Mechanical Processing Control in Manufacturing Nanofibrillated Cellulose by Interpreting its Rheological Properties

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Nanofibrillated cellulose (NFC) has generated significant interest due to growing concerns about low carbon emission, environmental issues, and the guaranteed outstanding performance of applied products. Because of this trend, the importance of NFC production from an industrial angle has also been emphasized. In this study, ground pulps (at -300 μm clearance, 40 passes) were homogenized by using a pilot-scale microfluidizer (at 1,500 bar, up to 5 passes) to produce the NFC, and its characteristics were investigated. Scanning electron microscope (SEM) images showed that the size and distribution of the NFC particles gradually decreased by up to three passes on account of the microfluidizer treatment and remained constant after that mechanical pass number. The viscoelastic properties (dynamic moduli) and viscosity of the NFC suspension steadily increased with three passes of the treatment, and the same trends as in the SEM images were observed after these passes. These results demonstrated that the NFC fluid behavior inside the equipment depends on the morphological properties of the manufactured NFC particles. Additionally, a good agreement between the morphological and rheological results implied that rheological analysis can be a reasonable approach to predicting the quality (size and distribution) of manufactured NFC particles.

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Keywords: Nanofibrillated cellulose (NFC); Rheological property; Pilot-scale production; Mechanical treatment

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INTRODUCTION

With increasing concerns towards environmental protection, the use of biological materials as a part of final products is inevitable. Nanofibrillated cellulose (NFC, also called cellulose nanofibril) is derived from sustainable and abundant lignocellulosic cellulose materials. Thus, interest in NFC particles has considerably increased in the nanomaterial fields. Nanocellulose particles have successfully been applied in various fields, such as biomedical applications, electronics, nanocomposites, and cosmetics

(Kangas *et al.* 2014; Kim *et al.* 2019; Cho *et al.* 2020) owing to their superior mechanical properties and their ability to easily achieve the desired surface characteristics by chemical tuning strategies (urethanization, silylation, amidation, polymer grafting, *etc*.), depending on the target applications (Park *et al.* 2020; Sun *et al.* 2020; Yook *et al.* 2020). NFC has shown its potential to be a leading material in this field.

The future perspective in the global market (Future Markets 2020) of NFC particles shows that their market size in the application fields is expected to grow by 3 to 20 times by 2030 compared to 2021. Although these positive market trends and many studies have demonstrated the potential of NFC, there seems to be no active market for final products that contain NFC except in Japan and a few other countries. This may be due to its several less favorable properties, such as incompatibility with polymer matrix materials, moisture sensitivity, and the high production cost compared to other competing nanoparticles. Therefore, it is necessary to study the application research to acquire desired properties and the economic production to revitalize the market of CNFs, a promising class of eco-friendly nanoparticles (Turbak *et al.* 1983; Nechyporchuk *et al.* 2016a; Blanco *et al.* 2018)

NFC is most often prepared from micron-sized cellulose fibers. Cellulose is a linear homopolysaccharide chain consisting of 1-4 glycosidic bonded glucose units, and the chains are packed into microfibrils and fibers by inter- and intramolecular hydrogen bonds. Mechanical disintegration of the cellulose fibers is performed in an aqueous medium. As disintegration progresses, the size of the fibers gradually decreases to the nano-level. Interaction between hydroxyl groups on the surfaces of the nanoparticles and water molecules strengthens with the individualization of the NFC. Hence, rheological differences of NFC fluids can occur for each process step. Currently, as NFC application research is successfully conducted, much attention to the importance of the processing-structure-property relationship from industry is increased to produce NFC suitable for a specific application field. A key factor affecting the mass production of NFC is the flow of NFC suspension in the tube inside the machine during the process. Hence, understanding its rheological properties can be essential to increasing production yield and to improving their quality through process improvement. However, most of the research for nanocellulose preparation is being conducted on a lab scale. The research trend has focused on the isolation of nanocellulose from various sources and evaluating its usage in different applications. Therefore, in-depth study for optimizing mass production accompanied by rheological interpretation from an industrial perspective is needed in order to expand the practical use of the nanoparticles.

