Dual Functions of CNF in Oil-in-Water Emulsion: Pickering Emulsifier and a Unique Dispersion Stabilizer

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Our CNF: RHEOCRYSTA®

Characteristics

TEMPO-CNF aqueous dispersion
Width: 3 nm, high aspect ratio
Introduced COONa groups on surface of fiber

Application as aqueous additives

High viscosity, shear thinning properties
Applied for ink of ball-point pen

Functions of our product

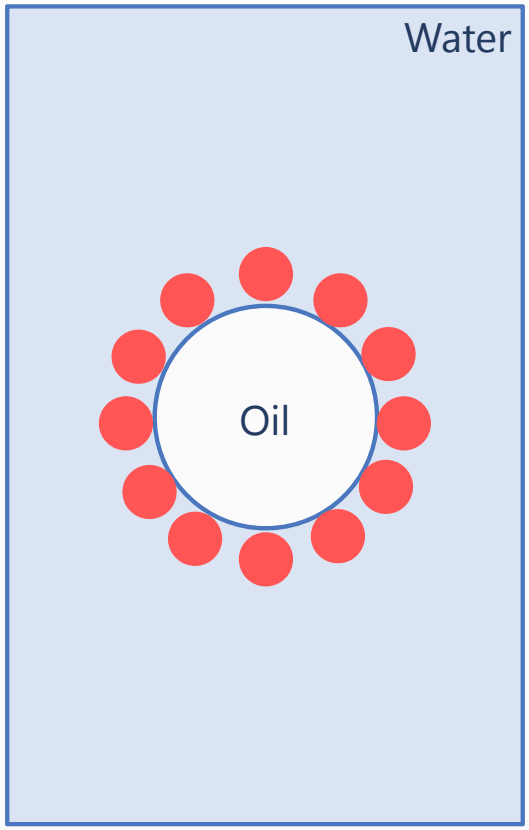
I. Rheology controlling with network structure of CNF
II. Emulsifying and dispersing
III. Dense and high strength film formation

Emulsifying and dispersing with CNF

About emulsification

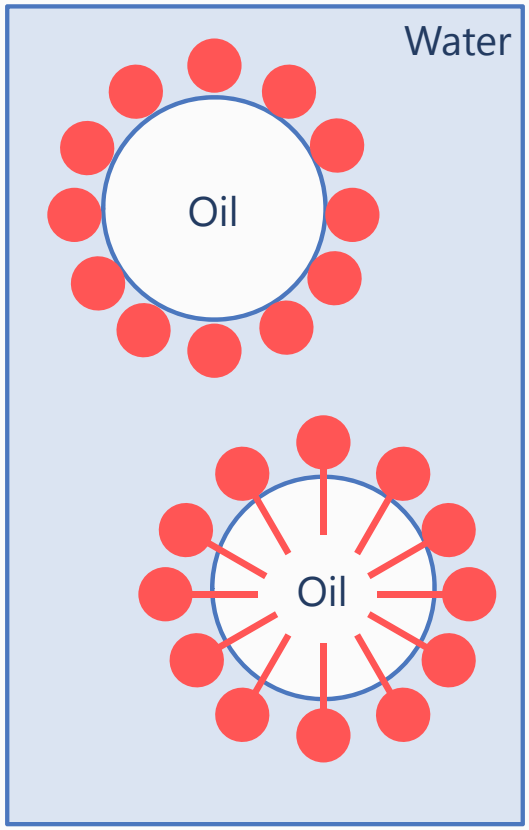
- Technique used in various fields
  such as foods, cosmetics and paints
- Mixing two liquids by micronization and dispersion uniformly
- In general, emulsion is prepared by reducing the interfacial tension between oil and water using surfactants

Emulsification without surfactants



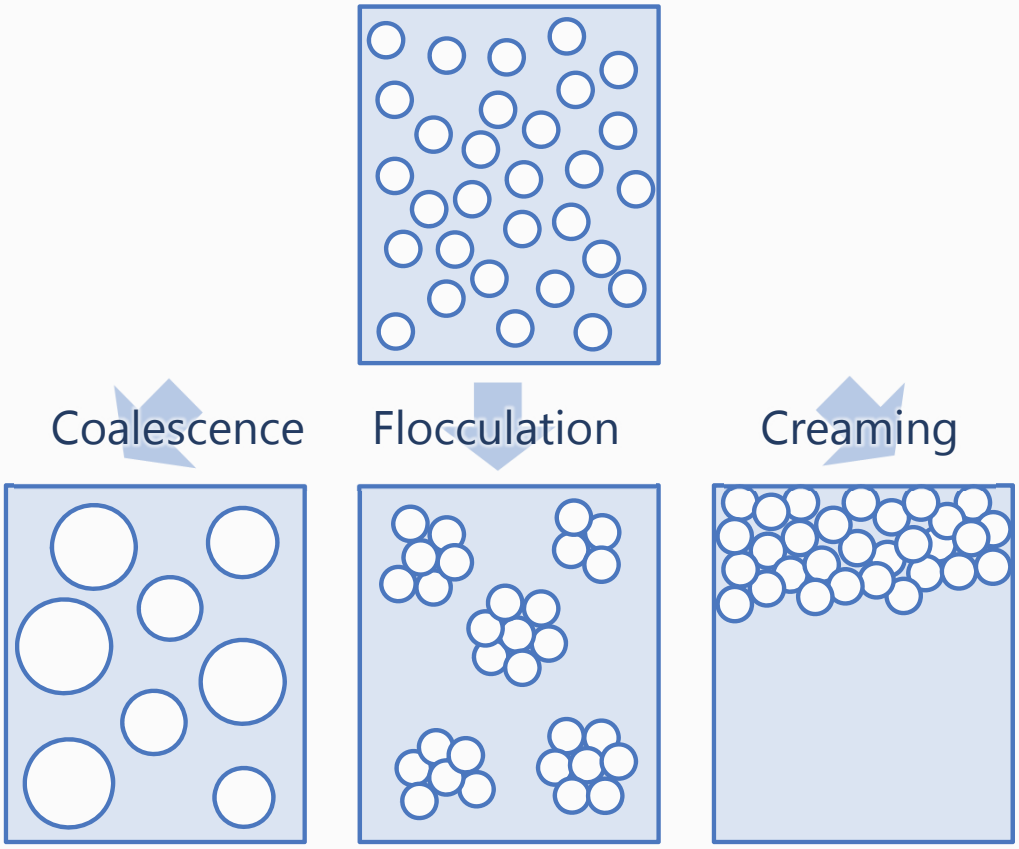
- Stabilization by adsorption of solid particles at the interface: Pickering Emulsion
- Found by Pickering *et al.*
- Pickering emulsifier:
  clay, $CaCO_3$, hydrophobized silica

