Estimation of Cellulose Nanofiber Length Using Steady Shear Viscosity of Fiber Suspensions

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ABSTRACT. In this study, a novel method was proposed for estimating the length of TEMPO-oxidized cellulose nanofibers using the steady shear viscosity of a nanofiber suspension in water. Two fiber suspensions were prepared: one sample contained fibers approximately 500 nm in length and the other sample contained fibers of approximately 200–300 nm in length. For each sample, the steady shear viscosity of the suspension was measured for 7–8 distinct volume fractions, and the viscosity was approximated using a power-law model. The relationship between the power index of the power-law model and the volume fraction of the nanofiber was used to estimate the fiber length. The measured lengths of the nanofibers were similar to those obtained using various other fiber length measurement methods, indicating that this method can be used for fiber length estimation.

I. INTRODUCTION

Cellulose nanofibers (CNFs) are biomaterials extracted from wood and other plants [1]. Various aspects of CNFs have been published in several journals [2-8]. Two methods are typically used to extract nanofibers from wood. One method is mechanical milling, and the other method is chemical treatment. In mechanical milling of pulp fibers, for example, the impact force from the collision of a jet of pulp fibers is used [9]. During mechanical processing, CNFs form clusters, and this fiber suspension generally scatters visible light, resulting in a cloudy appearance. Isogai et al. developed a chemical treatment method using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation in water [10] to break fibers into individual nanoscale fiber fragments. The fiber suspensions obtained by dispersing fibers in water using this method exhibit good transparency under visible light. Fiber suspension systems prepared by the TEMPO oxidation method are simpler than those prepared through mechanical processing because the fibers remain as individual entities. Therefore, the hydrodynamic and rheological properties of CNF-containing fiber suspensions can be studied easily. Therefore, TEMPO-oxidized cellulose nanofibers (TOCNs) were used in the present study.

Generally, the rheological properties of fiber suspensions containing short fibers are highly dependent on the aspect ratio of the short fibers in the suspension [11, 12]. This phenomenon is true for suspensions containing nanosized fibers such as cellulose nanofibers [13, 14]. Therefore, understanding the aspect ratio of CNFs is necessary for predicting the rheological properties of the suspension. Consequently, various methods have been investigated to measure the aspect ratios of CNFs. However, measuring the length and diameter of short nanoscale fibers is difficult.

Several methods have been devised for measuring the size of short nanoscale fibers. A simple method to measure the size of a short fiber is scanning electron microscopy (SEM). This method reliable because the length and diameter can be measured by directly observing the shape of the CNF. However, this method is also labor-intensive. Because observation under vacuum is necessary, the method requires considerable preparation for drying the fibers. Additionally, the method requires the application of a gold coating on the sample.

Boluk et al. proposed a simple method to measure the aspect ratio of cellulose nanocrystal (CNC) suspension fluids by measuring their intrinsic viscosity and obtained results consistent with those measured through atomic force microscopy [15]. This method of measuring the aspect ratio from the intrinsic viscosity is an application of the method for determining the molecular weight of polymers to CNCs. However, studies have reported that the length of the CNFs measured using this method is not always accurate [14]. Ishii et al. estimated the length of CNFs by measuring the dynamic viscoelasticity of CNF suspensions; the results were consistent with those obtained by transmission electron microscopy (TEM) [16, 17]. Araki et al. used microcrystalline cellulose suspensions to estimate aspect ratios based on the relationship between relative viscosity and concentration [18].

Other methods include dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) measurements [14]. A novel method was developed to determine the fiber length by measuring the birefringence of a CNF suspension [19]. In this method, fibers are oriented by applying shear to a semidilute or concentrated CNF

suspension. The degree of fiber–fiber interaction depending on the fiber concentration is measured as the birefringence, which is used to determine the length of the CNFs.

As described, various methods have been devised to measure the length and aspect ratio of CNFs. In this study, we proposed a novel method for measuring the average fiber length by measuring the steady shear viscosity, which is a rheological property of CNF suspensions.

II. TEST FLUIDS

The test fluids used in the experiment were two types of CELLENPIA, namely, TM-0101 and TC-02X, containing TOCN suspended in water supplied by Nippon Paper Industries Co., Ltd. TM-0101 is a fiber suspension containing fibers with an average length of 500 nm, while TC-02X contains fibers with an estimated average length of 200–300 nm. The average length of the fibers suspended in TM-0101 was measured by the supplier using a scanning electron microscope; however, the average length of the fibers suspended in TC-02X was not measured.