Various conditions and variables can be factors in scaling-up from the laboratory to industrial scale for nanocellulose. Inherent properties such as concentration and aspect ratio (length/width) of nanocellulose particles can be important variables controlling the rheological properties of nanocellulose suspension (Li *et al.* 2021). Dynamic moduli (storage (G') and loss (G'') modulus) and viscosity of nanocellulose suspensions increase with increased nanoparticle concentration due to the entanglement effect of the nanoparticles with long chains. Also, when their length is changed, the rheological properties of the suspension are directly proportional to their aspect ratio. The intrinsic properties of these nanoparticles can be changed during the process, which increases the rheological complexity of NFC fluids. However, several studies have experimented with NFC under the limited conditions of the Newtonian fluid and laminar flow (Kargarzadeh *et al.* 2017). As a high content of NFC suspension is produced at high pressure in the actual process, rheological analysis is required for the experiment considering the non-Newtonian fluid and turbulent flow conditions. In the actual process, the flow of NFC fluids is not

usually simple, and the fluid experiences a complex flow field in complicated geometries. Complex fluids depend on the Reynolds number (*Re*) and fluid characteristics. To define the flow behavior of the NFC suspension in the chamber of the microfluidizer used in the experimental design of this study, the *Re* was calculated, and 17,327 was obtained as the result. The *Re* was calculated according to Eq. 1,

$$Re = \frac{\rho \bar{v} D}{\mu} \quad (1)$$

where ρ is the density of nanocellulose (1.5 g/cm^3) (Moberg *et al.* 2017), D is the size of the chamber (500 µm), and μ is the kinematic viscosity (0.000223076 m^2/s) (Kargarzadeh *et al.* 2017). At a pressure of 1,500 bar and a flow rate of 3,643 mL/min, the velocity (v) has a value of approximately 7,731 m/s. The *Re* (>4000) obtained from Eq. 1 suggests that the NFC fluids in the chamber have turbulent flow. Therefore, NFC production must be studied based on rheological understanding because of the complexity of NFC fluids.

Size and distribution are key properties to determine the quality of the produced nanoparticles. These properties have been mainly evaluated using various microscopic tools. However, representing the entire characteristics of the final product using a few images from the microscopic tools can be difficult. As explained above, changes in these morphological properties of the nanoparticles can create differences in the rheological behavior of their suspensions. Consequently, presenting microscopic results of NFC particles together with fluid properties of NFC suspensions can be a positive approach to improve the reliability of their quality at the industrial level.

This work aimed to investigate the relationships between the morphological and rheological properties of NFC produced by mechanical treatments and to optimize their production based on these relationships. The results can provide a guideline for the economical mass production of CNF from an industrial perspective.

EXPERIMENTAL

Material

Microcrystalline cellulose, a purified cellulose powder for the preparation of NFC, with a particle size of 45 µm (Fig. 1), was purchased from Nippon Paper Chemicals Co. (KC Flock W-50, Tokyo, Japan). For the morphological analysis, tert-butanol (99%; Junsei Chemical Co., Tokyo, Japan) was used as received.

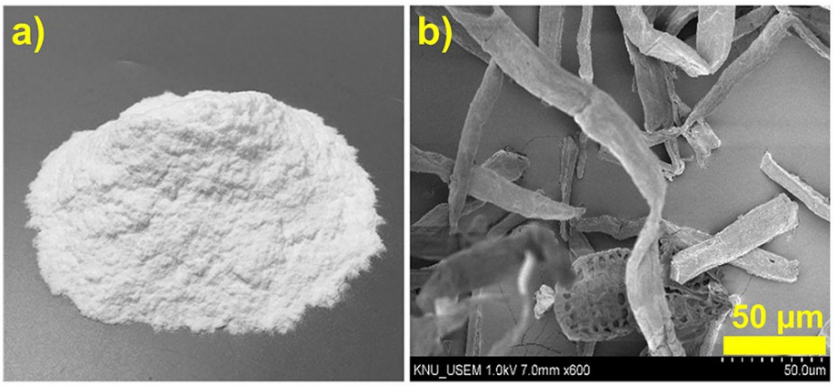

Fig. 1. a) Visual image of the cellulose powder and the b) scanning electron microscope (SEM) image of the cellulose powder

