

# PROPERTIES OF CELLULOSE NANOFIBRIL FOAM DEPENDING ON WET FOAMING CONDITIONS

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## ABSTRACT

Cellulose nanofibril (CNF) foam, which has advantages of sustainability and biodegradability, has a potential to apply to diverse fields including packaging, thermal insulation, and absorbent. In recent days, the oven drying of Pickering-stabilized CNF wet foam was proposed as an alternate approach to manufacture CNF-based porous foams. To produce CNF foam with uniform structure, the properties of wet foam are very important. In this study, carboxymethylated cellulose nanofibril (CMCNF) was used to prepare CNF foam. The effects of wet foaming conditions such as CMCNF consistency, surfactant amount, and shear rate on the properties of the wet and dry foams were investigated. A low addition level of surfactant led to insufficient generation of bubbles, whereas high levels of surfactant generated unstable wet foam. A proper amount of the surfactant and

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CMCNF consistency yielded wet foams with excellent stability. CNF wet foam with high stability resulted in CNF foam with uniform pore structure and high compressive strength. The shear rate during wet foam generation also had a significant impact on the foamability of wet foam, which determined the density and the pore size of the oven-dried CNF foam.

## **INTRODUCTION**

Foam and aerogels which are mostly produced from silica or petroleum chemicals are used in diverse industrial fields including packaging, thermal insulation, and absorbents [1–3]. To replace these materials by eco-friendly materials, cellulose nanofibril (CNF) can be used as raw material for producing foam and aerogels owing to its 3-D network forming ability [4]. CNF is known to have unique characteristics such as high specific surface area and aspect ratio, good mechanical strength, and biodegradability [5,6]. Many studies have reported that CNF foam or aerogels can be prepared via freeze drying which prevents hydrogen bonding between fibrils and compaction of the structure [7–9]. However, freeze drying requires several days for drying and consumes high amount of energy to maintain low temperature and vacuum during a drying process. In addition, CNF foams without crosslinking treatment usually has poor mechanical strength and brittleness.

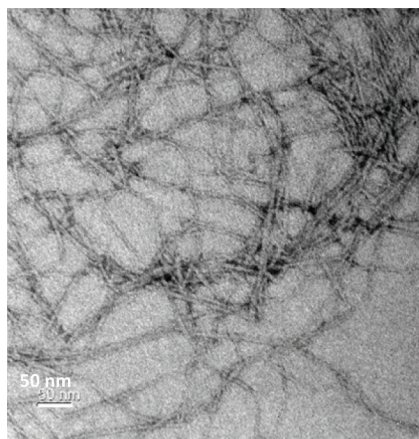
Recently, several studies proposed a process to make CNF foam via oven drying [10–12]. This process starts with the formation of a CNF wet form based on the Pickering stabilization concept. A CNF wet foam consisting of CNF-stabilized bubbles is converted to dry foam by evaporation of water between bubbles during oven drying process. The ability of CNF as a Pickering stabilizer of air bubbles made it possible. CNF is known to be an effective particle for Pickering stabilization owing to its excellent mechanical strength, high aspect ratio, amphiphilicity, and flexibility [13]. Many studies reported that CNF-stabilized Pickering emulsions show good stability by prohibiting the coalescence of oil droplets. It is also possible to stabilize the air-water interface using CNF with surfactant. If the wet foam structure has to be well converted to pore structure under hot temperature condition, CNF foam can be produced via oven drying which is a very attractive process in aspects of the possibility to scale-up due to its simple and low-cost drying process. However, high-temperature drying in the oven creates the Campbell effect derived from the capillary force, leading to aggregation and hydrogen bond forming between fibrils. Therefore, the preparation of highly stable CNF wet foam is very important because it has to endure the drying stress and bubble aging during oven drying. Nevertheless, the number of

studies on the preparation and application of oven-dried CNF foam using Pickering stabilization is very limited. Therefore, the studies on the preparation and the application of the Pickering-stabilized CNF foams are necessary to expand the potential applications of porous CNF materials as a next-generation sustainable material. In this study, the effects of wet foaming conditions on the characteristics of CNF wet and dry foams were investigated. CNF suspension consistency, the amount of surfactant, and shear condition were controlled to observe the influence of these conditions on the characteristics of Pickering-stabilized CNF wet foams. The wet foams were dried in the convection oven, and the characteristics of dry foam were also examined to determine the relationship between the characteristics of wet and dry foams.

## **MATERIALS AND METHODS**

### **Materials**

Carboxymethylated cellulose nanofibril (CMCNF) was prepared by grinding a carboxymethylated kraft pulp fibers using Supermasscolloider (Masuko Sangyo, Japan). The carboxyl group content of the prepared CMCNF was 870  $\mu\text{mol/g}$ . Octylamine (OA, Sigma Aldrich, USA) and sodium dodecyl sulfate (SDS, Sigma Aldrich, USA) were used as cationic and anionic surfactants to prepare wet foam, respectively.



**Figure 1.** Morphology of CMCNF observed using transmission electron microscope.

### **Preparation of CMCNF-stabilized Wet Foam**

CMCNF suspensions with different consistency (0.25 – 1.0 wt%) were prepared. Surfactant was added to 50 g CMCNF suspension by 0.01 – 0.06 wt% based on the weight of the suspension. The suspension was then vigorously stirred for 5 min with an overhead stirrer. The wet foaming was conducted at different stirring speed from 1500 rpm to 3000 rpm to examine the effect of shear rate during foaming.

The foamability was evaluated as the ratio of the volume increase induced by foaming, which is determined by given by:

$$\text{Foamability (\%)} = V_f/V_i \times 100 \quad (1)$$

Where  $V_f$  is the volume of the wet foam immediately after the foaming (ml) and  $V_i$  is the original volume of the suspension (ml).

### **Characterization of CMCNF-stabilized Wet Foam**

1 ml of each wet foam was transferred onto the glass slide and the bubble morphology was observed for 6 h using an optical microscope (Sometech, Korea). From images of the bubbles in each foam, the average diameter of these bubbles was obtained by measuring the diameter of more than 100 bubbles using the Image J program. To assess the long-term stability of the foams, each wet foam was placed in a 20-mL vial after foaming, and the change in the appearance of the foam was observed for 1 days. The oscillatory rheological properties of the wet foam was measured using a Bohlin CVO Rheometer (Malvern Panalytical Ltd., UK) with cone-plate geometry (4° angle, 40 mm diameter) and 300  $\mu\text{m}$  gap size. The storage modulus and loss modulus of each foam were measured for shear stress values ranging from 0.1 to 1000 Pa under an amplitude sweep mode at 1 Hz frequency. In addition, the yield stress was determined as the stress value that intersects two tangential lines of the viscoelastic region and flow region of the storage modulus curve. The average yield stress was obtained from three measurements.

