Transport Properties of Commercial Cellulose Nanocrystals in Aqueous Suspension Prepared from Chemical Pulp via Sulfuric Acid Hydrolysis

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ABSTRACT: A cellulose nanocrystal (CNC) sample prepared from chemical pulp via sulfuric acid hydrolysis procedures has been supplied by InnoTech Alberta Inc. in the shape of white dry powder as a prototype product. Some transport coefficients were precisely investigated for the CNC sample in aqueous suspensions at the room temperature of 25 °C such as the average rotational and translational diffusion coefficients (D_r and D_t) and viscoelastic relaxation times (τ_v) at dilute conditions. The determined values, D_r ≈ 2.3 × 10^10 cm^2 s^−1 and D_t ≈ 1.0 × 10^−11 m^2 s^−1, using depolarized and usual dynamic light scattering (DLS) techniques, respectively, proposed the consistent length and width of L ≈ 170 nm and W ≈ 7.6 nm via a theoretical model for monodisperse rigid rods dispersed in pure water. The viscoelastic behavior for aqueous CNC suspensions containing spherical probe particles was examined using DLS rheological techniques. The obtained value of τ_v = 1.0 × 10^−4 s fairly agrees with that of (6D_r)^−1 ≈ 7.4 × 10^−5 s. Because the theoretical model for monodisperse rods denotes the relationship τ_v = (6D_r)^−1, this observation strongly confirms that the CNC sample behaves as approximately monodisperse rigid rodlike particles. Transmission electron microscopy (TEM) images clearly demonstrated a bimodal distribution in rod length with major and small minor peaks at ca. 150 and 240 nm, respectively. Then, the reason for the observed disagreement between the L values resulted from the transport coefficients and the major peak in TEM images is the presence of the small minor component with L ≈ 240 nm. Consequently, individual nanosize rodlike crystalline particles in the CNC sample well disperse without forming large aggregations because of strong interactions and behave as isolated individual rods in dilute aqueous suspensions.

INTRODUCTION

Cellulose nanocrystals (CNCs) are nanosize crystalline rodlike particles made from cellulose via acid hydrolysis procedures by the use of several types of acidic agents.1−4 CNCs are highly potential nature base organic polymeric materials for a wide range of applications such as a high-performance reinforcement agent in common plastics because of their low density, ca. 1.6 g cm^−3;5 high strength, ca 10 GPa;5 and high modulus, ca 150 GPa.2,6,9 CNCs are also highly potential materials for optical applications because produced composites containing CNC particles can be transparent because of the size of CNC particles less enough than the wavelength of visual light.8,9 Moreover, it has been well-known that many kinds of CNCs have the ability to make a liquid crystalline phase in aqueous suspensions at concentrations higher than critical values depending on the CNC species.10,11 This liquid-crystalline-forming feature also fascinates many researchers who work in the field of basic science and also industrial practical applications.10,11 Moreover, CNCs have a highly promising future to be used in the fields of food and pharmaceutical industries.12−15 The fact that cellulose is the most abundant organic materials, that is, biomass, on the globe as the main component of the plant cell walls, which are generated repeatedly every year by a vast kind of plants infinitely, should be an important point to be deeply considered to develop a well-established sophisticated sustainable society on our globe.2,3,7

CNCs possessing different dimensions and morphologies are able to be prepared by choosing the source of cellulose samples, the kind of hydrolysis acidic agents and conditions.2−4 If one subjects higher plant cellulose samples originated from, for example, cotton and ordinary wood pulp to hydrolysis reactions, needle- or spindle-like CNC particles possessing lengths shorter than a few hundred nanometers and widths of a few nanometers are prepared.2−4 Enormously long whiskerlike CNC particles on the order of micrometers in length are obtained from tunicate and also green algae cellulose by hydrolysis reactions.2

