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ABSTRACT

Cellulose nanofibers (CNFs) produced by mechanical processing have a more uneven fiber shape, diameter, and length than those produced by chemical processing. Depending on the manufacturing conditions, CNFs containing insufficient fibrillated fibers may be produced. In order to find practical applications for CNFs containing unfibrillated fibers, it is important to understand how to control the rheological behavior of these systems. In this study, we investigated the relationship between the nanosized volume fraction and the rheological behaviors of CNF suspensions containing unfibrillated fibers prepared by a wet refining system (Water Jet System). The macroscopic structural changes in those suspensions under shear flow were also discussed based on rheo-optic measurements.

According to the frequency sweeps of the CNF suspensions, it was found that they were elastic-dominated gels, and the elasticity was attributed to the nanofibers. The elastic moduli increased with the volume fraction of the nanofibers, suggesting that the entanglement of the nanofibers was enhanced. The pseudo-plateau modulus $G_p'$ is proportional to the nanofiber volume fraction, with the constant $\alpha = 1.5$, suggesting that the entropic elasticity is dominant.

The viscosity curves of the CNF suspensions showed a shear thinning behavior, in which the viscosity linearly decreased with the increasing shear rate. From the Rheo-SALS measured at the same time, we found that the aggregates of the nanofibers elongated in the flow direction and deformed into an elliptical shape with the applied shearing. The shape change of the aggregates comprised of the nanofibers became more pronounced with the increased nanofiber volume fraction. However, the effect of the shape change of the aggregates was hardly observed on the viscosity curve.
We speculate that this is due to the fact that the unnanosized fibers, which exhibit a Newtonian flow, play a significant role in the flow behavior of the CNF suspensions.

**KEYWORDS:** nanocellulose / pseudo-plateau modulus / small angle light scattering (SALS) / shear thinning / Guinier plot / power law
**Introduction**

Cellulose is the most prolific biological resource on earth, and it has been reported that terrestrial plants produce 100 billion tons per year. Recently, cellulose has been reevaluated as an alternative biomass material to fossil materials because of its recyclability. In addition, the cellulose nanofiber (CNF) has attracted attention due to recent advances in nanotechnology. CNF is literally cellulose fibrillated to a nanoscale, and is expected to be used in a wide variety of fields, such as reinforcement materials for composites, heat insulators, optical and electronic devices, and medical materials, due to its light weight, high strength, and low linear thermal expansion coefficient (Eichhorn et al. 2010; Isogai et al. 2011; Klemm et al. 2011; Siqueira et al. 2010).

The manufacture of CNF can be roughly divided into chemical and mechanical treatments. As a chemical treatment, sulfuric acid has long been used in its manufacturing. In this method, cellulose fibers are treated at 30~40 °C for a long time to hydrolyze and remove the non-crystalline portions in order to obtain microcrystalline cellulose with the degree of polymerization of about 200~250. The product is called cellulose nanocrystal or cellulose nanowhisker. Recently, a catalytic oxidation method using TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) has been proposed; the TEMPO catalytic oxidation was reported in the 1990s as a reaction that can regioselectively convert the C6 primary hydroxyl group of polysaccharides to carboxylate groups under mild conditions (Isogai and Kato 1998). The CNF obtained by the TEMPO oxidation had a uniform fiber width of a few nm and an ultra-fine, high-aspect-ratio shape with a length of several μm, and their suspensions were found to be transparent and highly viscous (Saito and Isogai 2004; Saito et al.
2007). The oxidation reaction introduces a high density of carboxyl and aldehyde groups to the cellulose fiber surface, however, which may modify the fiber surface (Saito et al. 2006) and change its properties, thus there is concern about the environmental impact associated with the chemicals.