### **Drying and Characterization of Dry Foam**

A portion (20 g) of each wet foam was poured into a 55-mm-diameter polytetrafluoroethylene (PTFE) dish. The wet foam was dried at 60°C in a convection oven until it were completely dried. The characteristics of the dry foam including the appearance, porosity, and compressive strength were evaluated.

The pore structure of the foams was observed via field-emission scanning electron microscopy (FE-SEM; SUPRA 55VP, Carl Zeiss, Germany). Prior to observation, the dried foam was cut into cubes using a razor blade, and the cross-section of each specimen was coated with Pt (thickness: 10 nm). Using the Image

J software, the average pore size and the average pore-wall thickness were determined from the SEM images.

The apparent density, porosity, and shrinkage ratio in the thickness direction of the foam during drying were measured. The density of the foam was determined by weighing the 1 cm<sup>3</sup>-cubic foam. At least five cubic foams were tested for determination of the density of the dry foam. Furthermore, the porosity,  $\emptyset$  (%), was determined by:

$$\emptyset (\%) = (1 - \rho / \rho_c) \times 100 \quad (2)$$

where,  $\rho$  is the density of the dried foam (kg m<sup>-3</sup>) and  $\rho_c$  is the density of the cellulose (1500 kg m<sup>-3</sup>). The shrinkage ratio in the thickness direction of the foam was calculated by measuring the thickness of the foam before and after drying.

The compressive strength of the dry foam was evaluated by compression tests conducted on a Universal Testing Machine (Instron 5943, Instron, USA) equipped with a 1 kN load cell. The foam was cut into 1 × 1 cm cubic specimens and conditioned at 23°C, 50% RH for a day. A compression strain that was set to 90% of the foam height and a compression speed of 10 mm/min were employed. More than four specimens were tested for each condition. The compressive strength of the foam was determined as the stress value at 80% strain.

### **Preparation of Freeze-dried Foam**

Freeze-dried CMCNF foam was prepared to compare the characteristics of the foam with those of oven-dried CMCNF foam. 0.75% CMCNF suspension was put into disposable cuvettes (1 × 1 × 5 cm). The suspension was frozen in liquid nitrogen, and then freeze-dried using a freeze dryer (FD8518, Ilshin, Korea) at -80 °C under 5 mTorr.

## **RESULTS AND DISCUSSION**

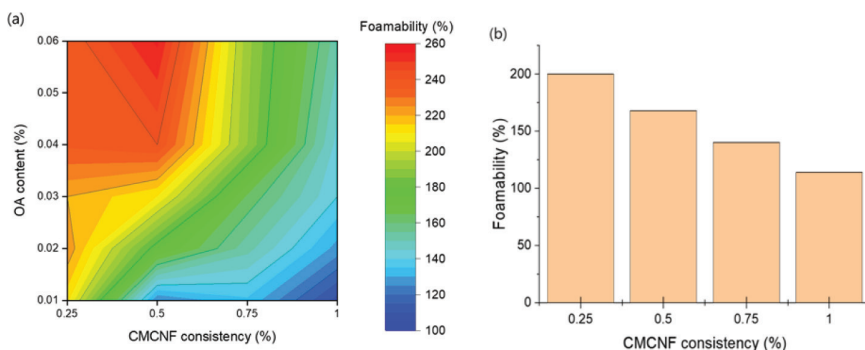
### **Effect of CNF Consistency and Surfactant Dosage**

#### *Characteristics of Wet Foam*

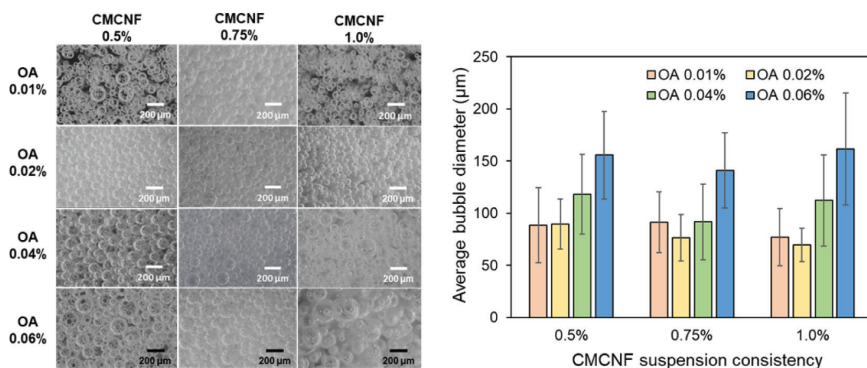
The effect of the CMCNF consistency and the amount of surfactant on the characteristics of wet foam was investigated by evaluating foamability, bubble morphology, bubble stability and rheological property. The volume of the CMCNF suspension with surfactant increased due to the generation of bubbles during vigorous stirring of the suspension. Figure 2 shows the foamability of the wet foam, which indicates the ratio of the volume before and after foaming. The

foamability of the CMCNF suspension with low consistency was relatively high. The foamability of the 0.25 wt% CMCNF suspension was >200% for all surfactant amounts. In the case of the 0.5 wt% suspension, the foamability was less than 125% at 0.01 wt% octylamine content, which was likely owing to the increased viscosity of the CMCNF suspension compared with the 0.25 wt% CMCNF consistency. However, when the octylamine content increased, the volume of the wet foam increased sharply with increasing amounts of octylamine. The foamability of the high consistency CNF (>0.75 wt%) was similar to that of 0.5 wt% CMCNF at 0.01 wt% surfactant content, but it increased slowly with the increasing amount of surfactant and remained below 200%, which may be resulted from the rapidly increased viscosity of the CMCNF suspension with increasing consistency: the viscosities of the 0.75 and 1.0 wt% CMCNF suspension were 5400 and 15000 cPs, respectively. The effect of CMCNF suspension consistency on the foamability was similar independently on the type of surfactant. When SDS (0.02%) was added to CMCNF suspensions with different consistencies, the foamability decreased sharply (Figure 2(b)). High viscosity corresponds to low mobility of CNF, and this may have contributed to low levels of foam generation at high consistency of the CNF suspension.

