Oven-dried carboxymethylated cellulose nanofibril foam with high water durability and its application for dye removal

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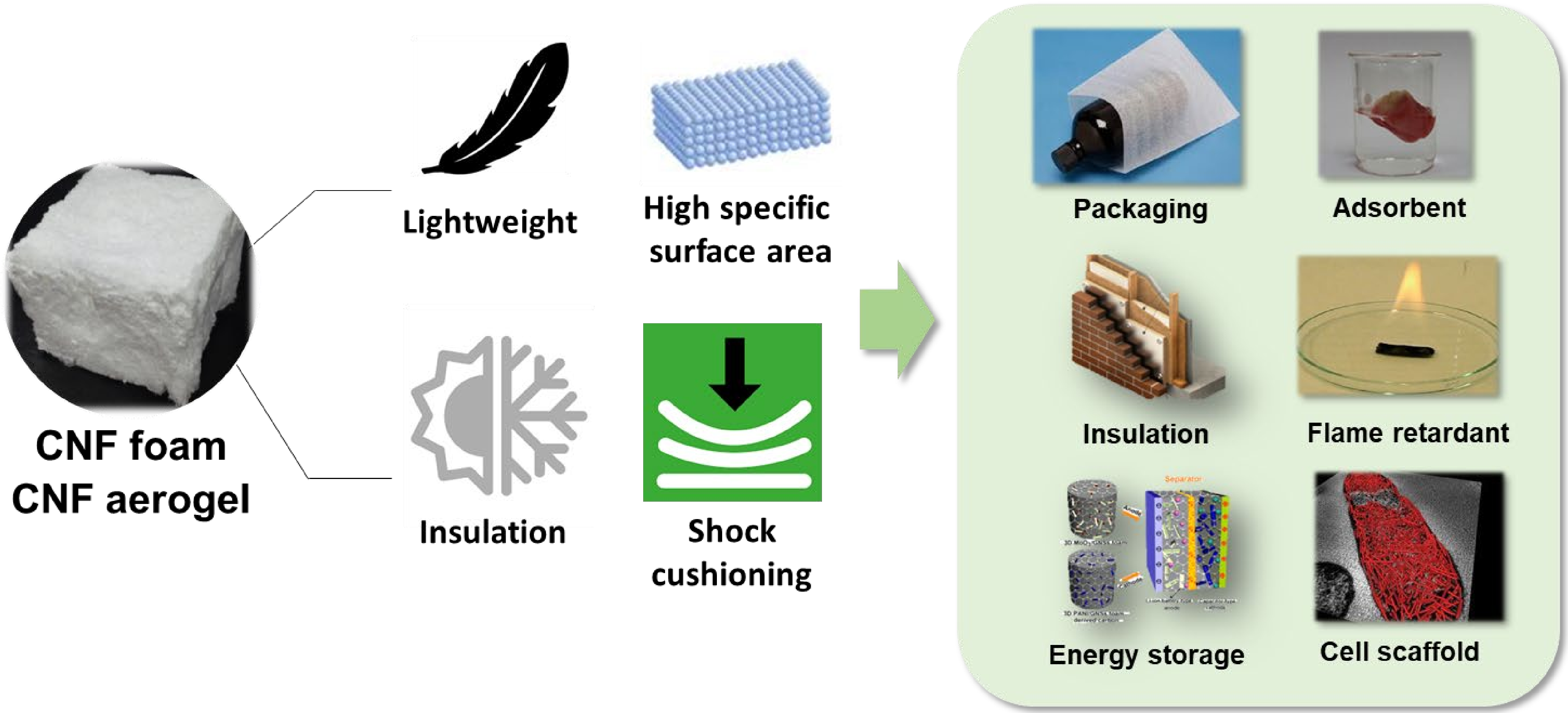
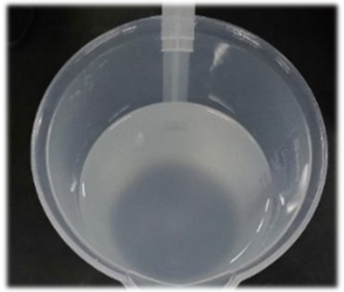
TAPPI NANO DIVISION

Cellulose nanofibril-based porous materials



Preparation of CNF-based foams

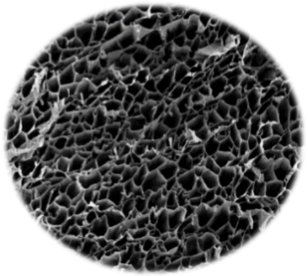
CNF suspension



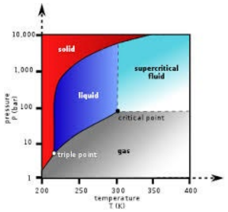
Substitution of water to air

Drying

CNF-based foams



- **Freeze drying**
  - ✓ Most widely used drying method for production of CNF aerogel and foam
  - ✓ Prevention of capillary forces and fibril aggregation
  - ✓ High porosity and small pore size
  - ✓ **Long drying time (several days), high energy consumption**

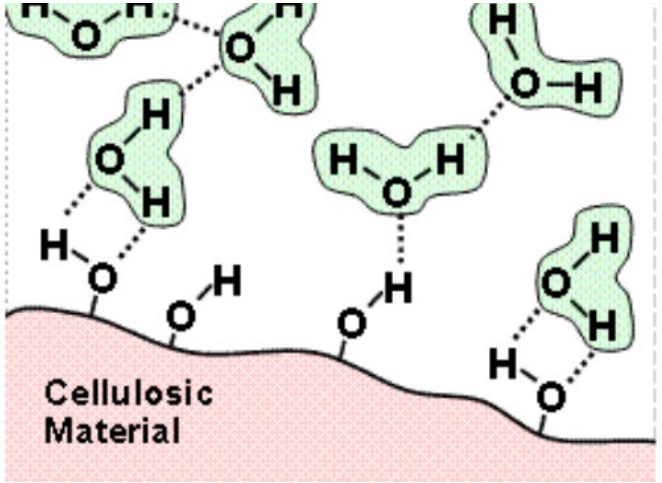


- **Supercritical drying**
  - ✓ Prevention of capillary forces during drying
  - ✓ **High cost technique, hard to scale-up**

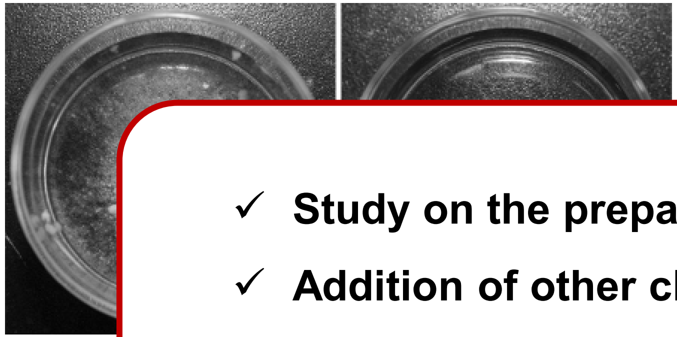
- **Oven drying**
  - ✓ Easy and low cost drying method
  - ✓ Relatively fast drying
  - ✓ **Aggregation of fibrils and deformation of porous structure**

  ➔ **Preparation of foam by drying CNF-stabilized bubbles**

Water durability of CNF foam

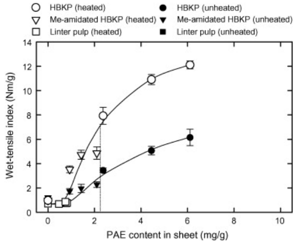


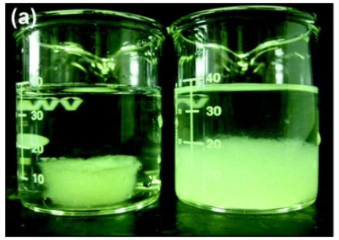
Hubbe et al. (2013)



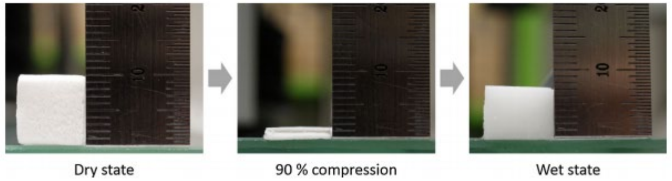
- Polyamide-epichlorohydrin (PAE) were most widely used crosslinkers to increase wet strength of the **CNF sheets**.
- PAE-crosslinked CNF foam prepared by **freeze drying** showed high water durability and wet resilience.