In this study, we pay attention to a white dry CNC sample obtained from wood pulp. InnoTech Alberta Inc. (Edmonton)
has started to operate a CNC pilot plant which can produce CNC samples as prototype products targeting commercially available products from any fibrous materials containing a high α-cellulose contentlike chemical pulp. They say that their CNC samples contain nanosize spindellike crystalline particles with a relatively monodisperse length distribution that maybe based on transmission electron microscopic (TEM) images. However, the dispersibility and stability of CNC samples in aqueous suspensions essentially important for practical industrial applications are highly dependent on the surface chemistry of CNC particles controlled by hydrolysis procedures and cannot be simply rated from only TEM images in general. Here, the distribution of length \( L \) and width \( W \) or diameter for nanosize spindellike CNC particles contained in a CNC sample that was kindly supplied by InnoTech Alberta Inc. were analyzed based on carefully taken TEM images, and the average, \( L_{\text{TEM}} \) and \( W_{\text{TEM}} \) values and their standard deviations were also evaluated. Then, transport coefficients for the commercial prototype CNC sample in dilute aqueous suspensions, such as rotational and translational diffusion coefficients \( (D_r \text{ and } D_t) \) and viscoelastic relaxation time \( (\tau_r) \), were determined to rate the dispersibility into aqueous media highly related to the efficiency of the CNC samples for industrial applications.

The determined values of \( D_r \), \( D_t \) and \( \tau_r \) were used to evaluate the consistent length, \( L_{\text{cf}} \) and width, \( W_{\text{cf}} \) of the nanosize spindellike particles contained in the CNC sample as rodlake ones using a theoretical model for monodisperse rodlake particles dispersed into viscous fluid.\(^{17}\) The average values of the length and diameter of rodlake particles, \( L_{\text{TEM}} \) and \( W_{\text{TEM}} \) of the CNC sample were compared with those of \( L_{\text{cf}} \) and \( W_{\text{cf}} \). Recently, theoretical models\(^{17}\) to discuss precisely the shape and dimension of dispersed particles at extremely dilute conditions have been established. However, some reported experimental transport coefficient data obtained at dilute conditions sometimes contain serious problems because of difficulties of experiments. Correct transport coefficients evaluated from carefully carried experiments are necessary to determine \( L_{\text{cf}} \) and \( W_{\text{cf}} \) precisely. Moreover, experimental studies to determine correct transport coefficients at dilute conditions are essential for especially newly obtained particles such as the CNC sample examined in this study for the investigation of transport and rheological features of moderate to concentrated suspensions.

Very recently, Mao et al.\(^{18}\) investigated the size and morphology of the particles contained in the same CNC sample as we examined. They used several kinds of scattering techniques, TEM observation, and also dynamic light scattering (DLS) experiments to obtain precise information on the morphology of the CNC particles and concluded that the length of the CNC particles in the sample derived from the \( D_t \) and \( D_r \) data did not coincide with each other. The values of consistent \( L_{\text{cf}} \) and \( W_{\text{cf}} \) determined in this study will be compared with their values and discuss the validity of our \( L_{\text{cf}} \) and \( W_{\text{cf}} \).

**RESULTS AND DISCUSSION**

**TEM Images.** Figure 1 shows a typical TEM image of CNC particles of the tested white dry CNC sample, which was highly diluted in water suspension and stained by the negative staining method. Many highly extended needle or spindellike shape objects, which seem to be individual primary CNC particles and possess the length, \( L \), and width, \( W \), less than 300 and 20 nm, respectively, are observed in Figure 1. The distribution of the \( L \) and \( W \) was quantified in the form of histograms, as seen in Figure 2. The observed \( L \) value shows the presence of a bimodal distribution: a major peak found at 150 nm and a small minor one at 240 nm. Similar bimodal \( L \) distributions in CNC samples were also clearly recognized in the previous systematic study.\(^4\) On the other hand, the \( W \) value has only one sharp peak at 10 nm. Then, the TEM image shown in Figure 1 looks similar to that previously published as CNC particles made from chemical pulp via sulfuric acid hydrolysis techniques including the bimodal distribution of \( L \) seen in Figure 2.\(^{2,18,19}\)