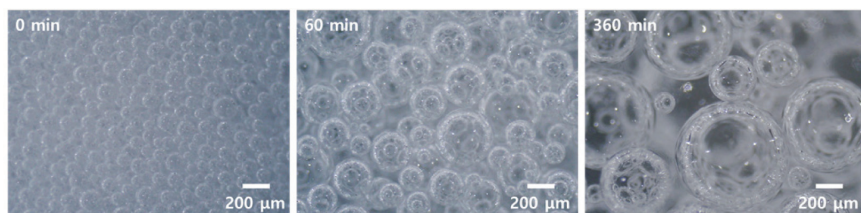
The morphology of the bubbles comprising each wet foam was affected by the CMCNF consistency and OA content (Figure 3). When observed using an optical microscopy, wet foam with 0.01 wt% octylamine was only partly composed of bubbles and the volume of liquid between the bubbles was large. This demonstrates that the amount of surfactant was not enough for sufficient foam generation. This insufficient foam generation seemed to contribute to the low number of bubbles, with a wider distribution of bubble sizes at 0.5 – 1.0 wt% CMCNF consistencies.



**Figure 2.** Foamability of carboxymethylated cellulose nanofiber (CMCNF) wet foam (a) depending on CMCNF consistency and octylamine content and (b) depending on CMCNF consistency with 0.02% SDS.



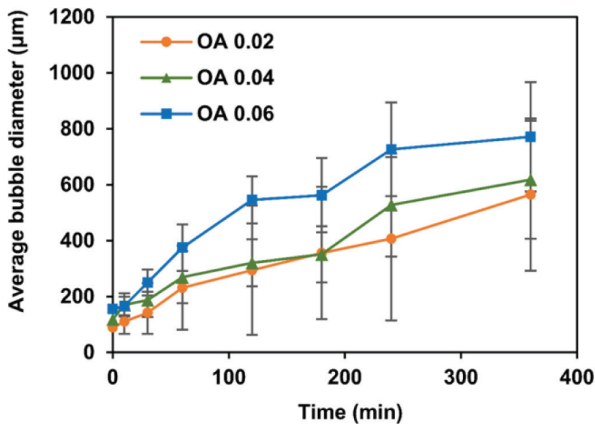
**Figure 3.** Microscopic images and average diameters of bubbles in CMCNF wet foam with different CMCNF consistency and octylamine (OA) contents [14].



**Figure 4.** Time-dependent changes in the bubble shape of the CMCNF 0.5 wt% + OA 0.02 wt% foam [14].

When the amount of octylamine increased from 0.01 wt% to 0.02 wt%, the wet foam was completely filled with bubbles, and the size of the bubbles decreased and the uniformity of the bubbles increased because of the increase in the number of bubbles by a proper interaction between nanofibrils and surfactant. For an octylamine content of >0.02 wt%, the average size of the bubbles increased and the size distribution of the bubbles widened owing to the generation of bubbles with instability.

Wet foam is thermodynamically unstable and destroyed with time [15]. Figure 4 shows the change in bubble shape of CMCNF (0.5%) wet foam with 0.02% OA. Owing to destabilization of the foam such as coarsening and coalescence of bubbles, the diameter of the bubbles increased. Therefore, wet foam should have good stability to maintain its structure during drying process. The stability of bubbles with different octylamine dosages was evaluated by measuring the time-dependent changes in the average bubble diameter (Figure 5). The average diameter of the bubbles increased over time, and the size distribution of the bubbles broadened, and correspondingly, the standard deviation of the bubble size increased.



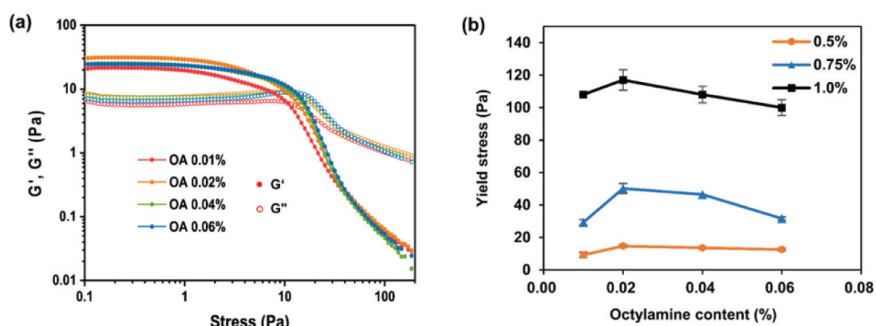
**Figure 5.** Time-dependent changes in the average bubble diameter of the wet foam with 0.5 wt% CMCNF suspension with 0.02 wt% (orange line), 0.04 wt% (green line), and 0.06 wt% (blue line) OA content [14].

This resulted probably from the aging of bubbles through coarsening, coalescence, and Ostwald ripening [10, 15, 16]. In fact, the size of the bubbles in the wet foam with higher octylamine concentrations increased more rapidly than that of the bubbles in the foam with lower concentrations; this indicated that a larger amount of the surfactant resulted in faster aging of the bubbles. It might be attributed to electrostatic interaction between the anionic CMCNF and the cationic octylamine. Higher addition of OA led to an aggregation of the fibrils due to interaction between positively charged octylamine and negatively charged CMCNF. It means that there is an appropriate addition level of a cationic surfactant to produce a stable wet foam. Cervin et al. [11, 12] have reported that the addition of OA corresponding to 33% of the total charge of CNF resulted in the wet foam with best stability. When the zeta potential of the CMCNF suspension was measured with increasing OA amount, the surface charge of the CMCNF was reduced by one-third by the addition of 4 % OA based on the oven-dried weight of CMCNF. A dosage of 4% OA based on CMCNF weight corresponds to a 0.02 % dosage in 0.5 % CMCNF suspension. In this study, an adequate amount of OA was considered as 0.02 – 0.04% based on the weight of CMCNF suspension (0.5 – 1%) from the viewpoints of foamability and wet foam stability. This result fits well with the works by Cervin et al. [11, 12]. Bubbles with excess dosage of the surfactant underwent coarsening, coalescence, or Ostwald ripening more frequently (than those with lower dosages), which led to a rapid decrease in the stability and increase in the size of the bubbles. Therefore, when using cationic surfactant, the electrostatic interaction between the surfactant and CMCNF must be well controlled.



In addition to the electrostatic interaction, the physical and rheological properties of CNF suspension affect the foamability and foam stability. The structure of wet foams prepared using 0.5 – 1.0 wt% suspension was maintained for a week without any drainage of water or destruction of structural features owing to high enough viscosity. However, water drainage occurred within a day for the foam prepared from 0.25 wt% suspension. Higher CNF consistency (higher viscosity) resulted in thicker lamellar features around the bubbles and strong entanglements in the foam [11,17]. When SDS was added to a CMCNF suspension, which there is no electrostatic attraction between SDS and CMCNF, stable foam could be obtained. It might be because of stable lamellar structure of CMCNF at the air-liquid interface. This prevented the destabilization of the bubbles and the drainage of water below the wet-foam layer, leading eventually to improved stability of the foam.