(Obokaka et al. 2007, Zhang et al. 2012)

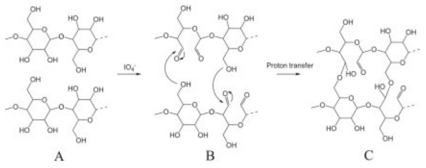


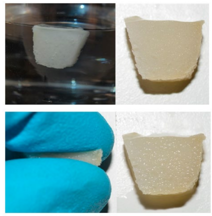


- Introduction of polycarboxylic acid produced ester linkage with CNF and increased the wet strength and wet resilience of **freeze-dried CNF foam**. (Kim et al. 2015)



- Partial oxidation of cellulose nanofibril generated aldehyde groups, and crosslinking of aldehyde and hydroxyl groups occurred.
- Water-durable, **oven-dried** CNF foam was prepared by crosslinking of aldehyde-introduced CNF. (Larsson et al. 2013, Cervin et al. 2016)





- ✓ **Study on the preparation and application of oven-dried foam with high water durability is required.**
- ✓ **Addition of other chemicals might affect the stability of CNF wet foam.**

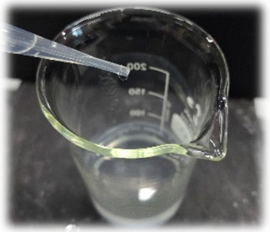
  ➔ **Proper crosslinking method for better foam stability should be selected.**

(Liang et al. 2020) (Wang et al. 2018) (Tian et al. 2017) (Mulyadi et al. 2016) (Lahtinen et al. 2017)

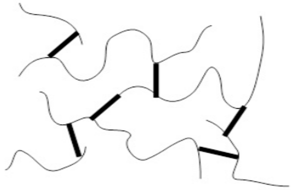
Objectives

Preparation of oven-dried CNF foams with high water durability via proper crosslinking and suggestion of their potential application