Design & role of interface membrane



- The interface membrane can be prepared by selecting an optimum surfactant according to the properties and purpose of the system
- Roles of the interface membrane
  - ✓ Reducing thermodynamic unstability by decreasing the interfacial tension between the oil and water
  - ✓ Formation steric and/or electric barrier
  - ✓ Addition of mechanical strength (elasticity of interface) that can withstand collisions between droplets

Unstabilization process of emulsions



Oil droplets formed by external mechanical forces become unstable in various processes

⇒Need solutions
to match each situation

Emulsification with CNF

Blank With CNF

- O/W emulsion can be prepared with CNF
- A candidate as new emulsifier for markets
- Detail mechanisms are unclear

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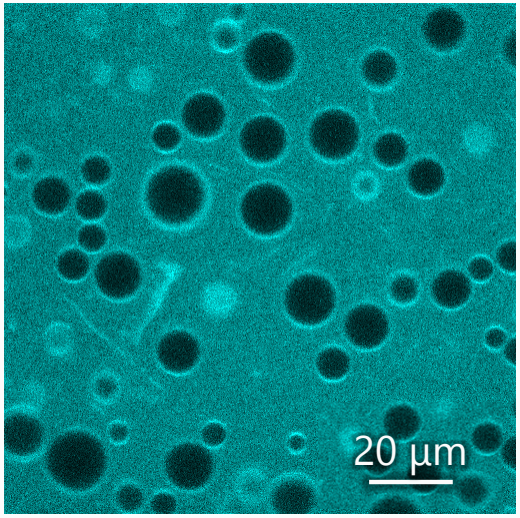
i. Mechanism of oil droplet formation

ii. Mechanism of emulsion stability

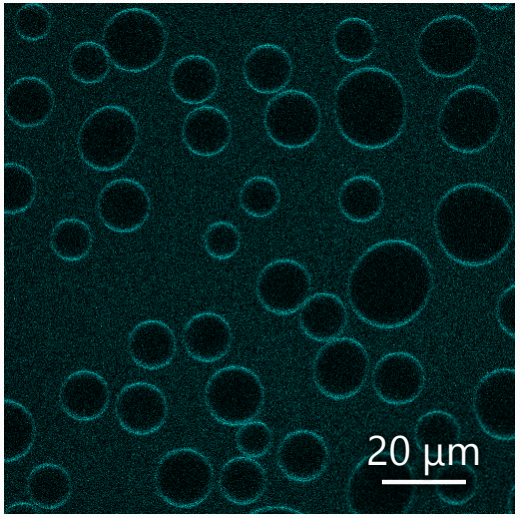
iii. Observation of emulsion

i . Mechanism of oil droplet formation

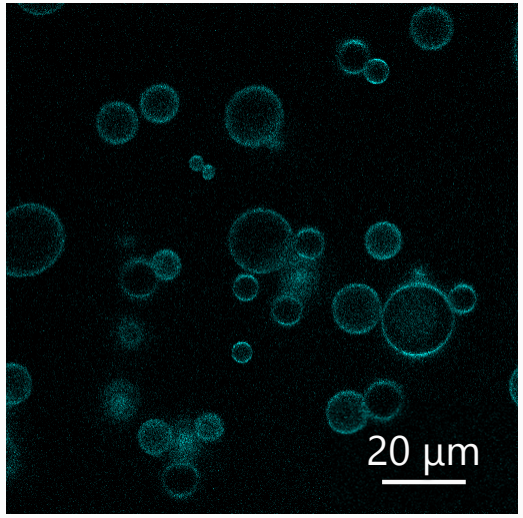
Fluorescence staining of CNF in emulsion



C_{16}/0.2% CNF dispersion



After x4 dilution



After washing of oil droplet

CNFs were localized onto the surface of the oil droplets

►CNFs adsorbed onto the oil droplets, then formed Pickering emulsion

Why CNFs adsorb onto oil droplets?