The storage modulus ( $G'$ ), loss modulus ( $G''$ ), and yield stress of the wet foam were evaluated (Figure 6). For all conditions, the storage modulus was higher than the loss modulus at the low stress level, indicating that the wet foam exhibited elastic behavior.  $G'$  was maintained until a certain level of stress was reached and decreased thereafter, and the curves of  $G'$  and  $G''$  intersect near the yield point of the foam. After the crossing point,  $G''$  was higher than  $G'$ , indicating that the foam behaved like a liquid due to the destruction of bubbles. The yield stress was determined from the intersection point between two tangential lines of the storage modulus. An octylamine content of 0.01 wt%, which was insufficient for foam generation, led to a low storage modulus. However, the storage modulus and the yield stress of the foam increased as the amount of octylamine increased to the optimal level. This suggested that, compared with the wet foam with an inadequate amount of surfactant, the foam with an adequate amount was more stable against the stress. However, increasing the octylamine content further led to reductions in the modulus and stress, owing possibly to a decrease in the stability

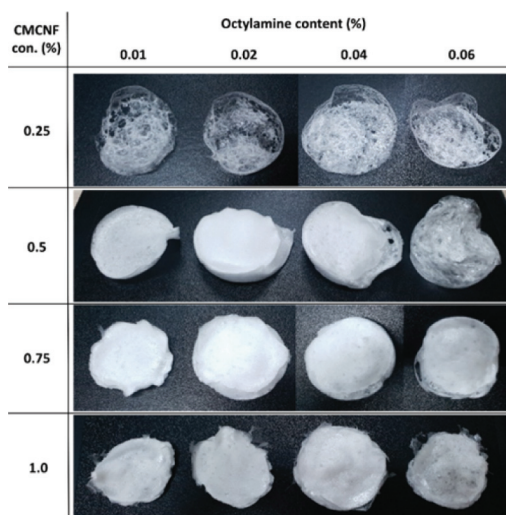


**Figure 6.** (a) Storage modulus ( $G'$ , filled circle) and loss modulus ( $G''$ , open circle) of CMCNF (0.5 wt%) wet foam and (b) yield stress of each CMCNF wet foam [14].

of bubbles. The rheology of the wet foam was also affected by the CMCNF consistency, i.e., the yield stress increased with increasing consistency, owing to the viscosity of the CMCNF suspension. Consequently, the stability of the wet foam could be estimated by evaluating the rheological property of the foam.

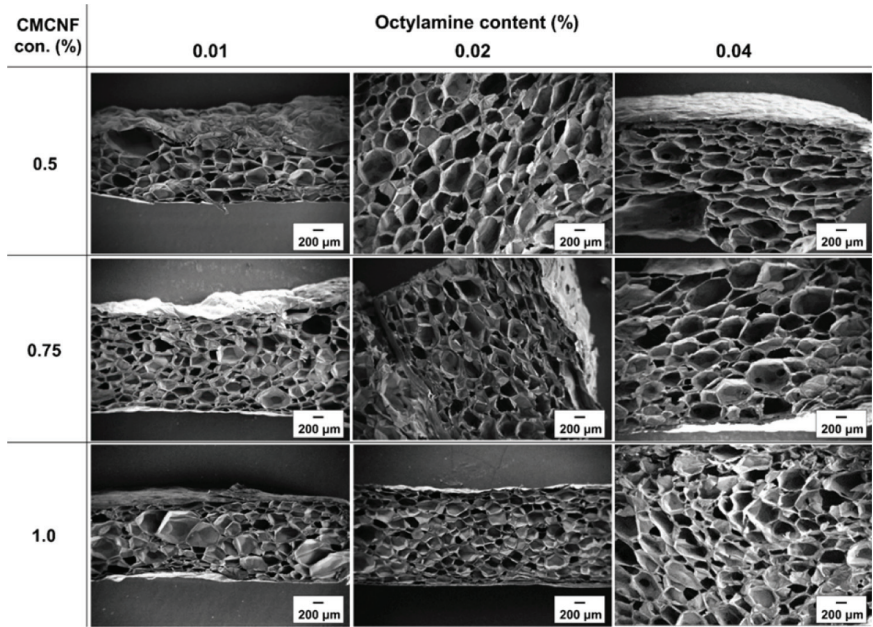
### Characteristics of a Dry Foam

Wet foams were placed in a PTFE dish, and then dried at 60°C in a convection oven. Under this condition, the structure of stable wet foams was maintained during the drying process, whereas the structure of unstable wet foams was destroyed or large cavities were generated (Figure 7). When the consistency of the CMCNF suspension was 0.25 wt%, all the bubbles were destroyed during drying and the foam collapsed due to the poor stability of the wet foam. The structure of foams prepared from 0.5 – 1.0 wt% consistency suspension was dependent on the CMCNF consistency and the amount of octylamine. The amount of the surfactant also influenced the drying behavior of the foam. In the case of the addition of an adequate amount of octylamine (0.02 wt% for 0.5 wt% and 0.75 wt% CMCNF suspensions and 0.04 wt% for 1.0 wt% CMCNF suspension), the foam structure could be maintained without large cavities or severe destruction because the stability of the structure was sufficient to endure the drying stress. Consequently, the stability of wet foam generated at adequate CNF consistency and octylamine levels was essential for producing oven-dried CNF foam.

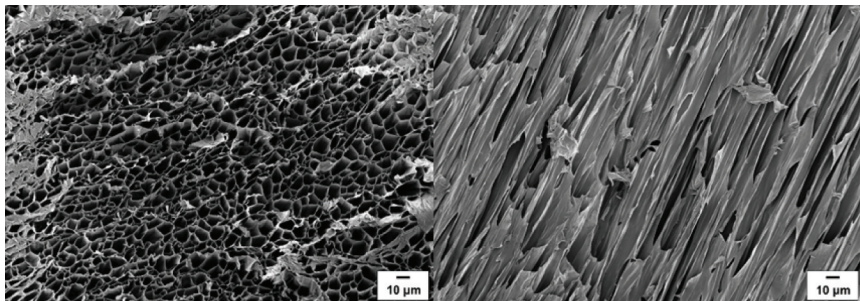


**Figure 7.** Dried CMCNF foams prepared at different CNF consistency and octylamine contents after 60°C oven drying [14].