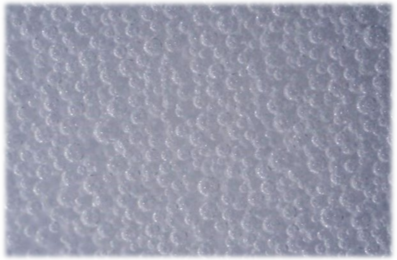
Crosslinking approach



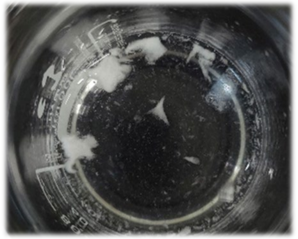
1. Addition of PAE

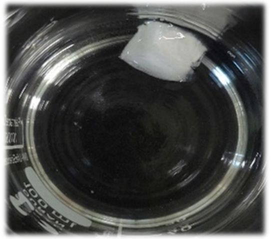


2. Self-crosslinking without crosslinkers

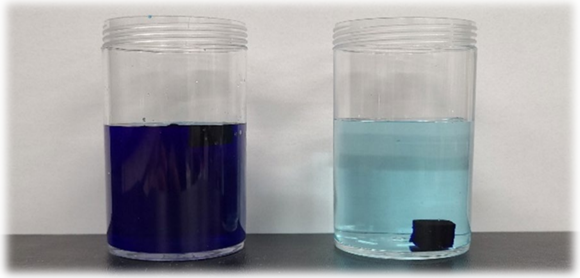


Wet foam characteristics





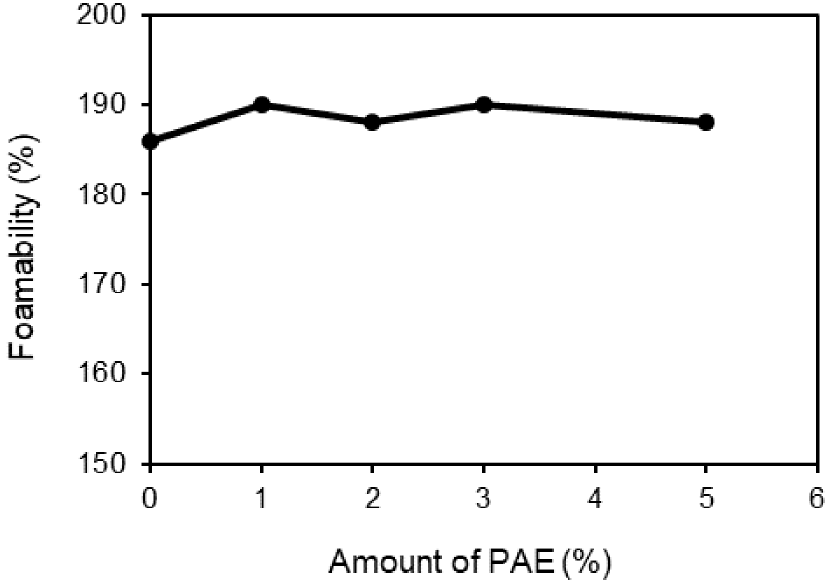
Water durability

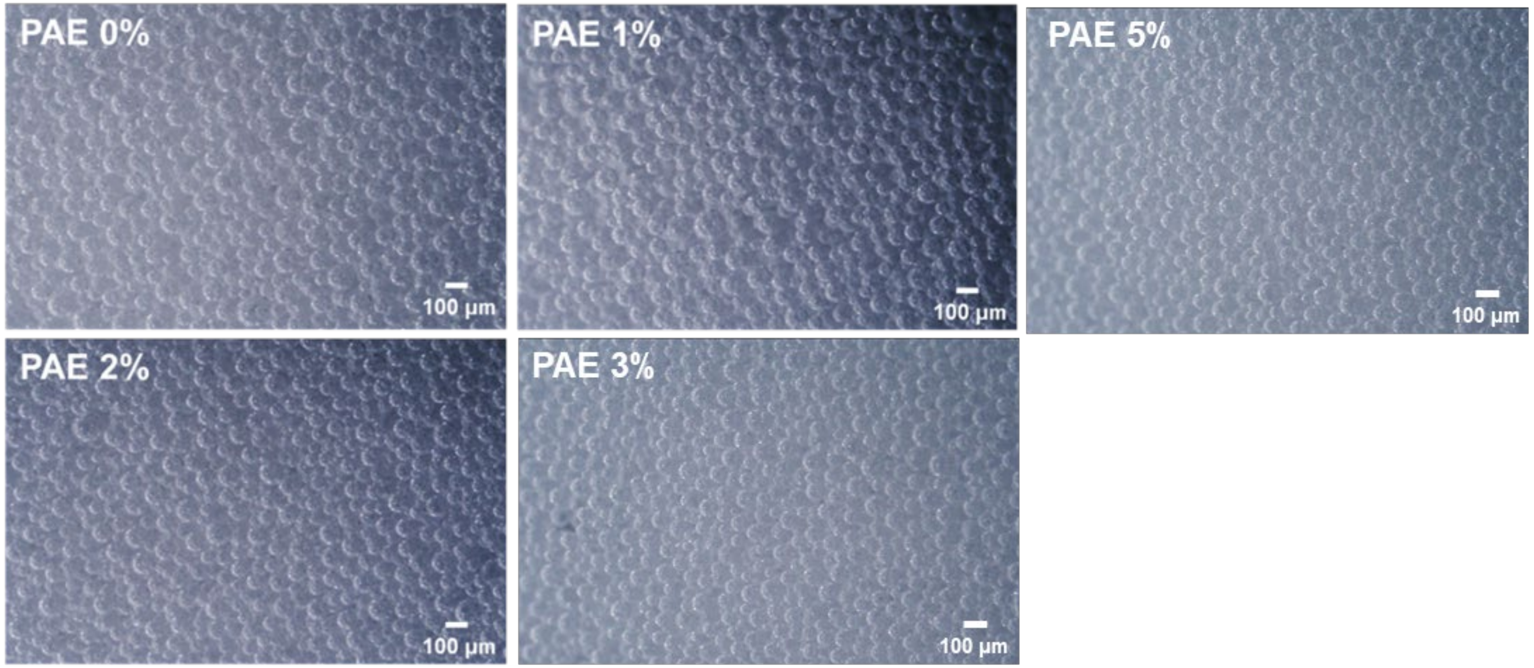


Dye adsorption ability

Effect of PAE addition on wet foam properties

➢ **Foamability and bubble morphology**

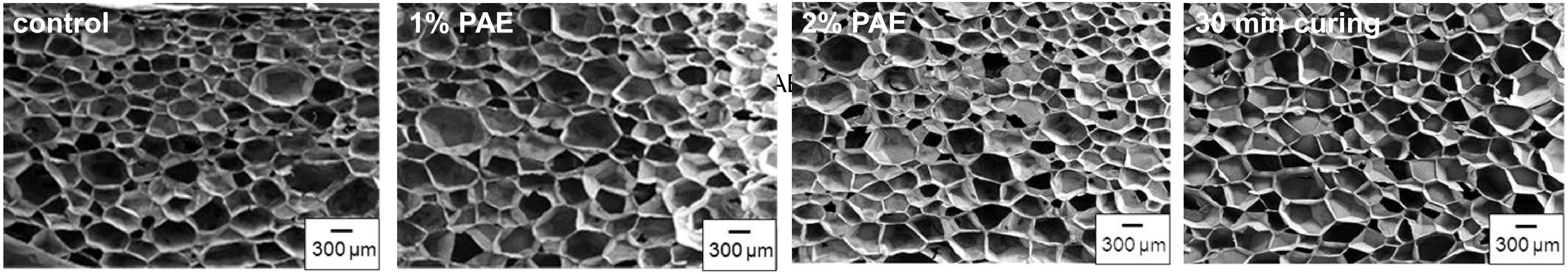




✓ Addition of PAE had no noticable effect on the generation of CMCNF wet foam.

Structural and mechanical properties

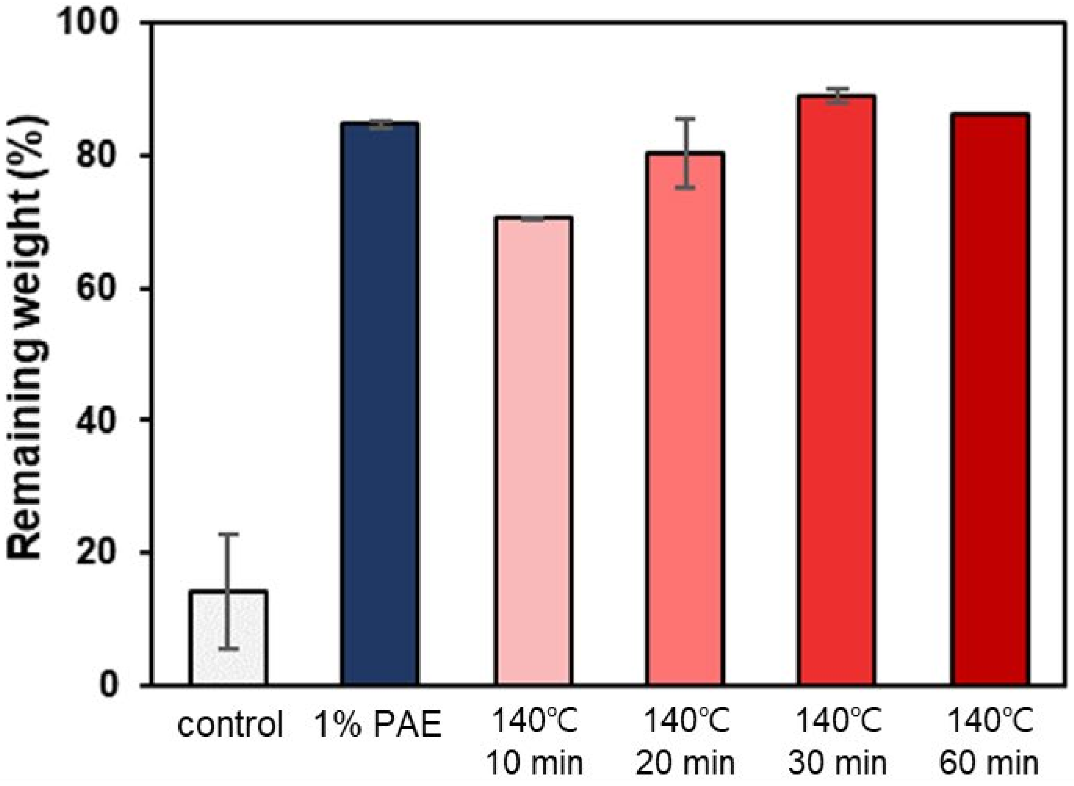
- **SEM images**

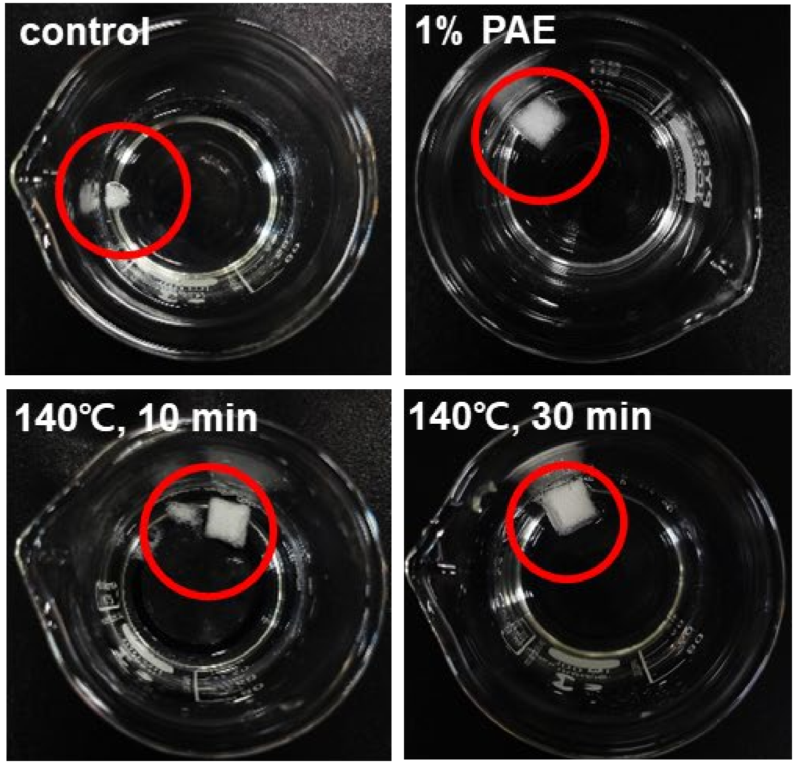


- **Structural and mechanical properties**

Drying method	Crosslinking condition	Density (kg/m³)	Porosity (%)	Compressive strength (kPa)
Oven Drying	-	9.1 ± 0.6	99.4	53.4 ± 7.5
	PAE 1%	8.9 ± 0.7	99.4	53.9 ± 0.4
	PAE 2%	9.0 ± 0.8	99.4	53.1 ± 2.6
	140°C curing for 10 min	9.0 ± 0.5	99.4	55.1 ± 10.8
	140°C curing for 20 min	8.9 ± 0.4	99.4	54.9±7.9
	140°C curing for 30 min	8.9 ± 0.5	99.4	55.3 ± 5.2
	140°C curing for 60 min	9.0 ± 0.3	99.4	54.6 ± 5.6