Discussion with interfacial free energy

Interfacial free energy G

$$G\ (\mathrm{Nm}) = \gamma_{\mathrm{OW}}\ (\mathrm{N/m}) \times A\ (\mathrm{m}^2)$$

Effect of interfacial tension γ_{OW}

Prepared emulsions with various oils with various γ_{OW} (8.5～53.3 mN/m)

Effect of interfacial area A

Prepared emulsions with various sizes of oil droplets by controlling the emulsifying conditions

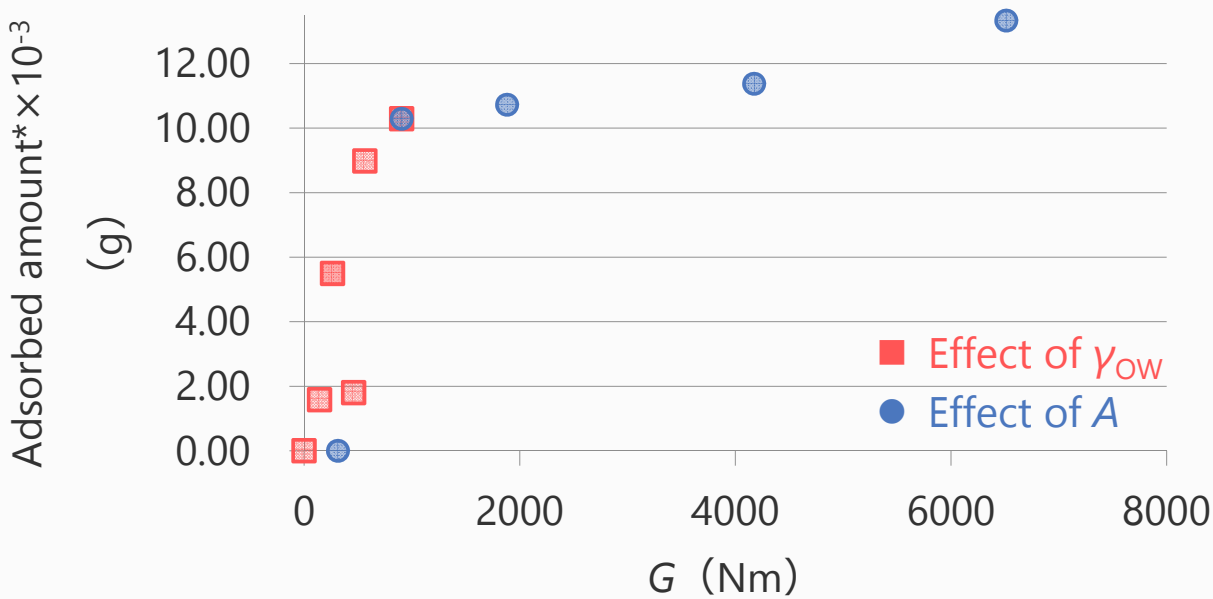
Preparation of O/W emulsion with various *G*

0.05% CNF dispersion (80%) + Oils with various γ_{OW} (20%)

Emulsification
(Homomixer 3,000-10,000 rpm x 5 min)

Evaluation of O/W emulsion (after 1 week)
Interfacial free energy *G*, Adsorbed amount of CNFs onto oil droplets

Effect of *G* to adsorbed amount of CNF



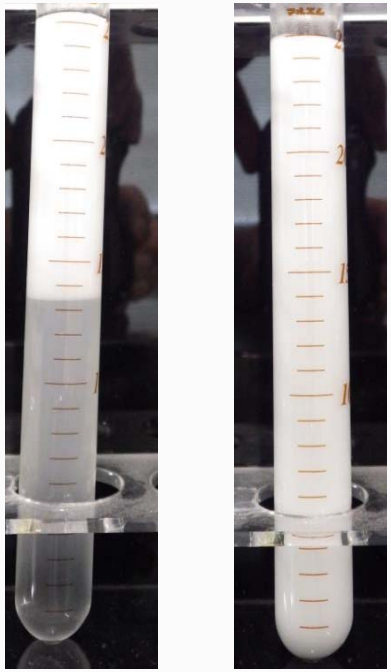
＊Calculated from the residual CNF concentration of water phase after emulsification

Higher *G* gave higher adsorbed amount of CNF (to stabilize the O/W interface)