In the case of dried out cellulose fibril samples made from kinds of higher plant resources such as softwood and hardwood pulp, ramie, cotton, and so on, cellulose microfibrils (or microfibril aggregates) are constructed by numbers of \((\alpha \text{-}1,4\) type) crystallites connected sequentially by amorphous (or disordered) cellulose chain regions along the elongated long-axis direction.\(^{26-4,19,20}\) In the short-axis (or a transverse sectional) direction, microfibrils (or microfibril aggregates) are constructed by one (or a few) microfibril(s) formed by, for example, 36–68 β-1,4-glucan chains for higher plants\(^{20,21}\) (or more β-1,4-glucan chains depending on the species of source plants\(^{21}\)) and held together by intra- and intermolecular hydrogen bonding, whereas β-1,4 glycoside linkages sustain the rod- or threadlike structure of cellulose microfibrils in the elongated direction. Then, it has been widely accepted that most disordered regions existing every ca 150 nm (approximately) periodically along cellulose microfibrils are effectively decomposed, and then isolated crystallites (CNC particles) possessing their length close to 150 nm are generated in the acidic hydrolysis procedures.\(^{20}\) Moreover, it has been well-known that a small amount of sulfate \((\text{OSO}_3^-)\) groups are introduced on the surface of CNC particles in the procedure of hydrolysis reaction using sulfuric acid, and the obtained CNC particles demonstrate rather higher dispersibility in aqueous suspension because of electrostatic repulsion between negatively charged sulfate groups than CNC particles without any ionic groups obtained by hydrochloric acids\(^{2-5,21,22}\). Consequently, one might expect high dispersibility for the examined CNC sample in aqueous suspension as in the form of isolated individual CNC primary particles, as seen in Figure 1.

The size of the transverse section of a microfibril formed by 36–68 β-1,4-glucan chains has been discussed by many researchers.\(^2-5,21,22\) Ding et al.\(^{22}\) recently estimated the size to be 3.2 nm × 5.3 nm. The observed \( W \) value for CNC particles

![Figure 1. TEM image of negatively stained CNC particles contained in the examined white dry powder sample resulted from the ordinary chemical pulp via a hydrolysis procedure with sulfuric acid. A black scale bar means 200 nm.](image-url)
in the sample markedly larger than the size of the microfibril, as seen in Figure 2b, clearly reveals that a couple of microfibrils are still bundled tightly by strong hydrogen bonding even after the hydrolysis procedure.

There are two possible explanations following the bimodal distribution of the \( L \) values observed in Figure 2a. The first explanation is that the amorphous or disordered regions exist perfectly in order with the constant periodicity of ca 150 nm along cellulose microfibrils, and the degradation process of \( \beta/1,4 \) glycoside linkages by hydrolysis reaction is not perfect. The second explanation is that the periodicity of disordered regions is not perfect, but the degradation process for glycoside linkages is perfect. Agarwal et al.\textsuperscript{23} recently discovered that crystalline domains are absent in the never-dried native-state wood cellulose samples based on the Raman spectroscopic data. Moreover, Horikawa et al.\textsuperscript{19} very recently claimed an idea that the disordered regions along dried out cellulose microfibrils are preferentially resulted from the drying out process of cellulose samples and are not there in the raw (or wet) native-state cellulose fibrils. Then, this idea\textsuperscript{19} is strongly supported by the discovery by Agarwal et al.\textsuperscript{23}. Then, the latter explanation for the bimodal \( L \) distribution seems plausible.