Water durability



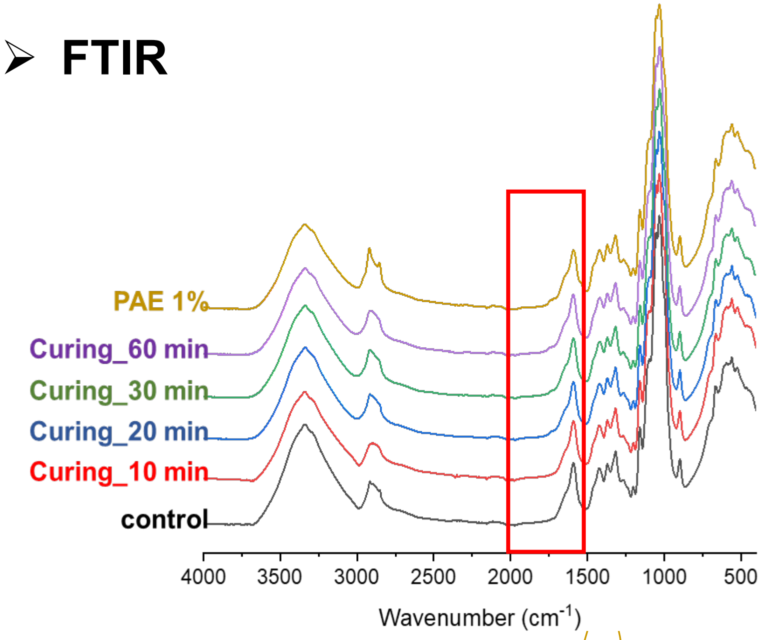


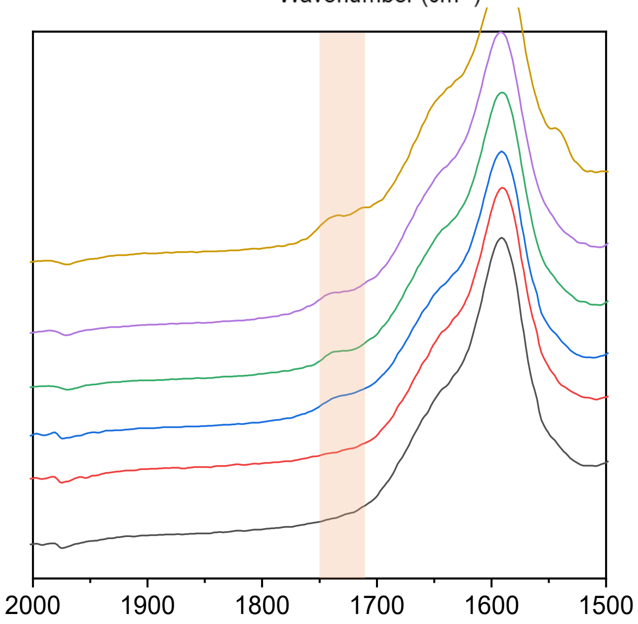
- ✓ Wet durability of the foam was evaluated by stirring the foam in DI water at 1000 rpm for 1 min.
- ✓ Wet durability of the foam improved as time for the heat treatment increased to 30 min.

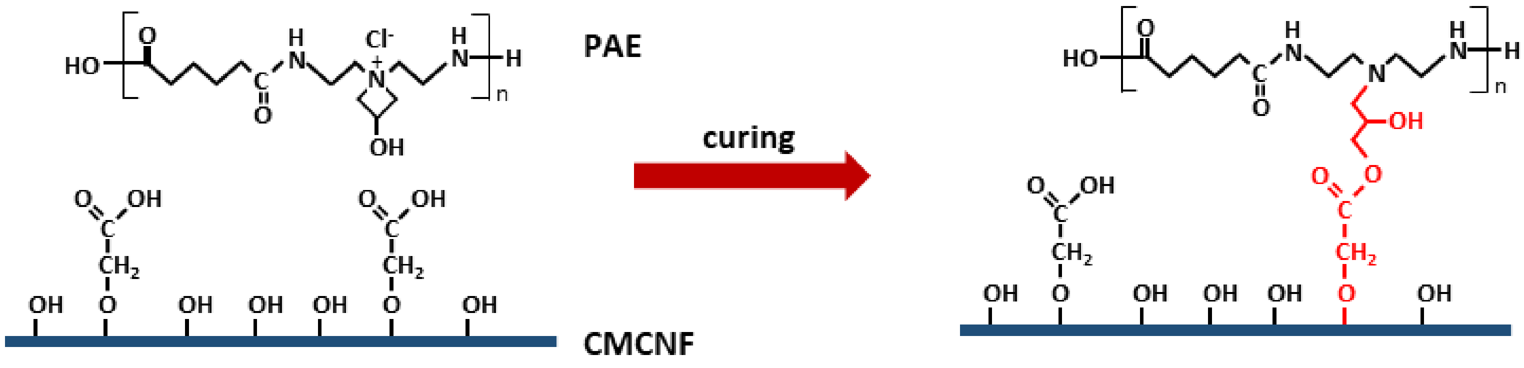
➔ Cured CMCNF foam and PAE-crosslinked foam showed similar wet durability.