2. Mechanism of emulsion stability

Effect of CNF concentration

Preparation & evaluation of O/W emulsion

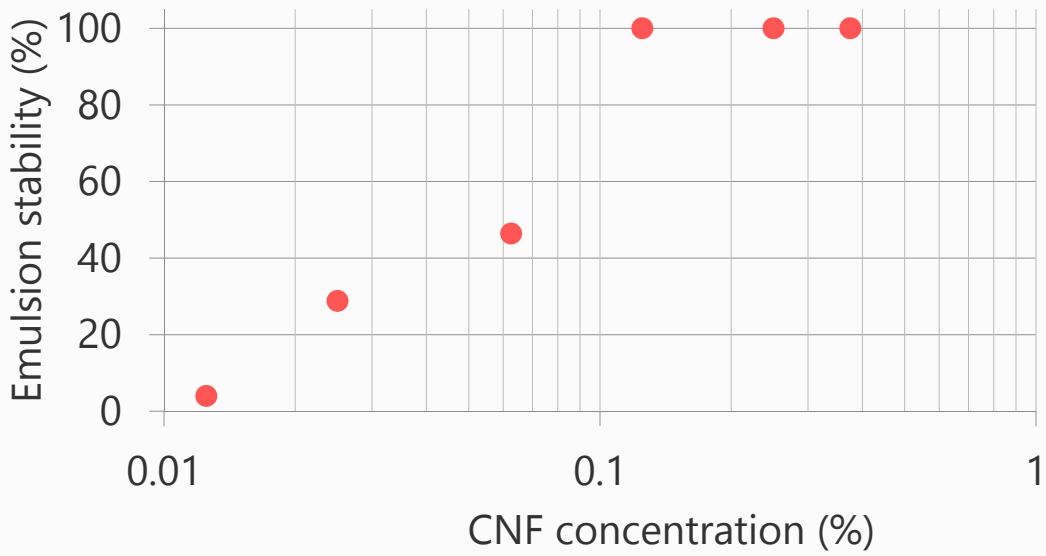


50% 100%

Determination of emulsion stability (after 1 week)

Emulsion stability (%) = Amount of emulsion phase (mL) / Total amount (mL) × 100

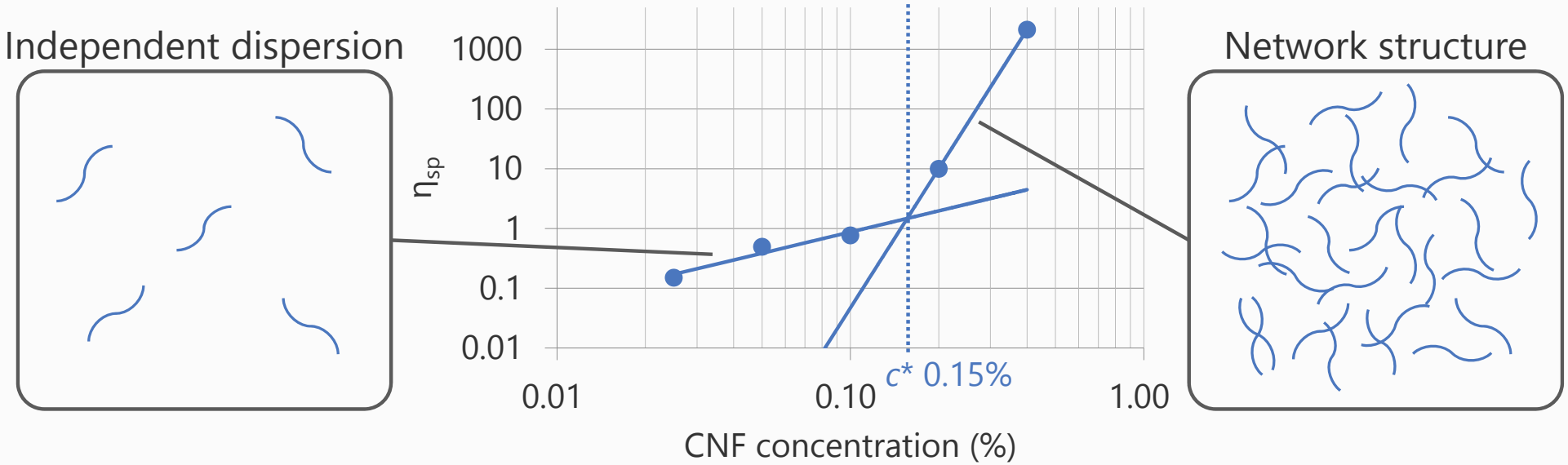
Effect of CNF conc. to emulsion stability



Higher CNF conc. gave higher emulsion stability

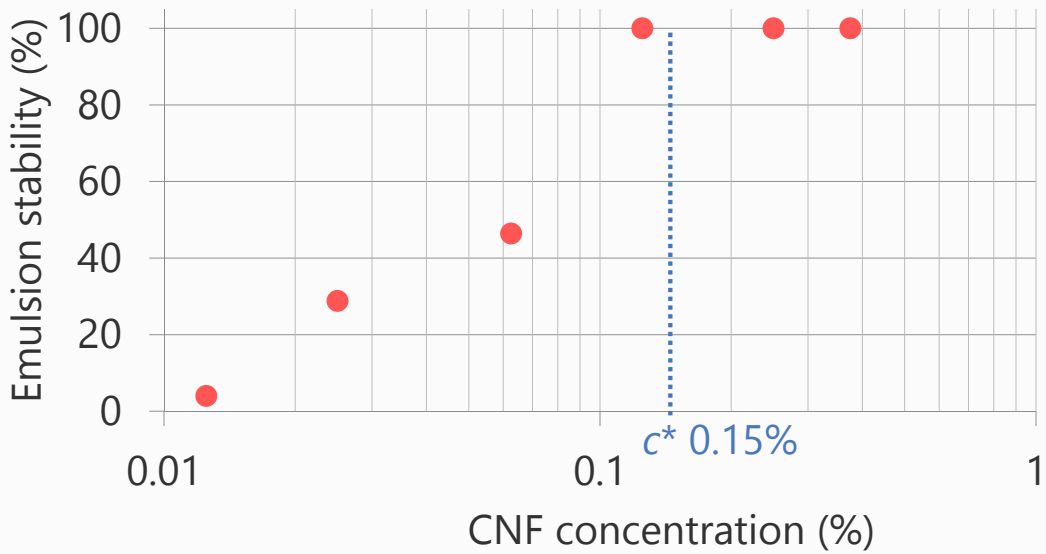
Emulsion stabilities are around 100% with >0.1% CNF