Production of the NFC

As shown in Fig. 2, the NFC production process consisted of grinder and microfluidizer operations. The aqueous suspension (170 kg of 0.5 wt%) prepared with the cellulose powder was pretreated using a grinder (MKZA15-40; Masuko Sangyo Co., Saitama, Japan). The grinding of the cellulose fibers was performed with –300 µm clearance (from the zero position of gab stones) at 1,740 revolutions for 40 passes. (Note that a negative value of the gap, as reported by the device, does not actually mean a negative value.) Disk stones can be operated at the negative clearance after the fibers loading as shown in Fig. 2 'Grinder operation'. Subsequently, the dispersed particles were homogenized using a microfluidizer (M-7250; Microfluidics, Westwood, MA, USA) consisting of two z-type chambers (the size of each chamber was 100 and 500 µm, respectively) at 1,500 bar for five passes. The process outlined by Villalobos-Castillejos *et al.* (2018) was followed. A sample was obtained for each pass to explore the morphological and rheological properties of the NFC. The samples are coded as shown in Table 1.

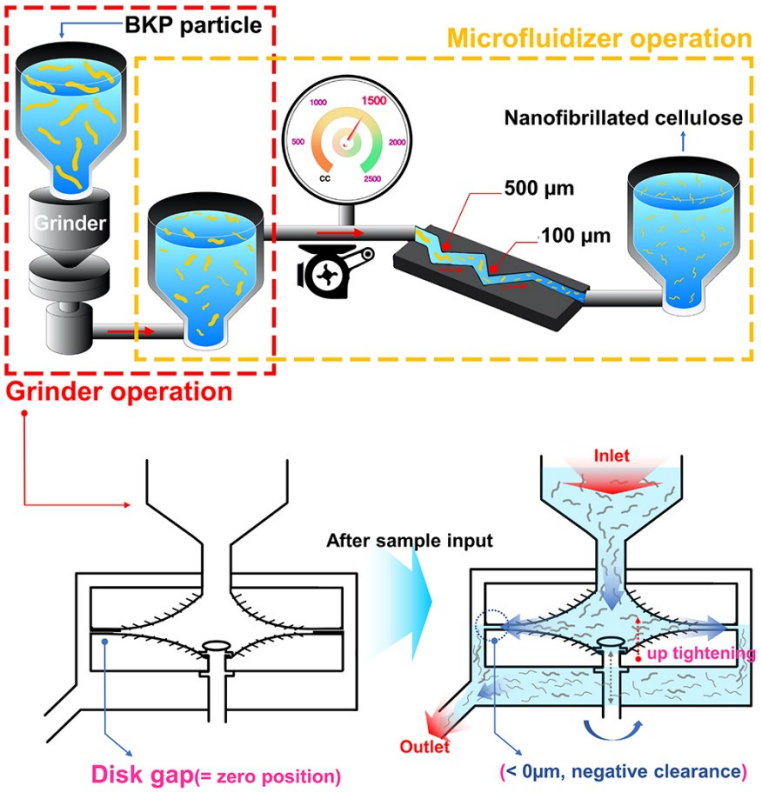

Fig. 2. Schematic diagram of the NFC production process

Table 1. Sample Codes According to the Conditions of NFC Production

Sample Code	Microfluidizing Cycles (Pass no.)
A1	1
A2	2
A3	3
A4	4
A5	5

SEM Analysis

The morphological characteristics of the NFC particles were examined using a field-emission SEM (JSM-7401F; JEOL, Tokyo, Japan). Nanofibers were gold-coated to a thickness of approximately 4 nm by ion coating. To obtain a clear image with well-dispersed CNFs, aqueous suspensions that contained the CNFs were solvent-exchanged to tert-butanol, and the samples were freeze-dried at –60 °C for 3 d. From the SEM images, 300 measurements of the CNF particles were randomly chosen to calculate the average diameter using ImageJ software (open source). Also, the uniformity of the particle size was judged using the standard deviation of its average size, which was expressed as 'distribution'.

Rheological Analysis

A rheometer (DHR-3; TA Instruments, New Castle, DE, USA) with parallel Peltier plates (diameter 60 mm, standard) was used to explore the rheological properties of the NFC suspension. The 60 mm-sized parallel plates were used for the gel-like samples to reduce the wall-slip. This geometry can yield identical results, except under a regime with a low-torque limit and occurrence of wall-slip. The temperature of the samples and the gap between the Peltier plates and fixture were maintained at 25 °C and 1 mm, respectively. It is crucial to confirm the linear viscoelasticity range (LVE, non-destructive deformation range) to prevent the deformation of materials by the rotating Peltier plate. The strain sweep test was performed in the γ range from 0.01% to 100% to determine the LVE of the NFC fluids at 5 rad/s (ω, angular frequency), as reported elsewhere (Jung *et al.* 2018).