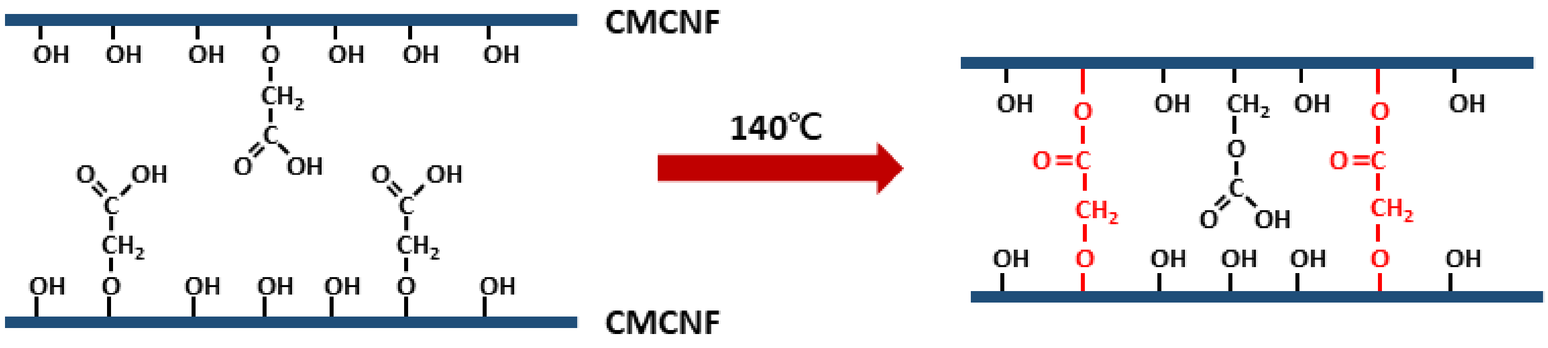
Crosslinking mechanism

- FTIR



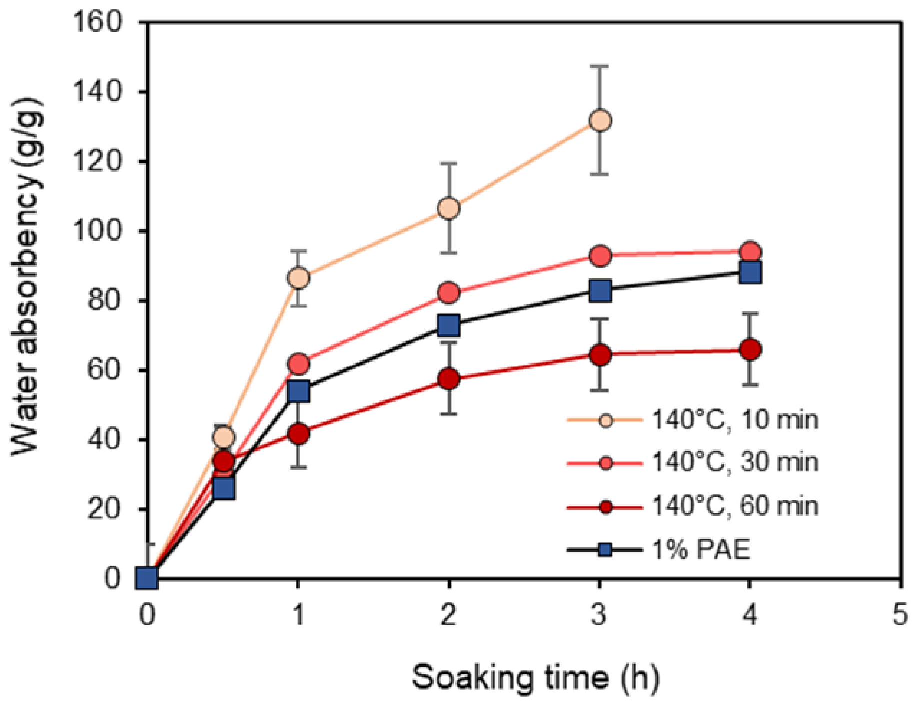


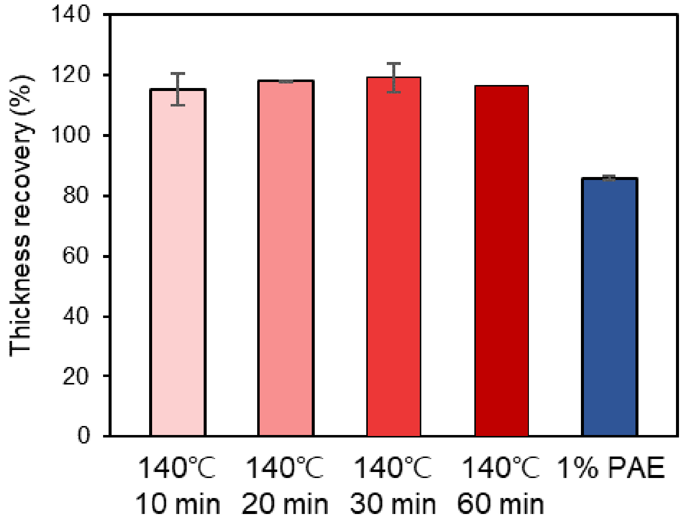


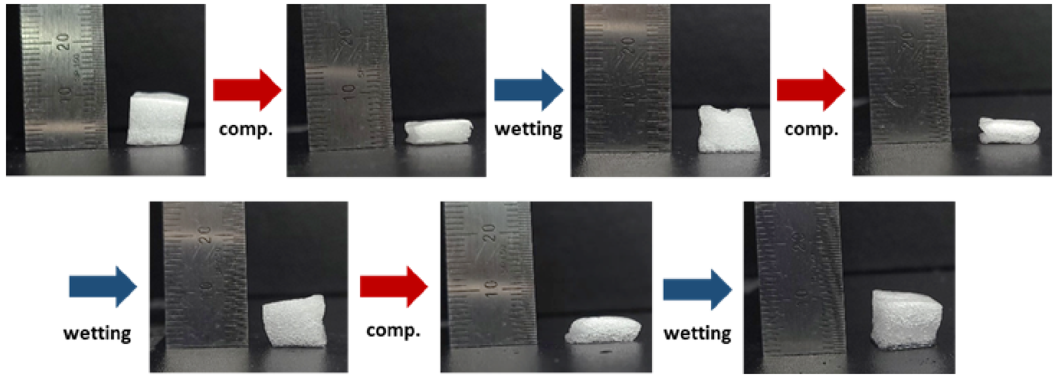


Performance in water

➢ **Water absorbency & wet resilience**





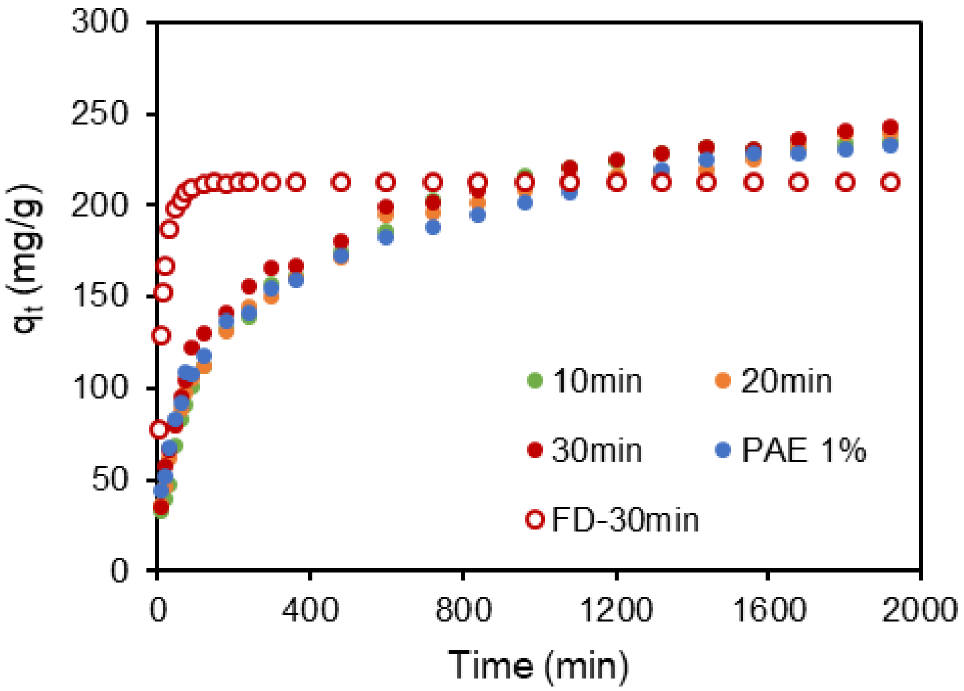


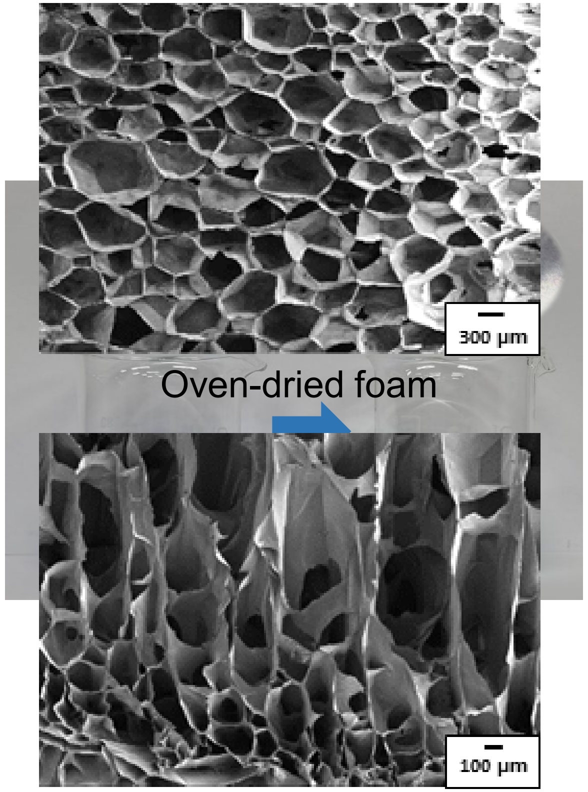
✓ Water absorbency of the foam decreased with longer heat treatment time.

✓ Oven-dried foam showed excellent wet resilience regardless of the curing time.