Determination of critical concentration *c**



CNFs form network structure by the interaction between fibers at more than the critical concentration *c**

Effect of *c** to emulsion stability

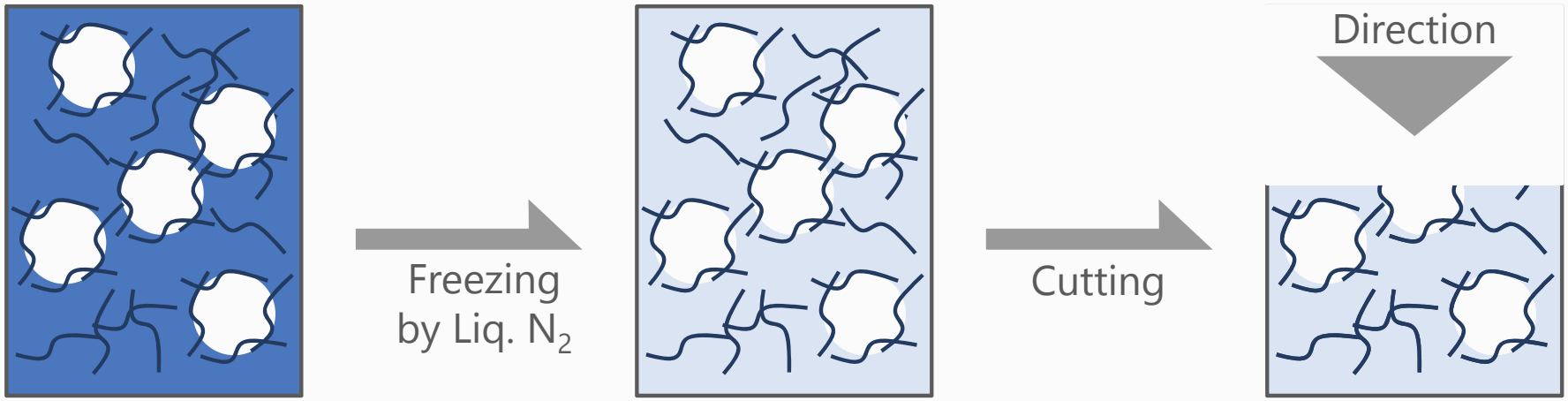


Networking ability of CNF contributes the stabilization of emulsion when CNF concentration is higher than *c**

