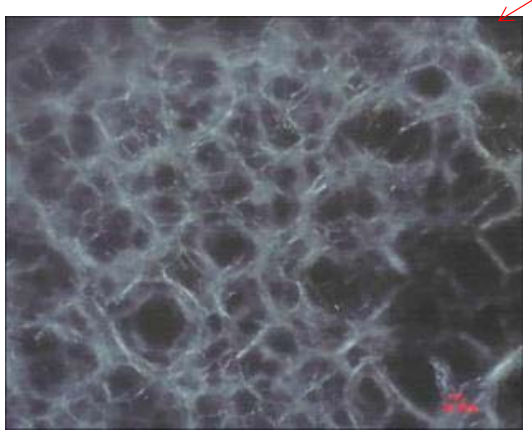
+

Silica aerogel

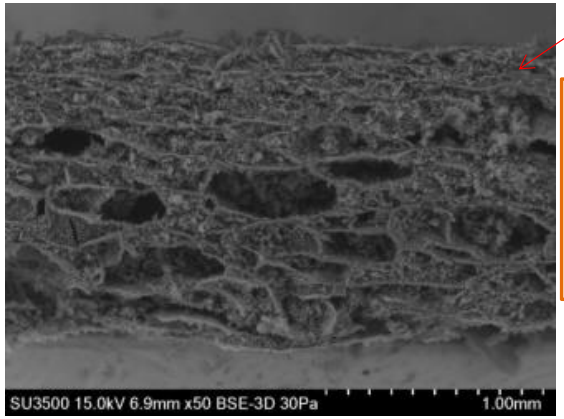
Sulfated CNF/silica aerogel colloid

dry

Sulfated CNF/silica aerogel composite



Microscope photo of sulfated CNF/silica aerogel colloid



SEM image of the cross section of sulfated CNF/silica aerogel composite

- Density: 0.05g/cm^3
- Thermal conductivity: 15mW/(m・K)
- Flexible
- Thickness: 100～1000μm

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Summary

- The sulfated CNF has a diameter of 4nm and an aspect ratio of more than 100 times.
- DS of sulfated CNF can be controlled by the concentration of sulfuric acid or reaction time.
- It can be used as surfactants, water-holding agent, reinforcing filler and matrix for the inorganic particle.
- It can also be used like the conventional saccharide sulfates in the medical and cosmetic areas.

Thank you

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TAPPI