Dye adsorption ability

➢ **Adsorption capacity**





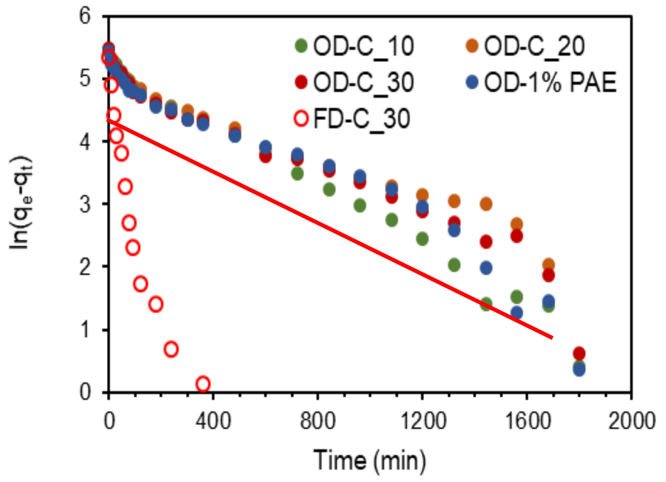
Freeze-dried foam

✓ MB adsorption rate of the oven-dried foam was slower than that of the freeze-dried foam because of the closed-cell pore structure.

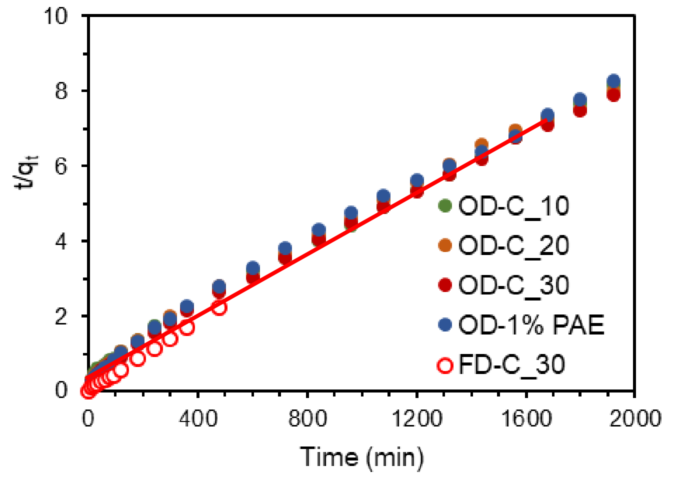
✓ Oven-dried foam showed higher maximum adsorption capacity (q_e), which was 230 – 250 mg/g.

➔ Oven-dried foam had higher specific surface area (SSA) than the freeze-dried foam.

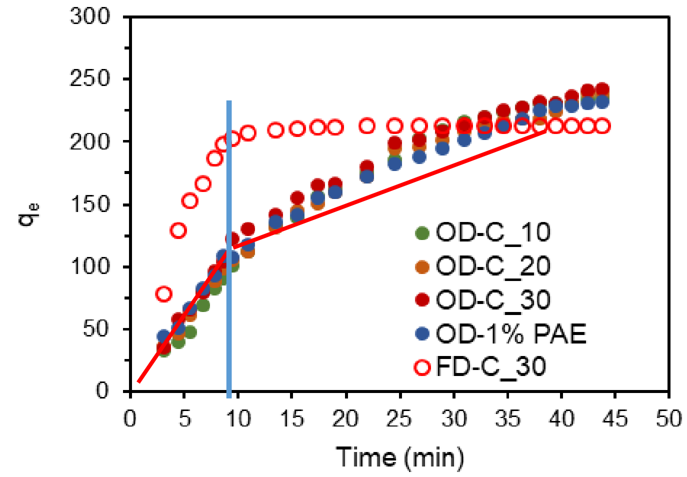
Dye adsorption kinetics



Pseudo-first-order



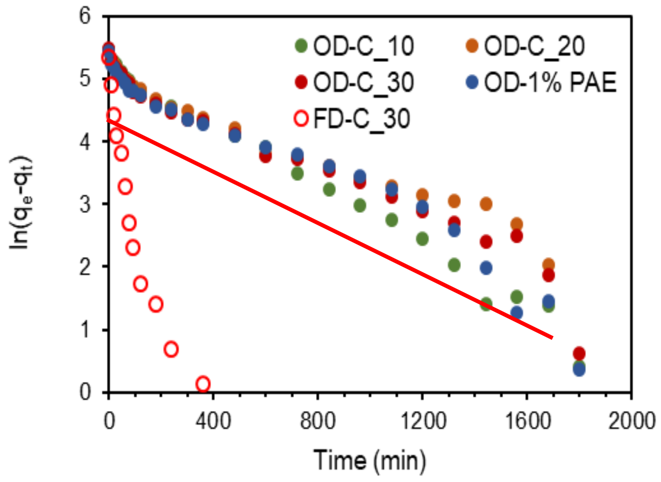
Pseudo-second-order



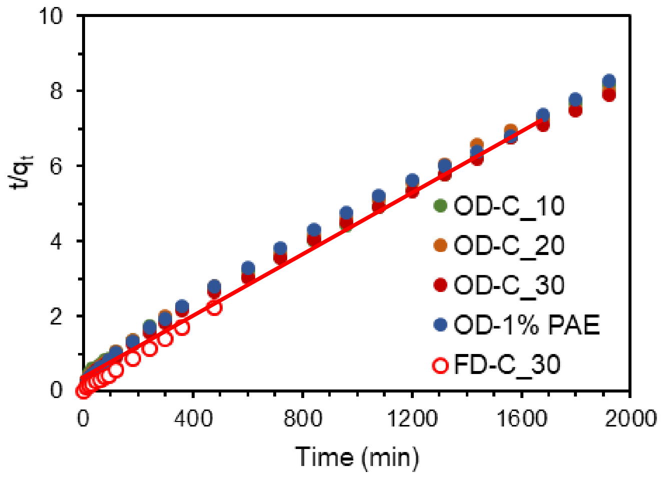
Intraparticle diffusion

Drying method	Crosslinking condition	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion model			
								$t^{1/2} < 10$		$t^{1/2} > 10$	
		k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/(mg·min))	q_e (mg/g)	R^2	k_3 (mg/g·$min^{1/2}$)	R^2	k_3 (mg/g·$min^{1/2}$)	R^2
Oven drying	curing_10min	0.0025	193.4	0.9877	2.9×10^{-5}	250	0.9956	11.2	0.9836	3.5	0.9376
	curing_20min	0.0021	183.0	0.8919	3.2×10^{-5}	243.9	0.9933	10.5	0.9773	3.4	0.9613
	curing_30min	0.0022	182.1	0.9429	3.5×10^{-5}	250	0.9952	12.5	0.9894	3.2	0.9675
	1% PAE	0.0023	186.2	0.9554	3.5×10^{-5}	238.0	0.9929	10.3	0.9681	3.3	0.9844
Freeze drying	curing_30min	0.0146	81.14	0.8871	4.7×10^{-4}	217.4	0.9992	18.7	0.9356	-	-

Dye adsorption kinetics



Pseudo-first-order



Pseudo-second-order

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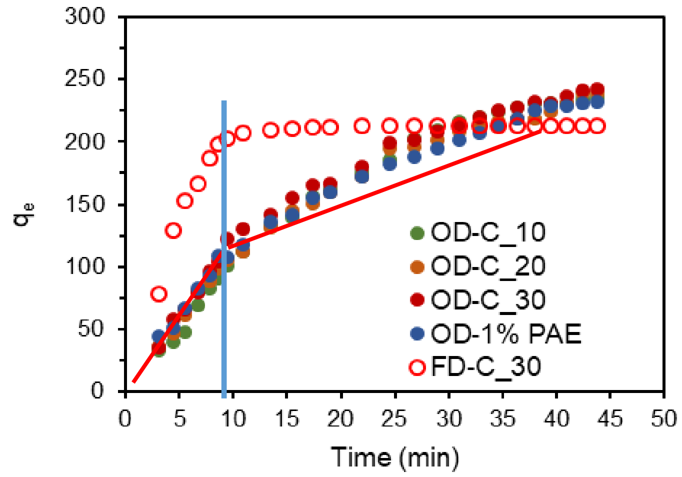