On the other hand, mechanical treatment is a method to tear the cellulose fibers mainly in the axial direction by using shear and collision forces, and cavitation caused by rapid decompression. Mechanical devices, such as a high-pressure homogenizer (Iotti et al. 2011; Turbak et al. 1983; Yano and Nakahara 2004), aqueous counter-collision (ACC) method (Kose and Kondo 2011; Kose et al. 2011; Tsuboi et al. 2014), and Water Jet System (Watanabe et al. 2011) are used. These mechanical methods caused high fibrillation by passing the fiber dispersion through the device many times, but in the case of the high-pressure homogenizers, pretreatment with enzymes is sometimes used because the fibers can clog the homogenizer and the energy consumption is high (Charani et al. 2013; Hayashi et al. 1998; Henriksson et al. 2007; Pääkkö et al. 2007). In the ACC method and the Water Jet System, cellulose dispersions are injected and collided with each other from opposite nozzles (injection speed: about 700 m/s, collision pressure: about 200 MPa), and the cellulose fibers are miniaturized only by the penetration force of the water between them. Although the force of collision is weaker than that of a covalent bond, the interaction between fibers is cleaved, thus the fibers can be nanosized without damaging the fiber surface. In addition, since all of these methods use only water and raw materials, the inherent properties of the raw materials, such as the degree of polymerization and crystallinity, can be maintained.
CNFs prepared from various types of cellulose sources using the above-mentioned process have been deployed in various industries due to their value-added properties, and studies have been conducted focusing on the rheological properties of the CNF suspensions (Bercea and Navard 2000; Boluk et al. 2011; Charani et al. 2013; Iotti et al. 2011; Iwamoto et al. 2014; Naderi et al. 2014; Pääkkö et al. 2007; Tanaka et al. 2020; Yamagata and Miyamoto 2021; Yamagata et al. 2020). In other words, it is important to understand how to control the rheological behavior of the CNF suspensions in order to fully exploit the potential of the material.

Factors that affect the rheological behavior of the CNF suspensions include the chemical composition of the fiber, including the surface functional groups, as well as the fiber shape and length distribution. Different starting materials have different chemical compositions, which results in a different fiber stiffness and interaction forces between the fibers. Therefore, even if the shape and the length distribution of the fibers are the same, the rheological behavior will be different depending on the fiber type. In addition, the viscosity and elastic modulus increase with the nanofiber concentration even if the starting material is the same (Charani et al. 2013; Iotti et al. 2011; Pääkkö et al. 2007; Yamagata et al. 2020).

However, there seems to be only a few quantitative and detailed studies of the effect of the fiber length distribution (containing poorly nanosized fibers) of the CNF on the rheological behavior. In particular, in the case of mechanical treatment, unlike chemical treatment, the shape, the diameter and the length of the produced CNF fibers are not uniform. From the viewpoint of reducing the production cost of CNF, it is important to find practical applications for the CNF that
contain fibers with insufficient nanosizing. In order to reduce the production cost of the CNF, it is essential to evaluate the physical properties of the CNF containing insufficiently nanosized cellulose fibers. In this study, we investigated the relationship between the CNF nanosized volume fraction and the rheological behavior of the CNF, which contain insufficiently nanosized fibers, and suspensions produced using a water-jet type wet refinement system. Furthermore, macroscopic structural changes of the CNF suspensions under shear flow were also discussed based on rheo-optic measurements.

Experimental

Preparation of fibrillated cellulose

Low-substituted hydroxypropyl cellulose (LODICEL®, Shin-Etsu Chemical Co., Ltd., hereinafter referred to as HPC) as the starting material, was added to ion-exchange water to prepare a dispersion of about 4 wt%. A water-jet type wet refinement device (Ultimaizer HJP25005, Sugino Machine Limited, Japan) was used as a mechanical refinement device, and the prepared dispersion was injected through two diamond nozzles (nozzle diameter: 0.13 mm) facing and collided with each other under a processing pressure of 180 MPa at room temperature (about 20 °C). The number of collisions was increased from 20 to 60 times to obtain the nanosized CNF suspensions.

AFM observation
CNF diluted with water to about a 0.001 wt% concentration was dropped onto a mica plate in a volume of about 1 mL, heated at 100 °C for 10 min, then air-dried at room temperature for a day and night. Fibers that adhered to the mica surface were obtained by this process. The samples were observed by an AFM system (Tosca 400, Anton Paar GmbH) in the tapping mode.

**Particle size distribution measurement**

The nanosized fibers were considered as spherical particles, and the particle size distribution was measured by a laser diffraction / scattering particle size analyzer (LS 13 320, Beckman Coulter, Inc.) equipped with a universal liquid sample module. The cumulative particle in the normal measurement range of 0.017~20,000 µm were set as 100 %. Among them, the CNF particles volume fraction of 0.017~1.047 µm automatically analyzed by the software was defined as the nanofiber volume fraction (Vn).