A frequency sweep describing the time-dependent behavior of a material in the LVE limit is a helpful test to estimate the long-term stability of the NFC network structure in the suspension. The frequency sweep of the NFC suspension was tested in the frequency range of 0.1 rad/s to 100 rad/s (ω) at 1% strain (γ). The viscosity (η) of the produced NFC suspension as a function of shear rate was measured in the range of 0.5 to 100 $s^{-1,}$ after conducting a steady-flow test for 60 s for each section.

RESULTS AND DISCUSSION

Morphological Characteristics of the NFC particles

The SEM images of NFC for each microfluidizing step are shown in Fig. 3. With increasing intensity of the mechanical treatment, the number of NFC bundles (which are not fully individualized nanofibers) gradually decreased. The average sizes and distributions of the nano-objects (obtained from the SEM images) were calculated from approximately 300 measurements, and the results are shown in Fig. 3f. The thickness and distribution of the NFC particles were reduced, and no further changes were observed after the NFC was processed with three passes *via* the microfluidizer, as expected from the SEM results. The NFC suspension in the chamber of the microfluidizer experiences a high shear rate and impact forces, and NFC particles in the suspension crash into the walls of the chamber. The particles subsequently disintegrate due to the breakage of hydrogen bonds between the cellulose fibrils. In general, the collision strength of particles at the same mass is proportional to their velocity. As the NFC size decreases, the number of exposed hydroxyl groups increases with their specific surface area, resulting in strong hydrogen bonding. The generation of strong interactions between the particles and water molecules increases the viscosity of their colloidal fluids. As a result, increments in the resistance of

the suspension flows (increase in the viscosity) can reduce the impact force that can break the hydrogen bonds of the particles. Therefore, the morphological behaviors shown in Fig. 3 suggest that the speed of the fluid flow caused by the NFC size processed with three passes reached a limitation in pulverizing the nanoparticles at the desired pressure. Additionally, it can be expected that the flow properties of the NFC suspension remain constant after that intensity. To test this assumption, a rheological assessment of produced NFC suspensions was performed, and the results are discussed in the following section.