Intraparticle diffusion

Drying method	Crosslinking condition	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion model			
								$t^{1/2} < 10$		$t^{1/2} > 10$	
		k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/(mg·min))	q_e (mg/g)	R^2	k_3 (mg/g·$min^{1/2}$)	R^2	k_3 (mg/g·$min^{1/2}$)	R^2
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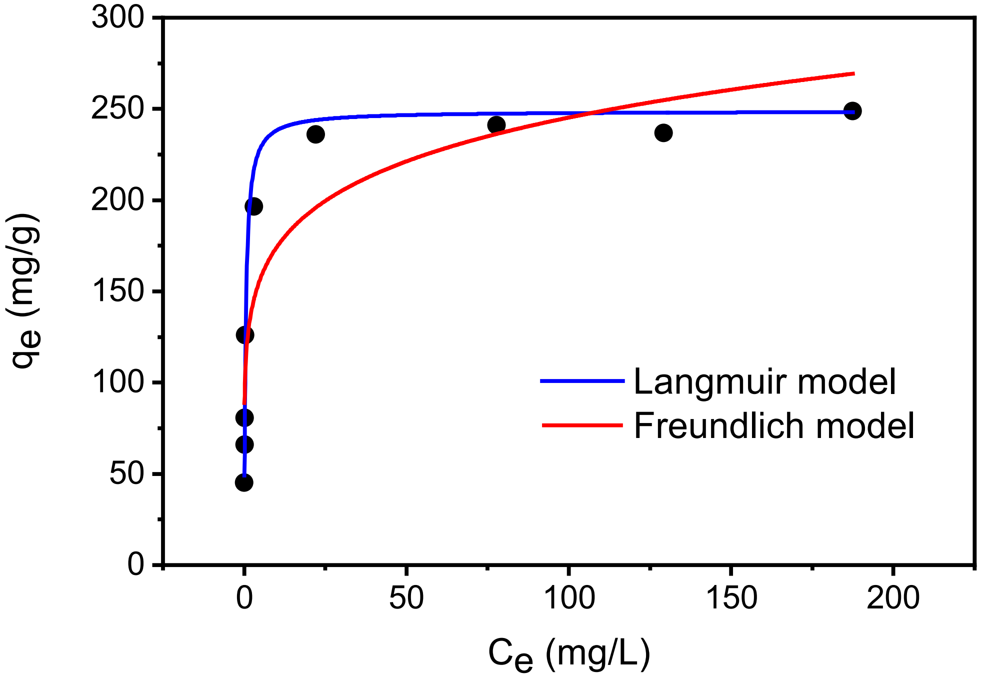
Freeze drying	curing_30min	0.0146	81.14	0.8871	4.7×10^{-4}	217.4	0.9992	18.7	0.9356	-	-

Dye adsorption isotherm

- **Oven-dried foam crosslinked with 1% PAE**



Freundlich isotherm		
K_F (L/mg)	n_f	R^2
123.68	6.72	0.8542

Langmuir isotherm		
q_{max} (mg/g)	b (L/mg)	R^2
248.81	2.26	0.9838

✓ MB adsorption of the oven-dried foam followed the Langmuir isotherm model, indicating that the MB adsorption behavior of the foam occurred by the monolayer adsorption at the homogeneous sites of adsorbent surfaces.

Summary

- **Crosslinking with PAE**
  - ✓ Addition of PAE did not have influence on the characteristics of CNF wet foam and dry foam.
  - ➔ PAE can be used as **a crosslinker for the oven-dried CNF foam**.

Addition of PAE → **CMCNF wet foam** → **Oven-dried CMCNF foam** → **PAE-crosslinked CMCNF foam**

- **Self-crosslinking of CMCNF**
  - ✓ **Heat treatment of CMCNF** produced **self-crosslinking** between carboxymethyl and hydroxyl groups**.**

CMCNF wet foam → **Oven-dried CMCNF foam** → **Heat treatment at 140℃** → **Self-crosslinked CMCNF foam**

- **Characteristics and performance of crosslinked CNF foams**
  - ✓ **Crosslinked CNF foam** exhibited **high water durability, high water absorbency (60 – 100 g/g)** and **excellent wet resilience**.
  - f the

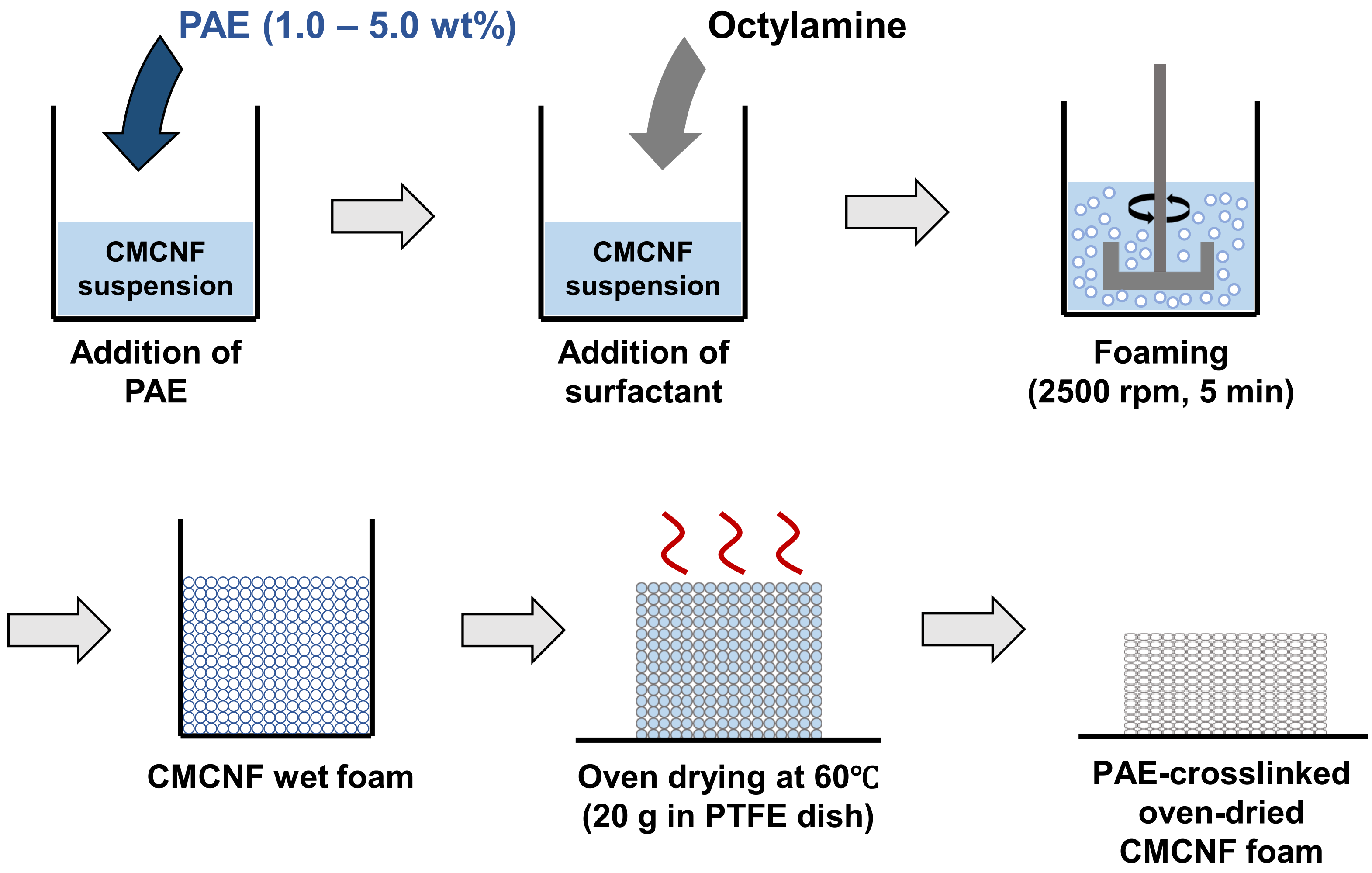
High water-durable, oven-dried CMCNF foam was prepared via crosslinking which can be used as a slow adsorption/release of the chemicals.