**Rheometry**

Rheological measurements were carried out at 20°C by a stress-controlled rheometer, MCR-102 (Anton Paar GmbH). Parallel plates of 25 mm diameter with a 0.5 mm gap between them were used for the viscoelastic measurements. For the shear flow measurements, a quartz plate of 43 mm diameter with a 0.5 mm gap between them were used to measure the time dependence of the apparent viscosity $\eta(\dot{\gamma})$ until a steady state was reached (1~5 min) at a fixed shear rate (Fig. S1). The effects of the sample evaporation were minimized by using a protective hood.

**Small Angle Laser Light Scattering (SALS)**
A small angle light scattering (SALS) system was attached to the above-mentioned rheometer and light scattering measurements were synchronously performed along with the viscosity measurements. A laser beam with a wavelength of 658 nm was irradiated from the top of the rheometer onto a sample sandwiched between the quartz plates, and the transmitted scattered light was directly recorded on a CCD camera chip at the bottom of the instrument. All the exposure times were 8.5 ms.

Results and discussion

Length of CNF

Fig. 1 shows AFM images of the samples obtained after 20 and 60 collision times. The 20 collision times sample (Fig. 1(a)) showed many fibers longer than several tens of microns, whereas the 60 collisions (Fig. 1(b)) showed few fibers longer than 10 μm. In addition, fibers with a width of more than 1 μm were observed in the 20 collision sample. However, it was difficult to accurately measure the fiber length from these images, so we measured the CNF fiber length by a laser diffraction / scattering size analyzer.

![Fig.1 AFM images of CNF prepared with (a)20 and (b)60 collisions](image)
The laser diffraction / scattering method cannot accurately determine the fiber length of a fibrous sample, such as the CNF, because the particle size distribution is based on the light intensity distribution pattern of the diffracted / scattered light, which is calculated assuming that the particles are spherical. However, it is possible to obtain information based on the behavior (spread and size) in water reflecting the fiber length as a particle size distribution. Fig. 2 shows the particle size distributions of the CNF suspensions with the different number of collisions. All the samples showed a bimodal distribution, with a single peak centered at about 0.3 μm and several peaks coexisting between 5 and 200 μm. The peak (volume fraction) near about 0.3 μm increased with the collision times, while the group of peaks coexisting at 5 to 200 μm decreased. These results suggest that the peak of about 0.3 μm and the multiple of peaks from 5 ~ 200 μm correspond to the size of the nanofibers produced by mechanical treatment and the starting material, HPC, respectively.

The relationship between the nanofiber volume fraction (Vn) smaller than about 1 mm and the number of collisions is shown in Fig. 3. Vn was 32.7 % for the 20 collisions, however, Vn increased with the number of collisions, reaching
74.8 % for the 60 collisions. At the same time, the cumulative medium diameter (D50) of the particles decreased by more than one order of magnitude, from about 10 μm at 20 collisions to about 0.3 μm at 60 collisions. These results indicated that a higher number of collisions is more effective for the nanosizing of the fibers.

![Graph showing nanofiber volume fraction Vn and average diameter, D50, of the CNF suspensions versus the number of collisions](image)

**Fig. 3** Nanofiber volume fraction Vn and average diameter, D50, of the CNF suspensions versus the number of collisions

**Viscoelastic behaviors of CNF suspensions**

Before measuring the frequency dependence of the viscoelasticity of the CNF suspensions, we performed the strain sweeps to confirm the linear region. The results are shown in Fig. S2. Both the storage modulus $G'$ and the loss modulus $G''$ increased with the number of collisions, i.e., with the nanofiber volume fraction Vn. The critical strain for the transition from linear to nonlinear was about 3 %, which was almost independent of Vn. Based on these results, the frequency sweeps were measured with the strain fixed at 1 %. The results are shown in Fig. 4. All the CNF suspensions have $G' > G''$ over the entire measurement frequency range, and both $G'$ and $G''$ are almost independent of the frequency $(G' \approx \omega^0, G'' \approx \omega^0)$, thus it is considered that they are an elastic-dominated gel, and the elasticity is attributed to the
nansized fibers. Thus, even for the sample with 20 collisions (Vn = 32.7 %), it is suggested that the nanosized fibers
physically entangled to form a three-dimensional network structure. The storage modulus $G'$ of the sample with 30
collisions (Vn = 47.4 %) was about $10^3$ Pa, which was similar to that of the 1.5 wt% suspension of CNF (fiber length:
827 nm, aspect ratio: 243) prepared by the TEMPO oxidation (Yamagata 2020) and the 2 % suspension of
microfibrillated cellulose (MFC) prepared by high-pressure homogenization by Iotti et al. (2011).