These samples were provided at concentrations of 3.12 wt% for TM-0101 and 5.20 wt% for TC-02X. TM-0101 was adjusted to seven weight fractions, namely, 0.50, 0.63, 0.75, 0.85, 0.93, 1.30, and 1.50 wt%, by dilution with ion exchange water to prepare the test fluids. TC-02X was adjusted to eight weight fractions, namely, 1.50, 2.00, 2.25, 2.50, 2.75, 3.00, 3.25, and 3.50 wt%.

The test fluids were stirred using a household hand mixer for approximately 30 min to allow the fibers to diverge fully. Because the sample fluid is highly viscous, as described, centrifugation was performed at approximately 3700 g (g is the acceleration due to gravity) for 3 min to remove small bubbles in the fluid before the experiment. Because these test fluids are almost colorless and transparent, the fibers in the sample fluid can be assumed to be well diverged.

Generally, in a fiber suspension, the mechanical interaction between the fibers significantly affects the rheological properties of the fluid. Therefore, the volume fraction within the liquid, rather than the weight fraction of the fibers, is a critical factor. Because the specific gravity of cellulose is 1.5, the volume fractions of each test fluid are 0.33, 0.42, 0.50, 0.57, 0.62, 0.87, and 1.0 vol% for TM-0101, and 1.0, 1.3, 1.5, 1.7, 1.8, 2.0, 2.2, and 2.3 vol% for TC-02X.

Because the TOCNs used in the present study existed almost as separate entities, the fiber diameters can be considered uniform and are approximately 3–5 nm [20]. However, the length is not uniform, with the existence of a length distribution [21].

In fiber suspensions, the rigidity or flexibility of the fibers is a critical factor when considering their effects on the rheological properties and flow of the fiber suspension system. The modulus of elasticity of the fiber is approximately 150 GPa [22], and the estimated tensile fracture strength is between 2 and 6 GPa [23]. Based on these values, the CNFs can be considered rigid.

III. CONCENTRATION CLASSIFICATION OF FIBER SUSPENSIONS

In fiber suspensions, the orientation state of the fibers during flow is significantly affected by the mechanical interactions between the fibers. When the fibers are rod-shaped, the values of nL^3 and L/D determine the magnitude of mechanical interference between the fibers. Here, n is the number density, L is the fiber length, and D is the fiber diameter. Using these values, the fiber suspensions can be classified into three concentration ranges, namely dilute, semidilute, and concentrated isotropic [24].

$$\begin{aligned} nL^3 &\precsim 1 : \text{dilute range,} \\ 1 \preccurlyeq nL^3 &\ll \frac{L}{D} : \text{semidilute range,} \\ \frac{L}{D} &\precsim nL^3 : \text{concentrated isotropic range.} \end{aligned} \qquad (1)$$

Here, the term “dilute” denotes the volume fraction of a fiber that does not cause mechanical contact with other fibers irrespective of any rotation of the fiber in the suspension at that volume fraction. The term “concentrated isotropic” indicates the concentration at which the fiber always causes mechanical contact with neighboring fibers regardless of how the fiber rotates. The term “semidilute” indicates the intermediate concentration. Furthermore, the relationship between these values and the volume fraction $\emptyset$ of the fiber is as follows:

$$\emptyset = nD^2L \qquad (2)$$

Based on Eq. (1), the following equation holds at the boundary between the semidilute and concentrated isotropic ranges:

$$\frac{L}{D} = nL^3 \quad (3)$$

Furthermore, solving Eqs. (2) and (3) simultaneously yields the following equation:

$$\emptyset = D/L \qquad (4)$$

When the volume fraction $\emptyset$ of the fiber at the boundary between semidilute and concentrated isotropic ranges is known, the aspect ratio of the fiber, L/D, can be obtained from this equation. Furthermore, assuming a fiber diameter D, fiber length L can be obtained.

IV. EXPERIMENTAL INSTRUMENTATION

In this study, the steady shear viscosities of test fluids were measured using a cone-and-plate rheometer (MCR-301, Anton Paar, Austria), where the cone diameter is 50 mm and cone angle is 1°. The sample temperature was maintained at 298 K.