The average \( L_{\text{TEM}} \) and \( W_{\text{TEM}} \) values were evaluated to be 152 and 8.84 nm, respectively, from the distribution functions, as shown in Figure 2. The standard deviations of the \( L \) and \( W \) were also calculated to be 34.0 and 2.37 nm, and these values mean the distribution of \( L \) and \( W \) rather sharp. However, it should be noted that TEM images obtained by negative-staining methods sometimes provide slight overestimation in object sizes, especially in the nanometer range similar to the \( W \) values, because of artifacts due to an essential problem for broad adsorption sites for heavy metal cations such as uranyl ions to objects in staining processes. Coagulative aggregation of primary CNC particles in the drying process during specimen preparation is of course another serious problem.\textsuperscript{27}

Rotational and Translational Diffusion. If suspended particles into viscous medium fluids have anisotropic structure such as spindle, rodlike, or rotational ellipsoidal shapes, the rotational diffusion constants of the particles can be determined by the use of depolarized DLS measurements.\textsuperscript{16,24–26} The incident light source is polarized in the vertical, \( v \), direction. Then, the depolarized, \( v_h \), condition is able to be set by placing a polarizing optical device in the horizontal, \( h \), direction in front of a photodetector. According to Berne and Pecora,\textsuperscript{18} the intercept of a plot of the first cumulant (\( \Gamma_v \)) is calculated from the autocorrelation function of scattered light electric field obtained under the depolarized condition \( [g_2^{(v)}(t)] \) converted from the autocorrelation function of scattered light intensity \( [g_2^{(2)}(t)] \) via the relationship \( g_2^{(2)}(t) = [g_2^{(v)}(t) - 1]^{1/2} \), against the square of the magnitude of scattering vector \( (q^2) \) provides the average value of \( D_v \) for anisotropic suspended particles in the manner of \( \Gamma_v |q^2|^{-1} |v| = D_v \) that is, the intercept of \( \Gamma_v \) versus \( q^2 \). On the other hand, the initial slope of the first cumulant under the usual DLS condition (\( \Gamma_h \)) against \( q^2 \) provides the average translational diffusion constant of suspended particles in the manner of \( \Gamma_h |q^2|^{-1} |v| = D_h \) irrespective of the shape of suspended particles. The dependencies of \( \Gamma_h \) and \( \Gamma_v \) on \( q^2 \) are plotted in Figure 3 for aqueous suspensions of the CNC sample at the concentrations of \( c = 1.0 \) and 5.0 g L\(^{-1}\). Although the \( \Gamma_h \) data were relatively scattered because of low scattering intensity under the depolarized condition, the intercept, \( \Gamma_h |q^2|^{-1} |v| \), was able to be evaluated irrespective of the \( c \) values. Then, we might conclude that \( D_h = 2.3 (\pm 0.2) \times 10^{-9} \) s\(^{-1}\) for...
the nanosized CNC particles in the sample. On the other hand, the initial slope between $\Gamma_i^{\text{nu}}$ and $q^2$, which is shown with a thin red solid line in Figure 3, provides the translational diffusion constant, $D_t = 1.0 (\pm 0.1) \times 10^{-11}$ m$^2$ s$^{-1}$. Moreover, it seems that the slope between $\Gamma_i^{\text{nu}}$ and $q^2$ shown with a blue thin broken line is identical to the value of $D_t$. This observation is confirmed theoretically because the relation $\Gamma_i^{\text{nu}} = 6D_t + D_rq^2$ has been derived theoretically.24–28

In the case of the usual DLS condition, the $q^2$ dependence of the $\Gamma_i^{\text{nu}}$ data approached that of $\Gamma_i^{\text{nu}}$ in the high $q^2$ range examined, as shown in Figure 3. If one ignores coupling between rotational and translation motions, the first cumulant, $\Gamma_1^{\text{nu}}$, calculated from the autocorrelation function of the scattered light electric field under the usual DLS condition, $g_1^{\text{nu}}(t)$, can be approximately described as follows