Fig. 4 Frequency $\omega$ dependence of storage modulus $G'$ and loss modulus $G''$ of CNF suspensions

The relationship between the elastic moduli of CNF and the nanofiber volume fraction Vn was discussed. As already
mentioned, since $G'$ and $G''$ are almost independent of the frequency, the elastic moduli at $\omega = 1$ rad/s are considered as
pseudo-elastic moduli ($G'_p$, $G''_p$). Both $G'_p$ and $G''_p$ increased with Vn as shown in Fig. 5. Many papers have been reported
the dependence of the elastic modulus on the concentration in fiber suspension systems (Guenet 2000; Tamai et al. 2004;
Tatsumi et al. 2002). In most cases, a scaling law is observed between the modulus G and the concentration c, as shown
in Equation (1).

$$G = Ae^c$$  \hspace{1cm} (1)
Here, $A$ is a constant that depends on the modulus and the aspect ratio of the fiber itself, independent of the concentration $c$. $\alpha$ is an index that reflects the network structure, and is reported to be about 2.25 in cellulose dispersion systems with a few $\mu$m fiber length regardless of the fiber type (Guenet 2000). The elastic moduli of the fibrillated CNF increased with $V_n$ and depended on the nanofiber concentration. The values of $\alpha$ for $G'_p$ and $G''_p$ were 1.5 and 1.7, respectively, which were lower than 2.25. Ramzi et al. found that the elastic modulus of the agarose cosolvent system can be represented by two straight lines with different exponents, $\alpha = 1.5$ for the agarose concentration below 20 g/L and $\alpha = 2.25$ for the agarose concentration above 20 g/L (Ramzi et al. 1998). According to morphological observations, agarose gels are composed of nearly linear fibrillar arrays and are known to be intrinsically rigid materials (Sugiyama et al. 1940). In light of Jones and Marque's theory (Jones and Marques 1990), it is concluded that the agarose gel is rigid and has an enthalpic elasticity in low concentrations, but exhibits an entropic elasticity due to the binding sites between the fibers being disordered and flexible at high concentrations (Ramzi et al. 1998). Considering these facts, the gelation of suspensions of the mechanically fibrillated CNF is attributed to the increased entanglement of the nanosized fibers, and the entangled junctions are disordered and flexible, suggesting that the system as a whole is gel dominated by an entropic elasticity.
Fig. 5 Pseudo-plateau moduli $G'_p$ and $G''_p$ at 1 rad/s of CNF suspensions as a function of the nanofiber volume fraction $V_n$

Shear flow behaviors of CNF suspensions

Fig. 6 shows the viscosity curves as a function of the shear rate for CNF suspensions prepared by 20 to 60 collisions. The apparent viscosity $\eta(\dot{\gamma})$ increased with the number of collisions in the entire measured shear rate range. $\eta(\dot{\gamma})$ at $\dot{\gamma} = 0.1\text{s}^{-1}$ was higher than $105\text{mPa.s}$ for all samples, but $\eta(\dot{\gamma})$ linearly decreased with the increasing $\dot{\gamma}$. At $\dot{\gamma} = 1000\text{s}^{-1}$, $\eta(\dot{\gamma})$ decreased by three orders of magnitude to $10^2\text{mPa.s}$.

These viscosity curves can be approximated by the power law shown in Equation (2).

$$\eta(\dot{\gamma}) = k\dot{\gamma}^{-n}$$

where, $k$ and $n$ are constants that have no physical meaning, but $n$ is also called the power exponent coefficient, and past papers have shown that $n \leq 0.8$ for polymer solutions and melts, and $n \approx 1$ for cohesive particle dispersion systems and liquid crystals. The $n$-values of the CNF suspensions ranged from 0.84 to 0.93. When the $n$ values were plotted...
versus the nanofiber volume fraction $V_n$, the $n$ values increased with $V_n$ as shown in Fig. 7. This suggested that as the number of nanofibers increased, the aggregation progresses with the entanglement of the fibers and the viscosity in the near-stationary state also increased, but when the aggregated structure is destroyed by the applied shearing, the viscosity decreases with the shear thinning behavior becoming more pronounced.