V. RESULTS AND DISCUSSION

Figure 1 depicts the steady shear viscosity at each TM-0101 concentration. This figure reveals that each test fluid has a shear-thinning viscosity. The results of fitting these viscosity properties to the power-law model are presented in the figure. The values of η_0 and n are also shown in the figure.

$$\eta = \eta_0 \dot{\gamma}^{n-1} \quad (5)$$

Furthermore, the value of n varies with the concentration of the CNFs.

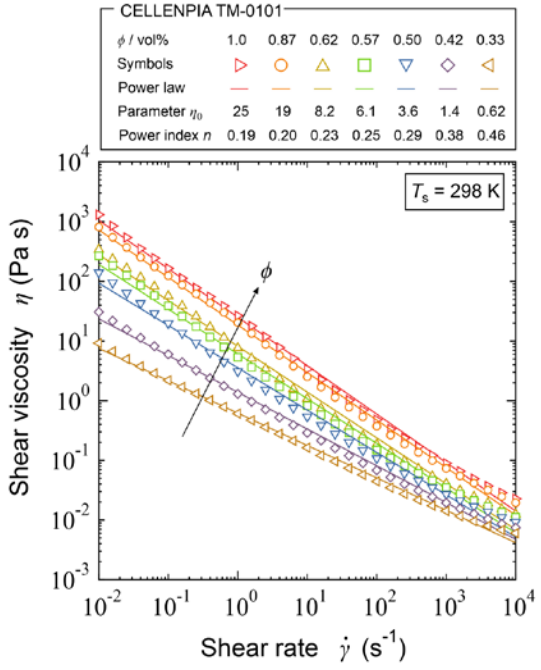

FIG 1. Dependence of shear rate on steady shear viscosities of test fluid: CELLENPIA TM-0101.

Figure 2 depicts the steady shear viscosity of the suspension at each concentration in the test fluids of TM-02X. As in the case of TM-0101, the test fluids at all suspension concentrations exhibited shear-thinning properties. However, unlike the case of TM-0101, the first and second Newtonian viscosities were observed for a test fluid with a low concentration. In such a case, the steady shear viscosity was approximated by the Carraue–Yasuda model [25]. However, we focused only on the range of shear rates that can be approximated by the power-law model and approximated the viscosity in that range using the power-law model. The values of η_0 and n, the parameters of the power-law model, are presented in the figure. As in the case of the TM-0101 suspension, the value of n varies with the concentration of the TM-02X suspension.

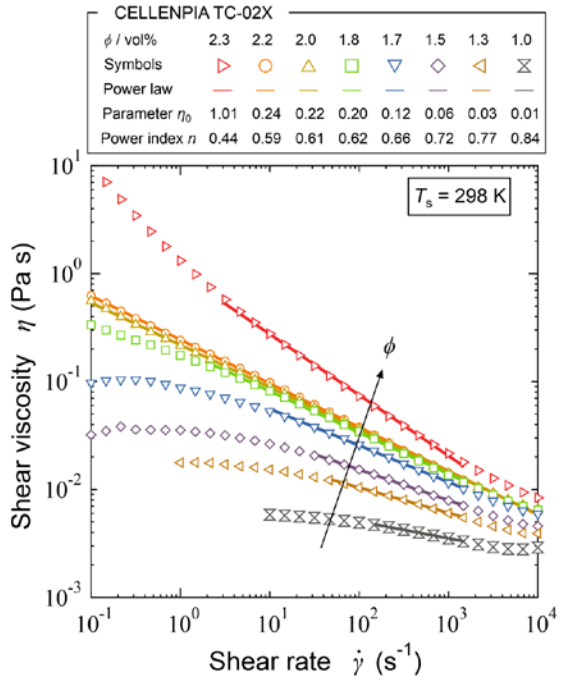

FIG 2. Dependence of shear rate on steady shear viscosities of test fluid: CELLENPIA TC-02X.

Using the results, the relationship between concentration $\emptyset$ and power index n is illustrated in Figs. 3 and 4 for both TM-0101 and TM-02X, respectively. As shown in Fig. 3, the power index n decreases with the increase in concentration. The decreasing trend changed abruptly at $\emptyset = 0.0057$. This boundary was considered the boundary between the concentrated and semidilute regions. Using Eq. (4), and assuming that fiber diameter D is 3 nm, the fiber length was calculated to be 523 nm. This value is close to the value of 500 nm measured using SEM. The hydrodynamic radius of the same sample fluid was measured using DLS and was 473 nm. The values measured by DLS were slightly smaller than those obtained by SEM. Fiber lengths of 500 and 517 nm were obtained according to fiber length measurements based on birefringence [19]. Both results revealed fiber lengths of approximately 500 nm, indicating that the method used in this study provided reliable results.