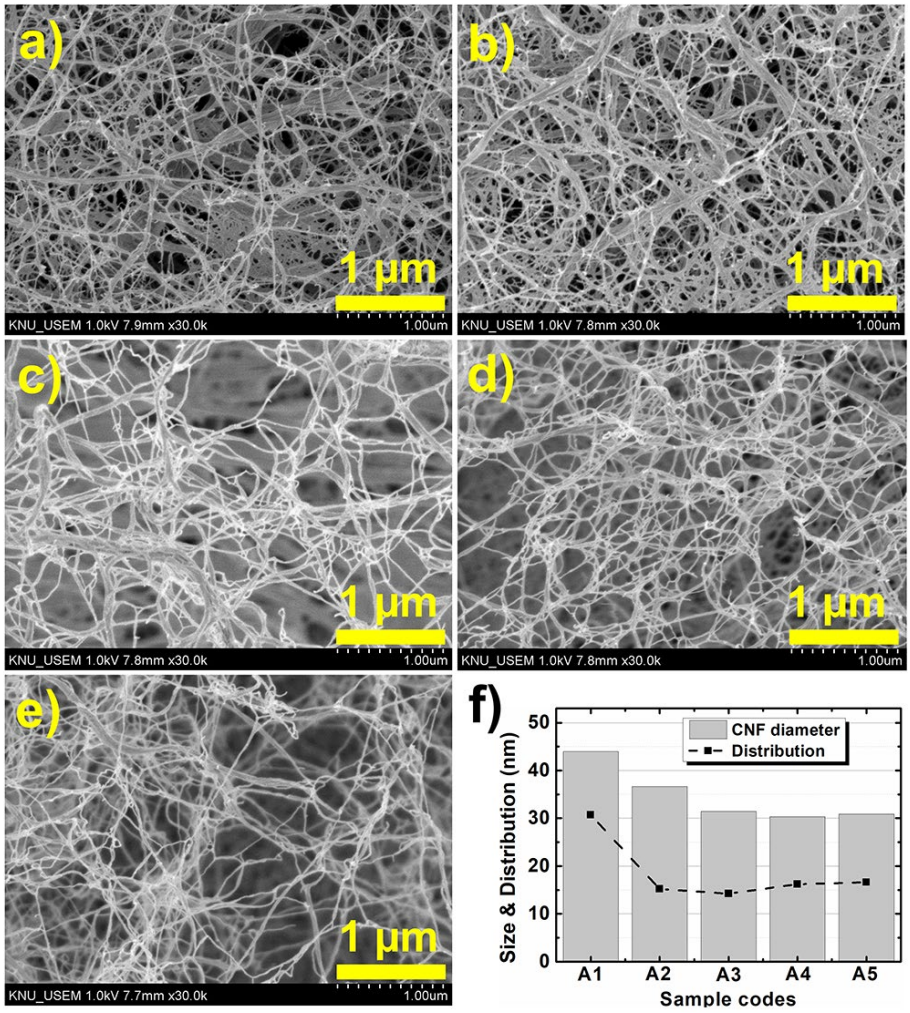

Fig. 3. Morphological results of the microfluidized CNFs. The SEM images at a) one pass b) two passes c) three passes d) four passes, e) five passe. f) shows the measured size and distribution (standard deviation) of each sample.

Rheological Properties of the CNF Suspensions

Obtaining the SEM results of NFC requires high proficiency and is time-consuming, as it requires a sampling technique that can individually disperse the nanoparticles. Morphological evaluations, such as SEM analysis, are mostly deemed a technique in microscopic angles because a target sample with a small amount is magnified. On the other hand, rheological evaluation uses bulk sample amounts compared to SEM analysis, and the preparation process for the measurement is also simple. As described above, the flow properties of the particle-containing fluids can depend on the

morphological properties of the particles. Therefore, if the trend of the rheological properties is similarly linked with the morphological properties, the rheological examination in NFC mass production can be a quick and easy approach to finding the optimal process of producing the smallest NFC.

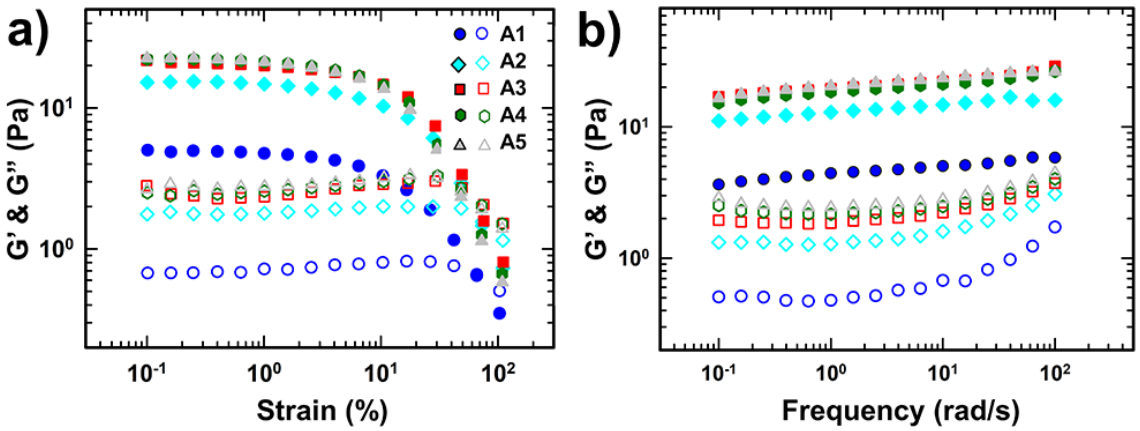

Fig. 4. Viscoelastic results of the NFC suspensions according to the a) strain swap test and b) frequency swap test (solid symbol *G*', blank symbol *G*")

The viscoelastic properties of the NFC prepared by the number of microfluidizer treatments were explored using the rheometer with parallel-plate geometry. Figure 4a shows the dynamic moduli (storage (*G*') and loss (*G*") modulus) as a function of strain. Regardless of the mechanical intensity, the *G*' and *G*" curves of the NFC suspensions had a similar LVE, indicating that the elastic structures of the suspensions remained stable (Nechyporchuk *et al.* 2016b). The stable structure of the NFC suspension collapsed after the critical strain (γ_c, approximately 10% strain), and the moduli were reduced successively. The critical strain can be used as a factor to identify the differences between the structural stability of materials (Li *et al.* 2021). Hence, the structural stability of produced NFC suspensions is similar regardless of the mechanical intensity. Figure 4b shows the changes in dynamic moduli as a function of frequency. The microstructure of the viscoelastic material can be predicted through the frequency sweep test (Nechyporchuk *et al.* 2016b). The frequency sweep curve of the suspensions indicates that *G*' was greater than *G*", with the curves nearly parallel to each other, so the suspensions had a gel-like structure with an interconnected network.