**Fig. 6 Viscosity curves for CNFs suspensions**

**Fig. 7 Power law index $n$ versus nanofiber volume fraction $V_n$**

Past studies about the rheological behavior of nanocellulose suspensions have confirmed that although they exhibit the shear thinning behavior, where the apparent viscosity decreases with the increasing shear rate, the behavior is not
monotonically decreasing, but rather shows a complex behavior where the plateau of the apparent viscosity appears in the
intermediate and high shear rate regions (Iotti et al. 2011; Li et al. 2015; Takai-Yamashita et al. 2021; Yamagata and
Miyamoto 2021). According to the work of Li et al. (2015), the reason for the appearance of the apparent viscosity
plateau in the intermediate and high shear rate regions is that the former is due to the formation of a more entangled
network structure of oriented fibers by the applied shearing, and the latter is due to the disruption of most of the
entangled network structure and the formation of a well-oriented structure. Iotti et al. (2011) also reported that the reason
for the appearance of the viscosity plateau in the intermediate shear rate region is the shear-induced structure formation,
i.e., since CNF is a long and thin fiber with a very high specific surface area covered by hydroxyl groups, the fibers are
organized by being very close to each other in the structure, influencing the suppression of the decreasing viscosity. We
also discussed the reason for the appearance of the viscosity plateau of the CNF suspensions prepared by the TEMPO
oxidation based on the results of the Rheo-SALS measurements. CNF forms an almost isotropic circular (three-
dimensionally spherical) aggregated structure in the low shear rate region. As the shear rate increases and reaches a
critical value, the aggregation elongates in the flow direction and deforms into an anisotropic elliptical shape in order to
reduce the flow resistance. We speculated that transient shear stress is generated at this time, suppressing the shear
thinning behavior and appeared in the viscosity plateau region. In other words, the appearance of the viscosity plateau is
considered to be caused by the organization and macroscopic structural changes of the nanosized CNF. However, the
plateau region of the apparent viscosity was not observed on the viscosity curve of the mechanical nanosized CNF
suspensions. Therefore, we decided to perform Rheo-SALS measurements of the CNF suspensions containing insufficiently nanosized fibers to confirm whether there is any structural change in the CNF aggregations under shear flow.

**Rheo-SALS measurements of CNF suspensions**

Small-angle light scattering (SALS) is one of the most widely used techniques to visualize changes in the internal structure of systems under shear flow by synchronizing it with rheological measurements. The intensity distribution of the scattered light caused by the incident primary laser beam is detected by a CCD camera during the light scattering. Various polarization components can be observed by changing the polarization directions of the incident light and the detector when making the measurements. The case where the polarization directions of the polarizer and the detector are orthogonal is called Hv, and the case where they are parallel to each other is called Vv. Based on the HV and VV scattering, we can obtain information about the optical anisotropy and density fluctuations and the optical anisotropy, respectively. The scattering images are omitted, but only the VV scattering results are shown below, since HV scattering, which indicates anisotropy, was rarely observed in the CNF suspensions.

Fig. 8 shows the scattering images obtained by the applied shearing from 0.1 to 1000 s\(^{-1}\) to the CNF suspensions prepared by 20 to 60 collision times. The flow direction is from left to right in the scattering image. The scattering images showed an almost isotropic circular regardless of the number of collisions at a shear rate of 0.1 s\(^{-1}\) as in the near static state. However, the scattering images transformed from a circular shape to a longitudinal elliptical shape extending...
perpendicular to the flow direction with the increasing shear rate. At the high shear rate, the elliptical scattering images became smaller with the number of collisions.

The shape and size of the scattered image are inversely related to those of the scatterers. In other words, a larger scattering image means smaller scatterers, and an elliptical scattering image extending along the y-axis means an elliptical scattering image extending along the x-axis (flow direction). We decided to calculate the size of the scatterer from the scattering image, however, since it is too qualitative to discuss the change in the structure of the scatterers from those of the scattering image.

![Fig. 8 Shear rate dependence of scattering images of CNF suspensions](image)

**Fig. 8 Shear rate \( \gamma \) dependence of scattering images of CNF suspensions prepared with a different number of collisions**

**Internal structure change of CNF suspensions under shear flow by Rheo-SALS analysis**

The observed scattering images were imported into Anton Paar's software, NewSALS ver.2.01, and the scattering intensity was calculated from the scattering vector \( q \), which corresponds to the distance from the center of the transmitted
light, and the average value of the light intensity in a specific angular range (±15°). The scattering intensity of CNF \( I(q) \) was calculated by subtracting those of water calculated in the same way. The scattering vector \( q \) can be calculated using equation (3), and the effective range of \( q \) for this device is 0.171 to 4.131 \( \mu m^{-1} \).

\[
q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \tag{3}
\]

where \( \lambda \) is the wavelength of the laser beam (658 nm) and the scattering angle \( \theta \) was calculated by Equation (4).

\[
\theta = \tan^{-1} \left( \frac{L/2}{l} \right) \tag{4}
\]

\( l \) is the camera length (15 cm) and \( \phi \) is the size (length) of the scattering image.