The pores of the dried foam were observed from SEM images (Figure 8). The dry foam was composed of elliptical, closed cell structures consistent with the findings of Cervin et al. [10], which differed from that of the freeze-dried CNF foam that consisted of directional, small, and open pores (Figure 9). The average pore diameter ranged from 220 to 380  $\mu\text{m}$  depending on the foam preparation



**Figure 8.** Pore structure of oven-dried CMCNF foam prepared under different CMCNF consistency and octylamine contents [14].



**Figure 9.** Pore structure of the freeze-dried CNF foam: (left) cross section, (right) longitudinal section [14].

condition. The pore diameter became larger than that of the bubbles in the wet foam because the bubbles underwent aging during drying. The cell wall of the oven-dried foam was composed of several layers of CMCNF film, which was created from the CMCNFs surrounding each bubbles in wet foam.

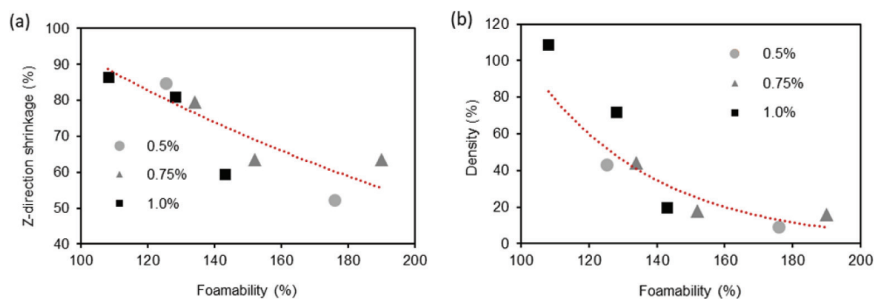
The structural properties including the density, porosity, z-directional shrinkage ratio, and average diameter of the pores are presented in Table 1. Most of the dry foams obtained via the oven drying of CMCNF wet foam exhibited >97% porosity. The z-directional shrinkage and density of the foam were strongly affected by the foamability of the wet foam (Figure 10). That is, the z-directional shrinkage and density of the dry foam decreased and the porosity of the foam increased with increasing foamability of the wet foam. Compared with low CNF consistency, higher consistency yielded foam with higher density and lower porosity, owing to the lower foamability, smaller pore size, and thicker pore wall. Regarding the amount of OA, the porosity of the foam with 0.01 wt% of surfactant was relatively low. This resulted from the fact that insufficient numbers of bubbles were generated when the amount of surfactant was low, thereby leading to significant shrinkage in the thickness direction during drying. The porosity of the foam increased with increasing amounts of OA which suggested that the higher foamability led to an increase in the porosity of the dry foam. In other words, the foamability and the bubble size of the wet foam had a significant effect on the

**Table 1.** Properties of dried CMCNF foams under different conditions [14]

<i>CNF consistency (wt%)</i>	<i>Octylamine content (wt%)</i>	<i>Density<sup>1</sup> (kg/m<sup>3</sup>)</i>	<i>Porosity<sup>1</sup> (%)</i>	<i>Thickness-direction shrinkage (%)</i>	<i>Pore diameter (μm)</i>	
					<i>Average</i>	<i>Standard deviation</i>
0.5	0.01	43	97.2	84.6	246.5	118.5
	0.02	9	99.4	52.2	372.4	129.5
	0.04	— <sup>2</sup>	— <sup>2</sup>	— <sup>2</sup>	339.0	119.3
0.75	0.01	44	97.1	79.6	223.6	79.4
	0.02	18	98.8	63.6	298.1	91.7
	0.04	16	98.9	63.5	353.6	150.8
1.0	0.01	109	92.7	86.5	247.1	108.0
	0.02	72	95.2	81.1	236.2	63.2
	0.04	20	98.7	59.4	330.2	119.3

<sup>1</sup> Density and porosity were measured with the cube cut foam.

<sup>2</sup> Deformed structure and large cavities in the foams prevented the determination of these values.



**Figure 10.** Relationship between (a) z-directional shrinkage and (b) density of the dry foam with the foamability of the wet foam [14].

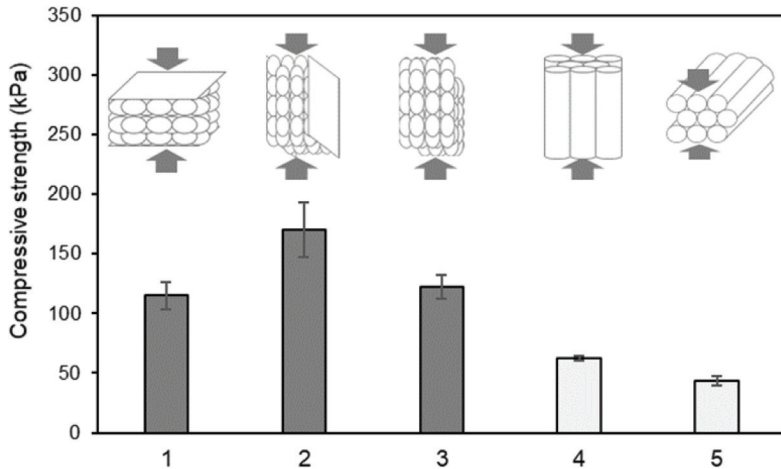
thickness-directional shrinkage during drying, and the density and porosity of the oven-dried CNF foam. This indicated that the structural properties of the oven-dried foam were determined by the consistency of CMCNF and the amount of the surfactant. The average pore size of the foam seemed to be related to the consistency of the CMCNF and OA dosage. When the CMCNF suspension consistency was low, the average pore diameter tended to be larger than the diameters occurring at high consistency levels. In addition, when the amount of OA was insufficient and the foamability of the wet foam was relatively low, the pores became small due to severe shrinkage in the thickness direction during drying. In contrast, the optimal amount of the surfactant improved the foamability of the wet foam, restrained the thickness-directional shrinkage, and preserved the pore structure without severe deformation, and thereby resulted in a relatively bulky and porous structure. Further increase in the concentration of OA led to a wide distribution of the pore size due to the presence of cavities or deformation of their structure. Therefore, the porous structure of the oven-dried CNF foam could be controlled by adjusting the preparation conditions of the CNF wet foam, and the suspension consistency and the amount of surfactant played an important role in the process.