A notable observation in the viscoelastic behavior was the intensity changes in the dynamic moduli (*G*' and *G*") of the NFC suspension when the number of mechanical treatments was. In both strain and frequency sweep responses, the dynamic moduli increased until three times in the mechanical treatment (A3), and a similar trend of the moduli was observed after that. Reduction in thickness of NFC particle (the enhanced degree of fibrillation) by mechanical disintegration strengthens entangled networks (Li *et al.* 2021), and thus resistance to flow of the fluid can be increased. Therefore, the lack of change in the dynamic moduli of the NFC suspension at the same concentration indicates that the properties related to the size of the particles were almost unchanged after the NFC suspensions were processed with three passes through the microfluidizer.

Figure 5 shows the viscosity responses of the manufactured NFC suspensions as a function of the shear rate. The trend in the viscosity curve with the increase in the number of mechanical treatments was similar to the morphological and viscoelastic responses.

Additionally, there were no major changes in the viscosity of the fluids that contained NFC after three passes of the disintegration process. The shear flow result can help account for the degree of fibrillation of the NFC particles (Grüneberger *et al.* 2014; Nechyporchuk *et al.* 2016b). Resistance to the flow of NFC suspensions increases with the fibrillation level of the NFC, which increases the viscosity. Hence, as a result of increasing the number of mechanical treatments, the viscosity is closely related to the morphological changes of the NFC, as demonstrated in Fig. 4.

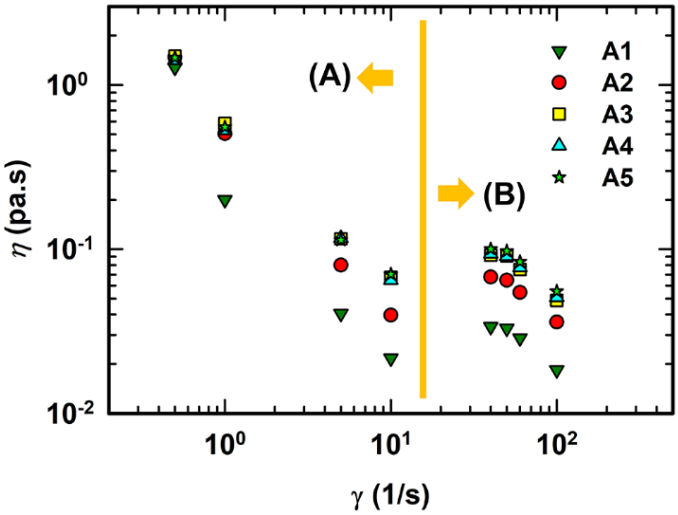

Fig. 5. Viscosity behavior with the shear flow

NFC suspensions generally exhibit shear thinning flow, which corresponds to a decrease in the viscosity with increasing shear rate. When a shear force is applied to the NFC fluid in a certain direction, oriented NFC particles flow towards the shear direction with the fluid (Fig. 6a) (Nechyporchuk *et al.* 2016b). As can be seen in Fig. 5, the flow of NFC suspensions exhibited shear thinning behavior up to approximately 10 s^{-1}. Interestingly, with further increment in the shear rate, some fluctuation of their curves was apparent. To accurately interpret this fluctuation, it is necessary to check the wall slip first. It is known that wall slip can occur in the fibrous suspensions, resulting from and measured with the parallel Peltier plates of the rheometer (Nechyporchuk *et al.* 2014). In the case of wall slip, the data will show disorder due to the variation. However, when the rheological properties were measured in this study, a specific shear rate was set, and the viscosity was measured by simple flow without raising the shear rate (Boukany *et al.* 2015; Jin *et al.* 2018). This was done to accurately observe the changes in the material properties depending on the shear rate. When measuring rheological properties, there is a phenomenon wherein the initially measured viscosity of the sample temporarily increases as the Peltier plate rotates. Thus, the viscosity point was set to reliably measured points. This measurement verifies whether the wall slip phenomenon actually occurs. Hence, wall slip can be excluded from the causes of the fluctuation.