Fig. 9 (a) Scattering profiles and (b) Guinier plots for CNF suspension prepared by 60 collisions (x-axis direction)

The curves are shifted vertically by the factor (0.01 ~ 50)

Fig. 9(a) shows the scattering curves for the flow direction of 0° to the x-axis with 60 collisions, and parts of the curves at the shear rate of 0.1 ~ 1000 s\(^{-1}\) are extracted. In addition, the y-axis is shifted upward and downward by
multiplying the scattering intensity by an appropriate factor (0.01 ~ 50), since the scattering curves overlap and are
difficult to understand. A plateau appeared around $q = 0.4 \sim 0.7 \, \mu m^{-1}$ at the low shear rates of less than 100 $s^{-1}$. However,
the plateau disappeared with the increasing shear rate, a maximum was observed around $q = 0.4 \sim 0.5 \, \mu m^{-1}$ and the
scattering intensity $I(q)$ decreased toward the wide-angle side. The gradient of the decreasing $I(q)$ becomes steeper with
the increasing shear rate. The scattering function in the small-angle region where $I(q)$ decreases can be approximated by
Guinier’s equation shown by Equation (5).

$$I(q) = I_0 \exp \left( -\frac{R_g^2}{3} q^2 \right) \quad (5)$$

Here $I_0$ is the scattering intensity when extrapolated to $q = 0$, and $R_g$ is the radius of gyration which is a measure of the
size of the scatterers. $R_g$ can be calculated from the slope of the straight line (red dashed line in Fig. 9(b)) when $\ln I(q)$ is
plotted versus $q^2$ from Equation (6), and the slope increased with the shear rate. The Guinier approximation is said to be
effective when the product of the scattering vector $q_{\text{max}}$ at the right end of the linear approximation region of the $\ln I(q)$ -
$q^2$ curve and the calculated $R_g$ is approximately 1.3 or less (Putnam et al. 2007; Zheng W and Best RB 2018). In our
experimental systems, $q_{\text{max}} \cdot R_g \approx 0.8 \sim 1.7$, which is a rather high value, but the measured values slightly deviate upward
from the approximate line, indicating that $R_g$ may be underestimated. We believe that the variation of $R_g$ with the shear
rate and the number of collisions can be well discussed, however, because the characteristic known as the Guinier region
in which the scattering intensity rapidly decreases from the plateau to the wide-angle region are observed on the
scattering curves.
The shear rate dependence of the radius of gyration of the major and minor axes of the scatterers, $R_g$, obtained from Equation (5) is shown in Fig. 10. The ● and ○ plots in the Fig. 10 show the $R_g$ of the scatterers obtained from the scattering intensity in the angle range of ±15° with respect to the x- and y-axis, respectively. In other words, ● corresponds to the magnitude of the short axis of the scatterer oriented perpendicular to the flow direction, and ○ corresponds to the magnitude of the long axis of the scatterers along the flow direction.

$R_g$ of the scatterers at the low shear rate was 1.2 μm when the number of collisions was 20 (Fig. 9(a)). This size is smaller than that of the starting material HPC and larger than that of the fibrillated fibers. In other words, the size of the scatterer was inferred to be that of the cluster-like aggregates formed by entanglement of the nanofibers. $R_g$ of the aggregates at low shear rates slightly increased with the number of collisions, but did not significantly change.

We now discuss the relationship between the size and shape of the aggregates and shear rate. In the case of 20 collisions, the size of the aggregates in the flow direction (0°) and the vertical direction (90°) were almost equal and its shape seemed to be spherical below 10 s⁻¹. As the shear rate increased, however, the size in the flow direction increased to 1.7 μm while the those in the vertical direction did not significantly change. Thus, the CNF aggregates elongated in the flow direction and deformed into an ellipse with the applied shearing. This shape change became more pronounced with the number of collisions, and the size of the aggregates in the flow direction grew to 2.5 μm for the 60 collisions.