Thank you

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MIST) (No. 2019R1A2C1085476)

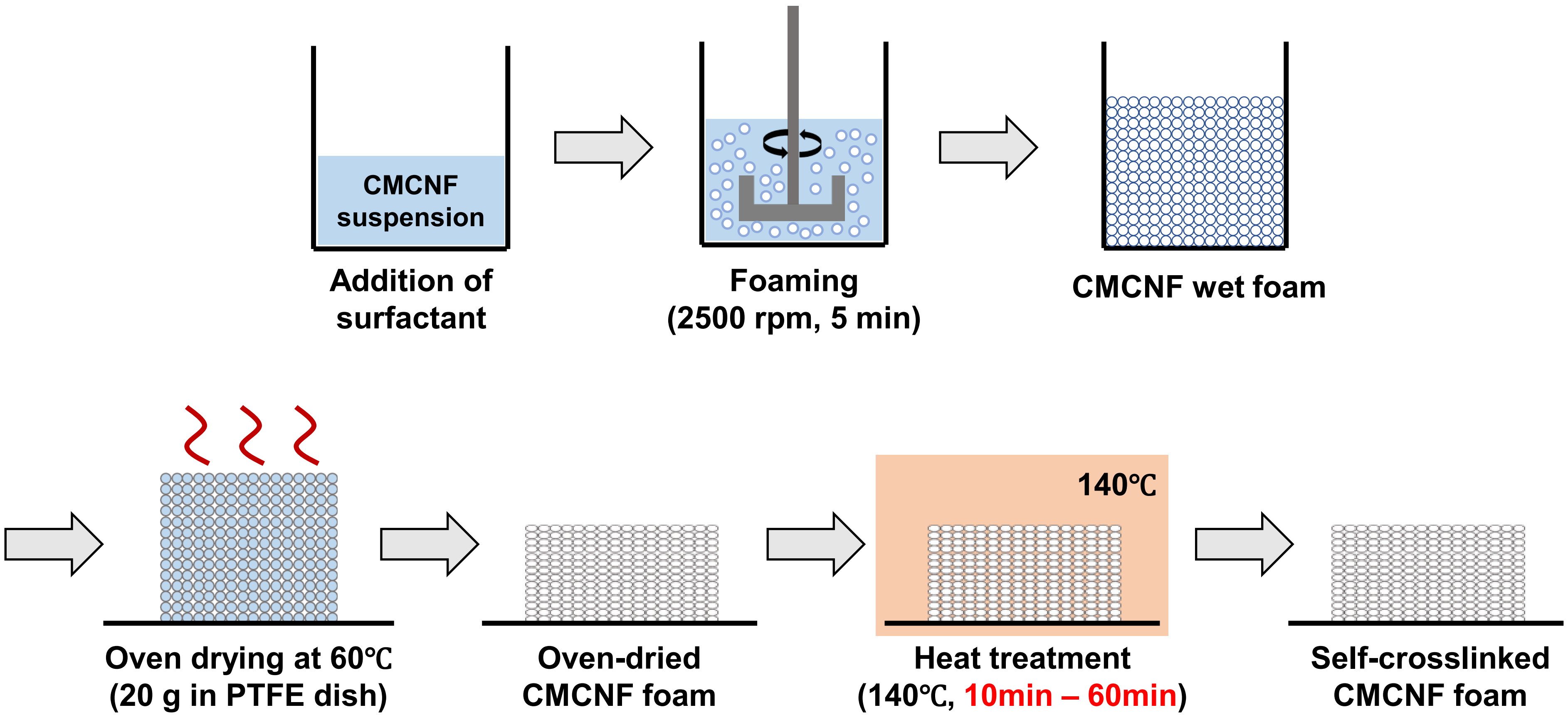
Preparation of crosslinked foams

➢ **Crosslinking with PAE**



Preparation of crosslinked foams

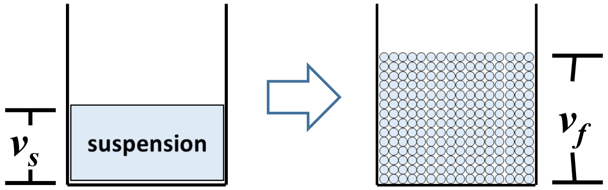
➢ **Self-crosslinking of CMCNF**



Foam characterization

➢ Wet foam characterization

- **Foamability**
  - ✓ Increased ratio of the volume of wet foams after foaming



$$\text{Foamability (\%)} = \frac{v_f}{v_s} \times 100$$

- **Morphology of bubbles (Optical microscope)**
  - ✓ Observation of the shape and size of bubbles
  - ✓ Calculation of the diameter distribution of bubbles (more than 300 bubbles were measured)
  - ✓ Measurement of the change in bubble size over time

➢ Dry foam characterization

- **Density and porosity**
  - ✓ Measurement of apparent density with 1 cm^3 cubic foam
  - ✓ Calculation of porosity of dry foam from the density of the foam (ρ) and cellulose (ρ_c)

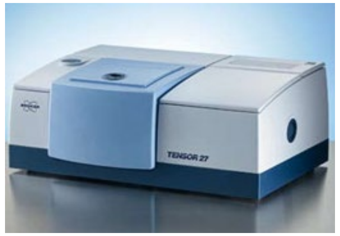
$$\text{Porosity } (\emptyset) = \left(1 - \frac{\rho}{\rho_c}\right) \times 100\ (\%)$$

- **Pore structure (FE-SEM)**
  - ✓ Observation of cross-section of the dry foam
  - ✓ Measurement of average pore size of the foam

- **Compressive test (UTM)**
  - ✓ Compressive strength and modulus of 1 cm^3 cubic foam
  - ✓ Compression speed : 5 mm/min, Compressive strength at 80% strain

Foam characterization

- **Chemical structure (FTIR)**
  - ✓ Investigation of the chemical structure of crosslinked CMCNF foam



- **Wet durability**
  - ✓ Agitating of 1cm^3 cubic foam at 1000 rpm for 1 min in water
    → Measurement of the weight reduction of the foam after agitation

$$\text{Wet durability (\%)} = {}^{m_f}/_{m_i} \times 100$$

m_i: initial mass of foam
m_f: mass of foam after agitation and drying

- **Water absorbency**
  - ✓ Soaking of 1cm^3 cubic foam into water for 4 h
    → Measurement of the weight of the absorbed water for every hour

$$\text{Water absorbency (g/g)} = {}^{m_w}/_{m_d}$$

m_d: initial dry mass of foam
m_w: mass of water-absorbed foam

- **Wet resilience**
  - ✓ 80% Compression of foam and soaking into water
    → Measurement of the recovery ratio of the foam thickness

$$\text{Wet resilience (\%)} = {}^{h_w}/_{h_d} \times 100$$

Dry foam 80% compression Soaked foam

Dye adsorption ability

- **Dye adsorption test**
  - ✓ Cubic foam into 50 mL methylene blue (MB) solution (50 mg/L concentration)

    → Evaluation of amount of MB adsorbed at various time (q_t) intervals by measuring MB concentration

$$q_t(\mathrm{mg/g}) = \frac{(C_0 - C_t)V}{m}$$

C_0: initial concentration of the MB solution,
C_t: concentration of the solution at time
V: volume of the MB solution
m: mass of the foam

- **Adsorption kinetics**
  - ✓ Pseudo-first-order kinetics $\ln(q_e - q_t) = -k_1 t + ln q_e$
  - ✓ Pseudo-second-order kinetics $\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$
  - ✓ Intraparticle diffusion model $q_e = k_3 t^{1/2} + c$

q_e: Adsorption capacity at equilibrium
k_1: pseudo-first-order rate constant
k_2: pseudo-second-order rate constant
k_3: rate constant for intraparticle diffusion model

- **Adsorption isotherms**
  - ✓ Freundlich isotherm $q_e = K_F C_e^{1/n_f}$
  - ✓ Langmuir isotherm $q_e = \frac{q_{max} b C_e}{1 + b C_e}$

K_F, n_F: Freundlich constant
C_e: MB concentration at equilibrium
q_{max}: theorical maximum adsorption capacity
b: Langmuir constant