3. Observation of emulsion

Observation using cryo-SEM

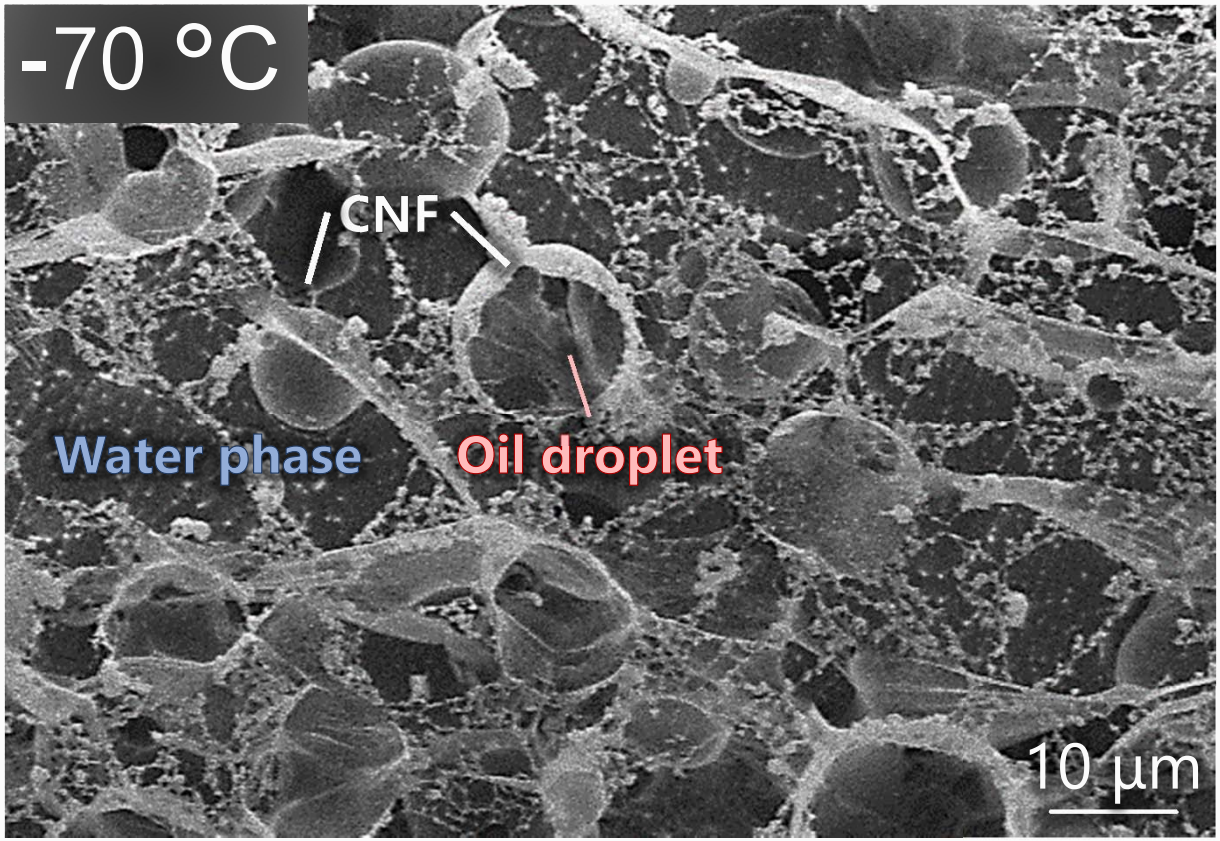
How to observe by cryo-SEM



O/W emulsion (20/80)
Oil: Cyclohexane
Water: 0.2% CNF dispersion

Observation
by cryo-SEM

Image of O/W emulsion



@-120 °C

Hole: oil phase
Ice: water phase

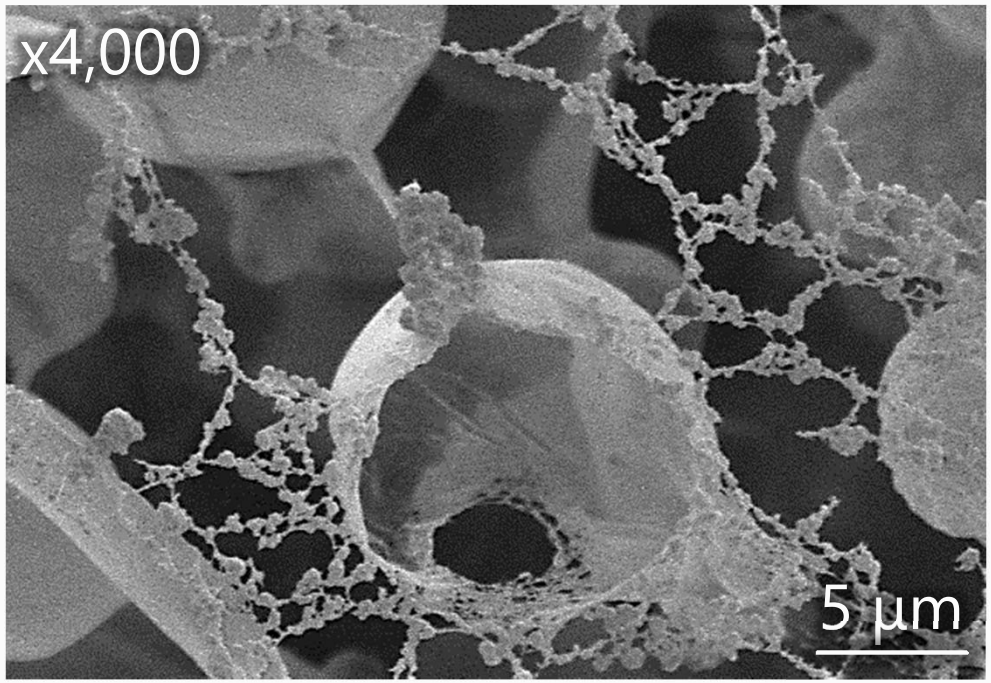
@-80 °C

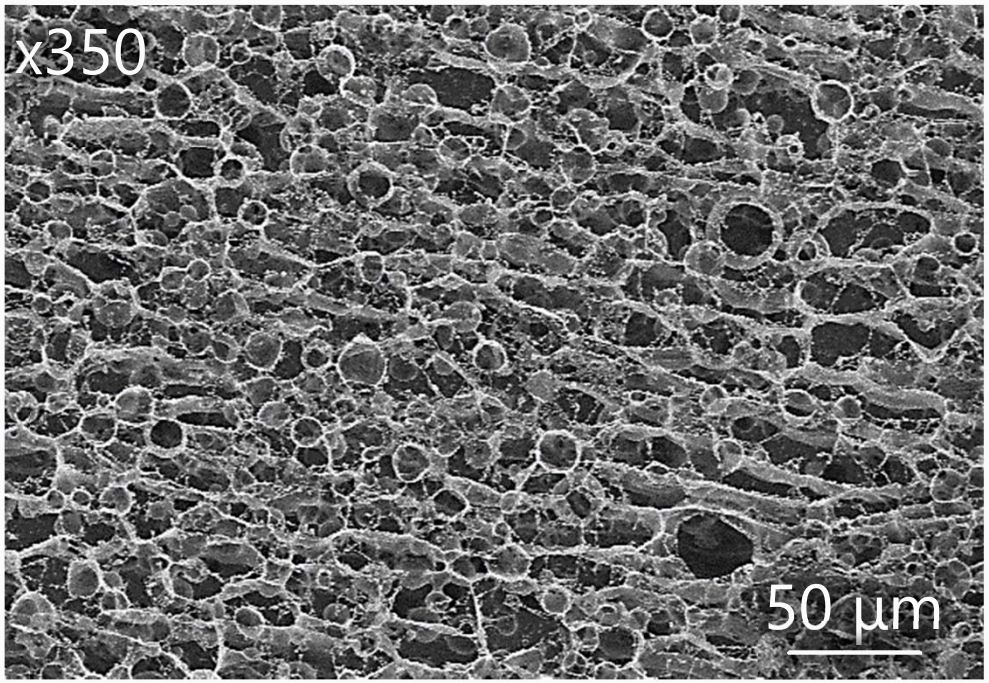
TOCN appeared in the ice phase &
the around of holes