Fig. 11 shows the dependence of the average aspect ratio of the CNF aggregates at 0.1 ~ 0.25 and 400 ~ 1000 s⁻¹ on the nanofiber volume fraction. As can be seen from the figure, the average aspect ratio of the aggregates showed a
constant value of about 1, which is a small concentration dependence, at the low shear rate, but increased with the nanofiber volume fraction at the high shear rate. In other words, in the high shear rate region, the aggregates elongate relatively more in the flow direction and the anisotropy increases with the increasing of nanofiber volume fraction.

![Graph showing relationship between radius of gyration \( R_g \) and shear rate \( \gamma \).](image)

**Number of collisions;** (a) 20, (b) 30, (c) 40, (d) 60

Based on the above results, the mechanically fibrillated nanofibers formed an isotropic spherical agglomerated structure in the static state. In addition, its structure becomes slightly larger with the nanofiber concentration. The aggregates deformed into an elliptical shape elongated in the flow direction with the applied shear rate above 10 s\(^{-1}\), and
its deformation is more pronounced for the nanofiber concentration. Therefore, it is not surprising that the shear thinning behavior is suppressed due to the transient shear stress induced by the shape change of the aggregates around $10 \text{ s}^{-1}$, and a plateau region appears on the viscosity curves. However, no changes were observed on the viscosity curve. This is probably due to the presence of long fibers with insufficient nanosizing. Fig. S3 shows the viscosity curve of a 4 wt% dispersion of HPC, the starting material before the fibrillization. Fig. S3 shows the flow behavior of a 4 wt% dispersion of HPC, the starting material before the fibrillization. The dispersion of the unfibrillated long fibers exhibits a Newtonian flow, and the shear stress $\sigma$ monotonically increases with the shear rate $\dot{\gamma}$. We speculated that the unnanosized long fibers, which remained more than 25% even after 60 collisions, absorbed the transient stresses caused by the deformation of the nanosized fiber aggregates, resulting in the monotonous shear thinning behavior of the CNF suspensions.

![Fig. 11 Relationship between aspect ratio of aggregates and nanofiber volume fraction Vn](image)

**Conclusions**
The relationship between the nanofiber volume fraction and the rheological behaviors of CNF suspensions containing poorly nanosized cellulose fibers produced using a water-jet type wet refinement system was discussed. Based on the frequency sweep, we found that the CNF suspensions behaved like an elastic-dominated gel, and the nanosized fibers were responsible for development of the elasticity. The elastic moduli increased with the nanofiber volume fraction, suggesting that the entanglement of the fibers was enhanced. The pseudo-plateau modulus $G_p'$ is proportional to the nanofiber volume fraction, and its constant $\alpha = 1.5$, indicating that the entropic elasticity is dominant.

The viscosity curve of the CNF suspensions showed a shear thinning behavior, in which the viscosity monotonically decreased with the shear rate. From the Rheo-SALS simultaneously measured, we found that the aggregates of the nanofibers elongated in the flow direction and deformed into an elliptical shape with the applied shearing. The shape change became more pronounced with the increasing nanofiber concentration, but the influence of those changes was hardly observed on the viscosity curves. We speculated that the unfibrillated fibers, which exhibit a Newtonian flow, are mostly responsible for the flow behavior of the CNF suspensions.

In conclusion, for the CNF suspensions containing poorly nanosized fibers, we speculated that the nanosized and unfibrillated fibers were largely responsible for the linear response under micro-deformation and the nonlinear response such as under shear flow, respectively.
Authors contributions Conceptualization: YY, SN, and KM; Data curation: YY and KM; Investigation: YY, SN, and KS; Project administration: YY; Resources: YY, SN, KS, and KM; Supervision: YY; Validation: YY, and SN; Visualization: YY, and KS; Writing—original draft: YY; Writing—review & editing: YY, SN, KS, and KM.

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Data availability All data generated or analyzed during this study are included in this published article and its supplementary information files.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflicts of interests/competing interests.

Code availability There is no code availability for software application or custom code.

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Fig. S1 Measurement program for steady flow.

Fig. S2 Strain dependence of dynamic moduli $G'$ and elastic $G''$. 
Fig. S3 Viscosity curve of 4 wt% HPC suspension without mechanical treatment.

○: $\eta(\dot{\gamma})$  ●: $\sigma$
Supplementary Files

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