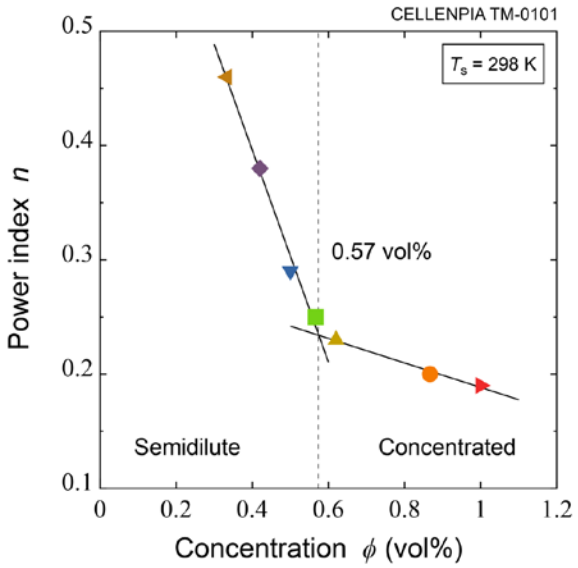

FIG 3. Relation between fiber concentration of test fluid and power index of power-law model used for approximation of shear viscosity for CELLENPIA TM-0101.

The concept demonstrated in Fig. 3 was also applied to Fig. 4. The test fluid with the highest concentration (2.3 vol %) and the test fluid with the lowest concentration (1.0 vol %) were excluded and not used in the calculations because they exhibited a trend distinct from the results for the other concentrations. Consequently, the fiber length was calculated to be 167 nm. Although SEM measurements were not available for TM-02X, the hydrodynamic radius of the same sample fluid was measured using DLS, yielding a value of 145 nm. The fiber lengths measured by the birefringence method were 169 to 182 nm [19], and the fiber lengths obtained in the present study are close to the values obtained by other measurement methods. Therefore, the measurement method used in the present study is assumed to yield appropriate fiber lengths. However, the proposed method does not allow measurements with very high or low concentrations of test fluids.

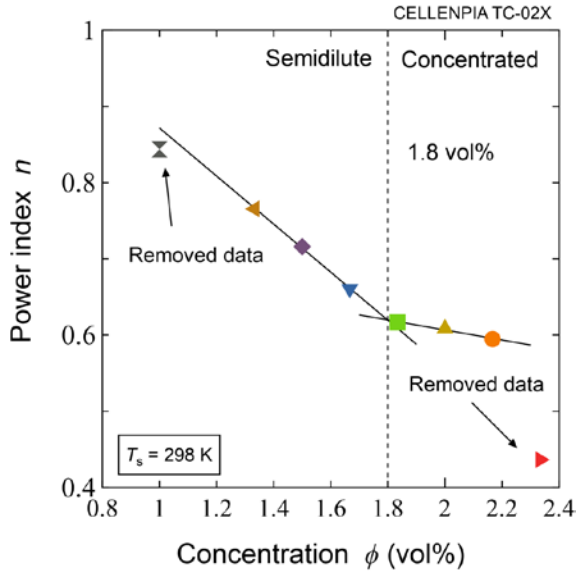

FIG 4. Relation between fiber concentration of test fluid and power index of power-law model used for approximation of shear viscosity for CELLENPIA TC-02X.

VI. CONCLUSIONS

In this study, we proposed a novel method to evaluate fiber lengths based on steady shear viscosity, which is a basic rheological property. The fiber lengths of the cellulose nanofibers obtained by this method were similar to those obtained through SEM, birefringence measurements, and DLS. Thus, this method is simple and effective for evaluating fiber lengths. In the future, it would be desirable to examine the applicability of this method on a larger number of samples with different average lengths.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

AUTHOR CONTRIBUTIONS

K.Y. conceptualization (lead), data curation (lead), formal analysis (equal), methodology (equal), project administration (lead), supervision (lead), writing the original draft (lead), and writing the review and editing (equal); T.H. investigation (equal), formal analysis (equal), methodology (equal), writing, review, and editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

STATEMENTS AND DECLARATIONS

The authors have no relevant financial or non-financial interests to disclose.

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