@-70 °C

TOCN covered the oil droplets & formed network structure

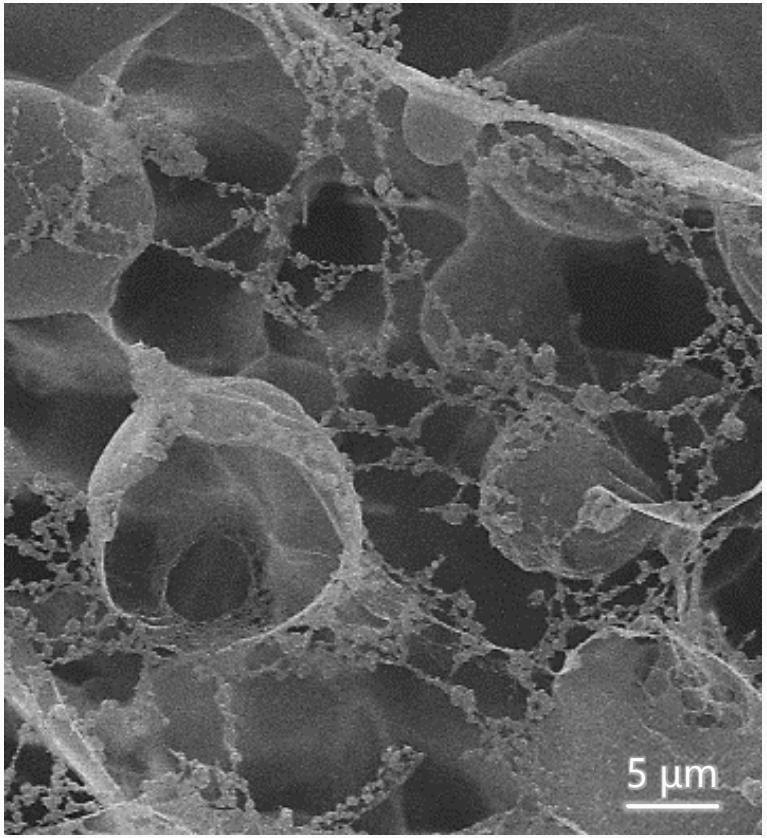
Image of O/W emulsion





CNFs adsorbed onto oil droplets & formed network structure

Dual functions of CNF in O/W emulsions



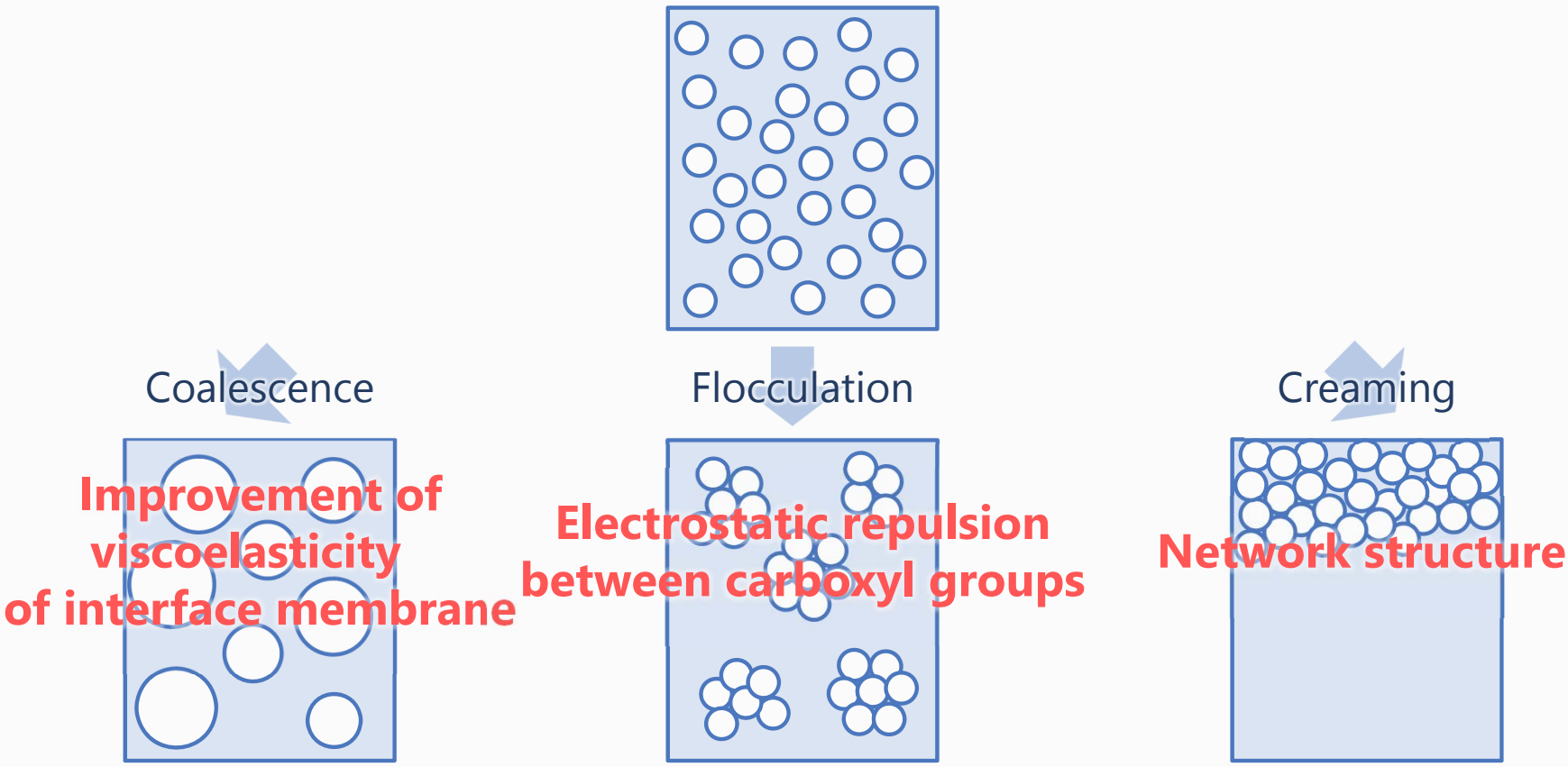
Pickering emulsifier

- CNFs adsorb onto oil droplets to decrease *G*, and then form Pickering emulsion
- Higher *G* gives higher adsorbed amount of CNF onto oil droplets

Dispersion stabilizer

- Networking ability of CNF contributes the stabilization of O/W emulsion when CNF concentration is higher than c^*

Effect of CNF to unstabilization process of emulsion



Thank you

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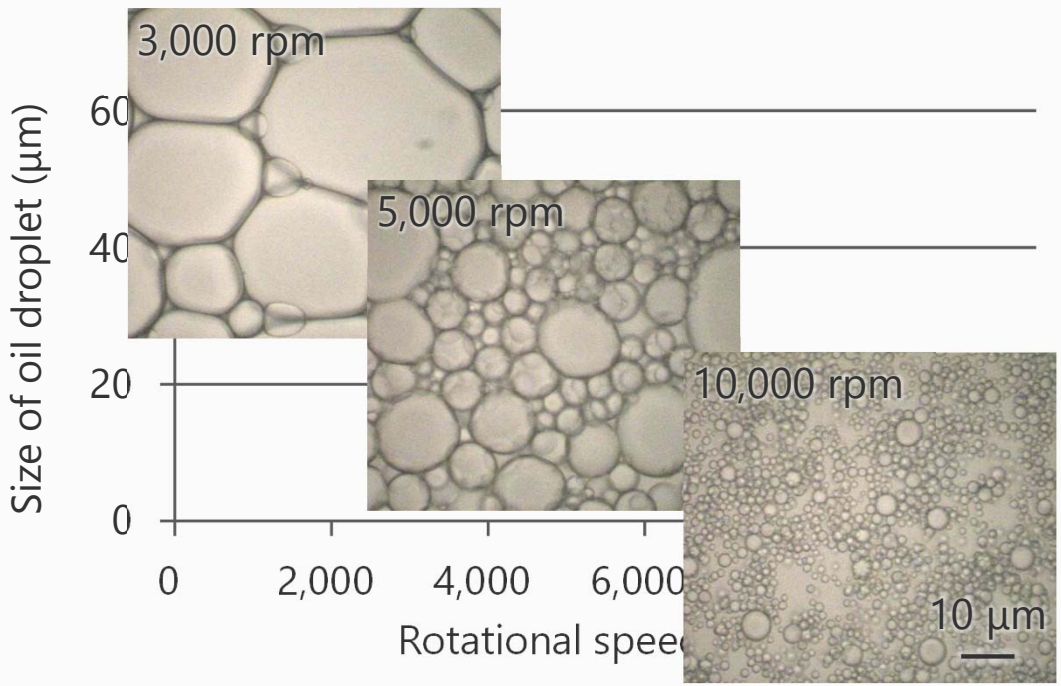
Properties of examined oils

Oil	Structure	Interfacial tension (mN/m)
n-Octanol	C_8OH	8.5
n-Decanol	$C_{10}OH$	9.0
Methyl Decanoate	$C_{10}OOMe$	17.9
Decanedioic Acid Diethyl Ester	$C_{10}(OOEt)_2$	23.9
n-Decane	C_{10}	52.3
n-Hexadecane	C_{16}	53.3

Effect of rotational speed to size of oil droplet



Size of oil droplet became smaller with higher rotational speed

Determination of the interfacial area dA

$$dA = \frac{V_T}{V_O} \times A_O = \frac{V_T}{\frac{4}{3}\pi r^3} \times 4\pi r^2$$

V_T: Total oil volume in emulsion phase (L)

V_O: Volume of an oil droplet (L)

A_O: Surface area of an oil droplet (m^2)

r: Diameter of an oil droplet (m)

Adsorbed amount of TOCN onto oil droplet

- Centrifugation for 10 min at 4,000 rpm (3,200 xg) of sample
- Determination of TOCN concentration in water phase by Phenol-sulfuric acid method
- Calculation by;

$$\text{Adsorbed amount (\%)} = \frac{0.05 - C_W}{0.05} \times 100$$

0.05: TOCN conc. before emulsifying (%)

Cw: Residual TOCN conc. in water phase after emulsifying (%)