The foams prepared in different CMCNF consistency were subjected to compressive tests and the mechanical properties of each foam were compared with those of the freeze-dried foam (Table 2). The compressive stress of the foams increased gradually until a compression strain of 70% and increased rapidly thereafter, owing to the significant densification of the foams. In addition, the stress in the curves obtained for the oven-dried foams slightly decreased at some points, resulting possibly from the crushing of closed pores in the foam during compression. The highest compressive strength, Young's modulus, and energy absorption were obtained for the oven-dried foam with 0.75 wt% CMCNF consistency that had relatively high density ( $18 \text{ kg/m}^3$ ) and small pore size ( $298.1 \mu\text{m}$ ). The density of the 1.0 wt% CMCNF foam with 0.04 wt% OA was similar to that of the 0.75

**Table 2.** Mechanical properties of oven-dried and freeze-dried CMCNF foams [14]

Drying method	CMCNF consistency (wt%)	Octylamine content (wt%)	Compressive strength at 80% strain (kPa)	Young's modulus (kPa)	Energy absorption (kJ/m <sup>3</sup> )
Oven drying	0.5	0.02	43.3 (4.2)	39.8 (5.0)	14.2 (1.2)
	0.75	0.02	115.0 (11.5)	80.6 (22.9)	37.3 (3.2)
	1.0	0.04	103.8 (14.1)	60.9 (5.9)	32.2 (1.4)
Freeze drying	0.75	–	62.8 (2.0)	29.9 (10.8)	13.9 (3.5)

Values in parentheses are the standard deviations.



**Figure 11.** Compressive strength of oven-dried (OD) CMCNF foam (CMCNF 0.75% + OA 0.02%) and freeze-dried (FD) CMCNF foam (CMCNF 0.75%) in different compressive directions: (1) OD in thickness direction, (2) OD in perpendicular to thickness direction, (3) OD in perpendicular to thickness direction after removing outer film layer, (4) FD in longitudinal direction, and (5) FD in radial direction.

wt% CMCNF foam, but the compressive strength was slightly lower owing to the relatively large pore diameters resulting from higher OA dosage. In addition, the compressive strength of the oven-dried CNF foam (0.75 wt%) was 83% higher than that of the freeze-dried foam with the same CMCNF consistency, indicating a greater compression resistance of the oven-dried foam.

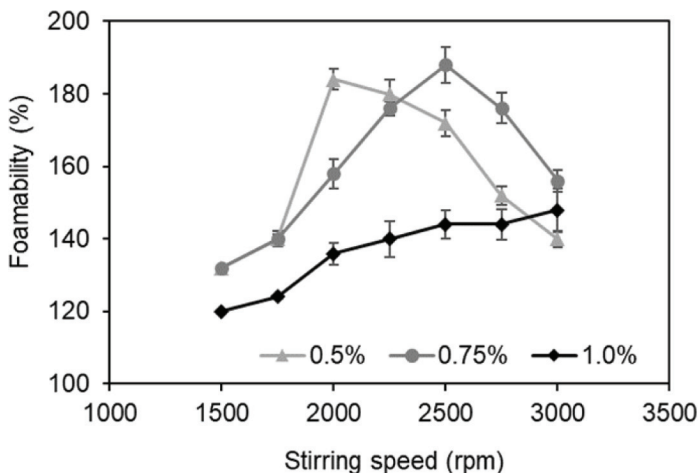
The mechanical strength of the oven-dried foam was also affected by the compressive direction of the foam (Figure 11). When the foam was compressed in a perpendicular direction to the thickness, it showed higher compressive strength. This is because of the CMCNF film layers present in the top and bottom side of

the oven-dried foam. This film layer gave higher resistance to compression, and improved the compressive strength of the oven-dried foam when it was compressed in perpendicular to the thickness direction [18]. However, when the film layers were eliminated, there was no difference in compressive strength of oven-dried CMCNF foam in different compression directions, indicating that the elliptical pore shape of the oven-dried foam had no influence on the compressive strength of the foam. On the contrary, the freeze-dried foam, which exhibited anisotropic pore structure resulted from the growth of ice crystal during freezing, showed different compressive strength when it was compressed in axial direction or radial direction.

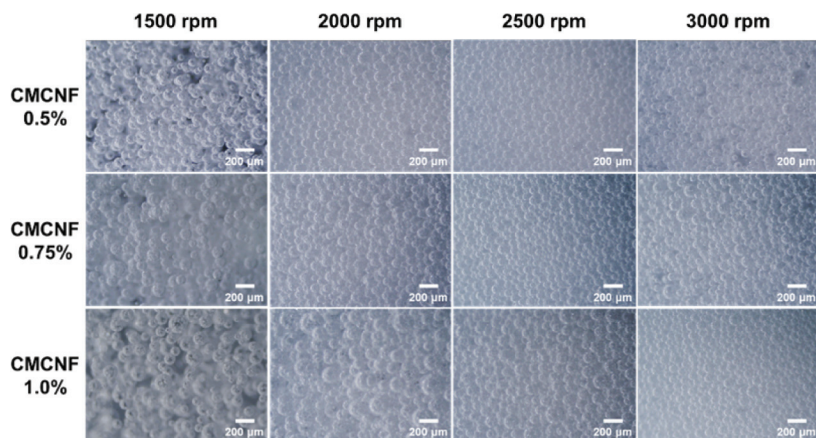
### **Effect of Shear Rate**

#### *Characteristics of Wet Foam*

The CMCNF wet foam was prepared at different stirring speed conditions, and their characteristics were evaluated. Figure 12 shows the foamability of the CMCNF wet foam depending on the shear rate during foaming. In general, high shear rate is beneficial to obtain a wet foam with high formability. The formability was very low at 1500 rpm because of insufficient generation of bubbles. The shear rate to reach a maximum foamability was dependent on the CMCNF consistency. In the case of 0.5 wt% CMCNF suspension, the maximum foamability was obtained at 2000 rpm. On the other hand, the shear rates at maximum foamability



**Figure 12.** Foamability of the CMCNF wet foam prepared under different stirring speed. The OA was added by 4 wt % based on the oven-dried weight of CMCNF.



**Figure 13.** Morphology of bubbles in CMCNF wet foam prepared under different CMCNF consistency and stirring speed conditions.