Consequently, the similar data behavior regardless of the number of treatments in Fig. 5b indicates that it was not the wall slip phenomenon but a rheopectic behavior in which the viscosity increases and then decreases at a specific shear rate (40 s^{-1}), which is an intrinsic rheological property of NFC suspensions. Cellulose nanofibers are characterized by a long chain structure with a high aspect ratio and many hydroxyl groups. Cellulose nanofiber aggregation can occur instantaneously at a high shear rate due to chain

entanglement and interactions such as hydrogen bonding between NFC particles (Fig. 6b). This agglomeration phenomenon increases the instantaneous viscosity, implying that it may clog the channels of the microfluidizer without inducing dispersion and crushing of NFC in the microfluidizer inner tube. From an industrial perspective, this phenomenon makes the automated process of NFC difficult. Therefore, it is essential to verify the characteristics and concentration of the pulp, which can affect the rheological properties of NFC and the pressure in the microfluidizer during mass production of NFC.

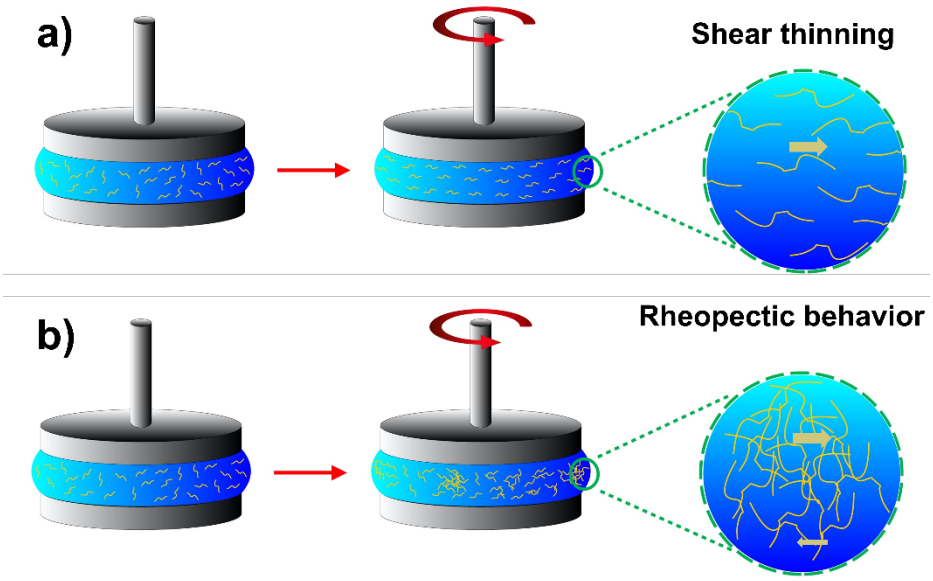

Fig. 6. Schematic of shear thinning and rheopectic behavior of the NFC suspension

CONCLUSIONS

1. This paper investigated the size change of nanofibrillated cellulose (NFC) particles prepared according to the number of the mechanical treatment and the rheological properties of suspensions containing them. The behavior of the NFC particle size change according to the increase in the number of the treatment was well-matched with the change in the rheological properties of the suspension including particles. Hence, it was confirmed that rheological characterization using a rheometer could be a powerful tool to support the morphological description of the NFC particles. Also, these results demonstrated that it is possible to control and optimize the NFC production process by considering the rheological properties to prevent aggregation of the NFC suspension that can be clogging narrow tubes of microfluidizer under high pressure and shear stress.
2. The scanning electron micrograph (SEM) images showed that the width of individual NFC particles prepared from grinder-treated pulp and treated with a microfluidizer decreased by up to three times with the number of microfluidizer processes. No major change in the sizes of the individual NFC particles was observed thereafter.
3. The analysis of the viscoelasticity and viscosity of the NFC suspension according to the number of microfluidizer processes showed that the changing behavior of the

dynamic modulus and the viscosity of the NFC suspension was similar to that of particle size obtained through morphological analysis. Through the analysis of the viscosity behavior according to the shear rate, it can be confirmed that at a specific shear rate (40 s^{-1}) or higher, the NFC suspension exhibits a rheopectic behavior that is caused by the agglomeration of NFC particles, rather than the shear thinning behavior of a general NFC suspension.

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