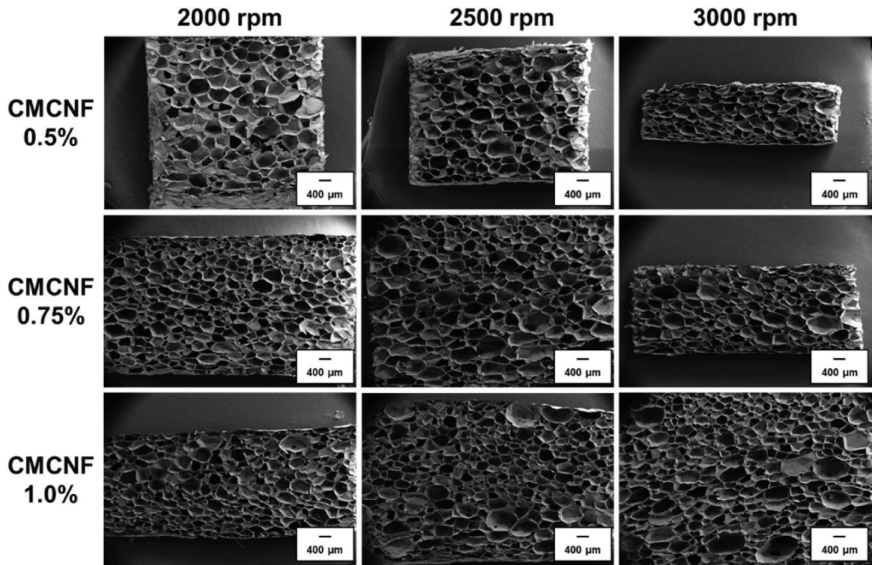
were 2500 and 3000 rpm for the 0.75 wt% and 1.0 wt% CMCNF suspensions, respectively. It indicated that CMCNF with high consistency required high stirring speed to reach the maximum foamability owing to low mobility between fibrils. It is worthy to note that the foamability decreased when the shear rate was higher than that with the highest foamability. This indicates that too high shear rate might destroy some of bubbles. Accordingly, shear conditions applied to foaming must be carefully determined to obtain the optimal foamability.

The morphology of bubbles prepared at different stirring speed was observed (Figure 13). The bubbles tended to become smaller with increasing the stirring speed. The size of bubbles appeared to be uniform at the condition with the highest foamability, and it had a rather wide distribution at the conditions which exhibit low foamability. Therefore, it revealed that the shear condition in wet foaming affected the bubble morphology and foamability.

### *Characteristics of Dry Foam*

The dry foams were prepared via the oven-drying of each wet foam. The microstructure of the dry foams observed by SEM was presented in Figure 14 and the physical and mechanical properties were shown in Table 3. All foams had porosity >98% because they were prepared with adequate amount of surfactant. The thickness and average diameter of pores of the foam were highly related to the foamability of the wet foam. The foam with bigger pore size and the higher thickness was created at the conditions which exhibited higher foamability, which resulted





**Figure 14.** Pore structure of the oven-dried CMCNF foams prepared under different CMCNF consistency and the stirring speed.

in the higher porosity of the foam. In addition, the foam prepared at high shear rate were composed of both small pores and large pores, which corresponded to the morphology of bubbles in wet foams. This indicates that the structural property of the oven-dried foam can be affected by the shear condition in wet foaming as well. It is also notable that the pore size of the oven-dried CNF foam was varied along the thickness direction. Pores in the top and bottom layer of the foam exhibited smaller pores that those in the middle section of the foam. When the CNF wet foam was dried in the oven, the top and bottom layer of the wet foam were firstly exposed to heat and dried earlier than the middle section of the wet foam. Therefore, the bubbles at the both end sides might be less susceptible to bubble aging, resulting in smaller pores.

Mechanical property of each foam was evaluated by compression test. The compressive strength at 80% compression and the thickness recovery rate after removing compressive force were shown in Table 3. The compressive strength was highly dependent on the thickness and density of the foam, which were determined by the foamability of the wet foam. The foam prepared at the condition with the highest foamability exhibited relatively lower compressive strength as well as the lower shape recovery rate due to their higher thickness and porosity than the foams with lower foamability. The dry foam prepared at higher shear rate

**Table 3.** Characteristics of oven-dried CMCNF foam prepared under different CMCNF consistency and the stirring speed

<i>CMCNF consistency (wt%)</i>	<i>Stirring speed (rpm)</i>	<i>Thickness (mm)</i>	<i>Density (kg/m<sup>3</sup>)</i>	<i>Porosity (%)</i>	<i>Compressive strength (kPa)</i>	<i>Thickness recovery (%)</i>
0.5	2000	7.5	9	99.4	43.3 (4.2)	21.3
	2500	5.4	11	99.3	81.2 (19.9)	39.3
	3000	1.9	21	98.6	170.1 (3.8)	61.0
0.75	2000	5.3	12	99.2	184.0 (14.3)	67.9
	2500	7.5	9	99.4	57.1 (4.3)	38.4
	3000	4.6	14	99.1	265.9 (28.3)	88.1
1.0	2000	5.8	20	98.7	103.8 (14.1)	42.0
	2500	6.9	13	99.1	61.9 (11.5)	36.2
	3000	8.4	11	99.3	67.7 (17.7)	38.0

than that of the maximum foamability showed the improved compressive strength and the thickness recovery although their thickness was low. High thickness of the foam means a relatively thin layer of CMCNF surrounding each pore. Therefore, the resistance to the compressive load might be weak and it caused the collapse of the structure, resulting in low compressive strength and thickness recovery. That is, the mechanical property of the oven-dried foam could be controlled by the stirring speed during wet foaming.

## CONCLUSIONS

In this study, CNF foams were prepared via oven drying of Pickering-stabilized CNF wet foam and the effects of wet foaming conditions on the characteristics of wet and oven-dried CMCNF foams were investigated. CMCNF wet foam could be prepared by addition of cationic OA surfactant and anionic SDS surfactant, respectively. A low addition level of surfactant led to insufficient generation of bubbles, whereas high levels of surfactant generated unstable wet foam. The formability of wet foam decreased with an increase in the consistency (viscosity) of CNF suspension at a given amount of a surfactant. The wet foams with enough high CMCNF consistency (>0.5 wt%) and optimal dosage of the surfactant (0.02–0.04 wt% based on the suspensin weight) exhibited high stability with uniform morphology of bubbles, which could maintain their structures during oven drying. The oven-dried CMCNF foam had a closed-cell structure with pore diameters of 200–400 μm and high porosity above 97%. The stirring speed in wet

foaming process affected the foamability of the wet foam. When the CMCNF suspension with high consistency (low mobility) was used, high stirring speed was required to obtain high foamability and uniform bubbles. When the shear rate further increased after reaching the maximum foamability, the foamability decreased. When the wet foams were dried in the oven, the pore size and the thickness of the dry foam were strongly related to the foamability of the wet foam and they affected the compressive strength. The compressive strength of the oven-dried foam was 83% higher than that of the freeze-dried foam, showing the advantages of the oven-dried CNF foam. These results revealed that structural and mechanical properties of the oven-dried CNF foam were determined by the properties of wet foam which could be controlled by the consistency of CMCNF, a dosage of the surfactant, and stirring speed during wet foaming.

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# PROPERTIES OF CELLULOSE NANOFIBRIL FOAM DEPENDING ON WET FOAMING CONDITIONS

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How confident are you that these are Pickering-stabilised foams? The high stability of a conventional Pickering emulsion made with solid particles is driven by the extremely strong adsorption of the particles to the interface. To achieve this, the contact angle at the particle surface should be around 90 degrees. The reason that the emulsions are stable is that, in order to make the droplets (or bubbles in your case) coalesce, the particles have to be desorbed from the interface, and if they are strongly adsorbed that is very difficult. It also means that the droplet or bubble size is very dependent upon the concentration of the particles. The more particles there are, the smaller the droplets or bubbles are after shearing, because there is more interfacial area available to adsorb the particles. It also makes the emulsions extremely resistant to Ostwald ripening. In your case, you start with cellulose which is extremely hydrophilic, and you modify it so that it has a zeta potential of  $-50$  mV. So there does not seem to be a strong driving force for it to adsorb at the interface. You also show that the bubble size is not very dependent on the cellulose concentration, and if you have a low-cellulose

## *Discussion*

concentration you do see a lot of bubble coalescence. So, I wonder if there is an alternative mechanism; perhaps the reason that the foams are stable is because the interstitial phase, the water phase, has got such high viscosity at low shear rate that the bubbles themselves cannot actually coalesce. I wonder if you had any evidence that you do have adsorption of the CNF to the interface and that you have a genuine Pickering-stabilised foam rather than one that is primarily stabilised by the interstitial viscosity?

## *Hye Jung Youn*

First of all, thank you for your comment and the question. As you mentioned, Pickering stabilisation is performed by solid particles that are strongly adsorbed on the interface between air or oil and water. In general, surface chemistry is important for forming Pickering emulsions, but we think other mechanisms are also effective for forming Pickering emulsions, especially for CNF. We believe that our CNF particles stabilise air bubbles well. We can explain it for several reasons. One is the aid of surfactants, the second is the morphological feature of CNFs, and the last is the high viscosity of the CNF suspension. We tried to make CNF wet foams using different types of CNFs (different fibril widths, different charges) and different types of surfactants. Most of the results of this presentation are about using negative charged CMCNF and cationic charged octylamine. Octylamine has a low HLB value, which means it is more lipophilic. Therefore, we think it helps CNF to make a good wet foam. In addition, the anionic, more hydrophilic SDS (HLB=40) also contributes to sufficient bubble generation. Regarding morphological features, CNF with smaller and more uniform size would make a good Pickering emulsion by the improved adhesion by the capillary force. The high viscosity also favours the formation of Pickering emulsions and imparts mechanical rigidity to maintain the wet foam structure. And we confirmed that CNF particles were adsorbed at the interface by observing the bubble surrounded by CNFs dyed with a fluorescent dye using a confocal laser scanning microscope. The cell wall of the dry foam has a lamellar structure of CNF layer, so we think that CNF stabilised the air well. We think there are various mechanisms affecting this CNF stabilised wet foam and we will think and consider it further according to your comments.

## *Lars Wågberg*      KTH Fiber and Polymer Technology

The question I have is related to your very elegant method of controlling the quality of the foams, i.e. rheology. You said that the highest  $G'$  was the best for the foam stability, how did you establish this connection?

*Hye Jung Youn*

Thank you for the question. From our experience with different wet foaming conditions such as surfactant level, stirring speed, or cellulose nanomaterial types, we found that rheological property ( $G'$ ) can be used as one of the quality indicators of wet foam stability. For example, we prepared a CNC suspension and a CNF suspension of the same viscosity by adjusting the consistency. However, the storage modulus of the CNC wet foam was lower than that of the CNF wet foam, which resulted in dry foam with non-uniform structure due to poor stability. A higher modulus of the wet foam means a stronger resistance of the wet foam network to external or internal forces that induce deformation. When we want to evaluate the stability of a wet foam over time, observation of the appearance of the wet foam is generally used, but it takes a relatively long time and is not a quantitative value. Therefore, we think that the measurement of  $G'$  would be a good way to find the appropriate surfactant dosage or stirring energy, which leads to a wet foam with good stability. However, this  $G'$  is strongly affected by the consistency of the CNF suspension. Therefore, comparisons of the absolute value of  $G'$  should be avoided when the suspension consistencies are different.

*Lars Wågberg*

As you know we have been active in this field and one lingering question I have is that the aspect ratio of the cellulose fibrils seems to be extremely important. Did you look into that at all?

*Hye Jung Youn*

Yes, I agree with your opinion. Although I didn't show any data on the effect of aspect ratio in this presentation, we compared the wet foams made of CNC and CNF particles, respectively. Compared to CNFs, CNCs (cellulose nanofibre with low aspect ratio) required a higher consistency suspension to prepare a wet foam. Although a high consistency (viscosity) suspension was used, the CNC-wet foam collapsed during oven drying, which means the wet foam structure could not be maintained during the oven drying process. Therefore, we think cellulose nanofibres with high aspect ratio are suitable for the manufacture of foams via oven drying.

*Gil Garnier*      Monash University

Two short questions: the first one, have you investigated the effect of cellulose charge on the foamability? Second, have you investigated repulpability and re-foaming of your material?

## *Discussion*

*Hye Jung Youn*

In answer to your first question, to investigate the effect of cellulose charge, we prepared wet foams using cellulose nanofibres with different charges: the CNC which has sulfonate group, the carboxymethylated CNFs (CMCNFs) with carboxyl group contents of 400  $\mu\text{mol/g}$  and 870  $\mu\text{mol/g}$ , TEMPO-oxidised CNF (TOCN) with carboxyl group content of 1.1 mmol/g, and quaternised CNF. The CNC particles showed high foamability but did not show a porous structure because of drying deformation, and the quaternised CNF showed low foamability, resulting in the final dry foam with low porosity. CMCNF and TOCN had relatively high foamability and high porosity, which was also affected by the type and addition level of surfactant. Based on these results, we thought that cellulose charge could affect the foamability, but its impact was not significant. Other factors such as aspect ratio, fibril width, and viscosity appear to be more important for foamability.

As to your second question; we haven't investigated re-foaming. When no crosslinking agent was added, the dry CNF foam was easily disintegrated in water by stirring. That is, the repulpability was good. Therefore, for example, to use this foam as dye adsorbent, it was necessary to add a crosslinking agent to the CNF suspension. Regarding re-foaming, we did not attempt to make a foam again using this disintegrated foam. We will try it according to your comment. Thank you for the good comment.