$$\Gamma_1^{\text{nu}} = -\frac{S_0D_rq^2 + S_1(D_q^2 + 6D_t)}{S_0 + S_1}$$

where $S_0$ and $S_1$ mean dynamic structure factors depending on the magnitude of the scattering vector, $q$. Because the value of $S_0$ is much greater than that of $S_1$ at small scattering angles leading to low $q$ value conditions, the relationship $\Gamma_1^{\text{nu}} = D_rq^2$ holds as described above. However, it is expected that the value of $S_1$ increases gradually with increasing $q$ and becomes much greater than that of $S_0$ at higher scattering angles. At the condition satisfying $qL > 3$, where $L$ means the length of rodlike particles, the same relationship $\Gamma_1^{\text{nu}} = D_rq^2 + 6D_t$ as $\Gamma_1^{\text{nu}}$ holds in accordance with Berne and Pecora.27 The fairly good agreement between the $\Gamma_1^{\text{nu}}$ and $\Gamma_1^{\text{nu}}$ data observed at $q^2 > 8 \times 10^{-14}$ m$^{-2}$, as shown in Figure 1, reconfirms that the nanosize CNC particles of the tested sample possess the average values of $D_t = 2.3 (\pm 0.2) \times 10^{-11}$ s$^{-1}$ and $D_r = 1.0 (\pm 0.1) \times 10^{-12}$ m$^2$ s$^{-1}$, respectively, as characteristic transport coefficients in dilute aqueous suspensions.

**Evaluation of Length and Diameter.** Methods to evaluate the length, $L$, and width, $W$, of monodisperse rodlike particles dispersed in a viscous fluid have been established based on theoretical models taking account of the hydrodynamic effect of rodlike particles using numerical calculation methods.17,29,30 Then, the $D_t$ and $D_i$ values can be calculated as functions of $L$ and $W$ in an explicit form. Both of the $D_t$ and $D_i$ values are referred to determine consistent $L$ and $W$ precisely. According to TEM images which have been described in detail in a previous section, the values of $L$ and $W$ for individual primary CNC particles distributed in a range from 100 to 300 and 5 to 10 nm, respectively. Then, the values of $D_t$ and $D_i$ were calculated in the range, as shown in Figure 4, at 25 °C assuming water as a medium fluid. If one assumes a $W$ value ranged from 7 to 8 nm, both of the experimental $D_t$ and $D_i$ values are perfectly reproduced by an identical $L$ value close to 170 nm simultaneously.

Then, the consistent $L_{tr}$ and $W_{tr}$ values, which reasonably satisfy both of the experimental $D_t$ and $D_i$ determined for the CNC sample in this study, are determined to be 170 and 7.6 nm, respectively, and fairly agree with the values of $L_{\text{TEM}}$ and $W_{\text{TEM}}$, as shown in Figure 2. Differences between the values, $L_{tr}$ and $W_{tr}$, and the TEM average ones, $L_{\text{TEM}}$ and $W_{\text{TEM}}$, are calculated to be +21 and $-1.6$ nm, respectively. The reason for the 14% increment found in the $L_{tr}$ from $L_{\text{TEM}}$ should be the presence of the small minor component with its length of $L = 240$ nm. Because the depolarized DLS (DDLS) and DLS...
techniques used in this study provide the weight average $D_w$ and $D_n$ in general, the presence of the minor component of $L = 240$ nm possessing higher weight than the main component of $L = 150$ nm slightly increases the $L_n$ value than the $L_{TEM}$ value, which is simply calculated as the number average. On the other hand, the reason for the substantial decrement of 19% found in the $W_n$ from $W_{TEM}$ is not clear at present. Because the transport quantities, $D_w$ and $D_n$, determined in dilute aqueous suspensions strongly assure a high dispersibility of the examined CNC sample into water, uncontrollable processes in the drying and staining procedure during specimen preparation for TEM observation possibly induce some artifacts increasing the $L_{TEM}$ value, such as coagulation of primary CNC particles and excess smearing. Consequently, we might conclude that CNC particles originated from the examined sample well-disperse in dilute aqueous suspension individually, as shown in Figure 1.

Elazzouzi-Hafraoui et al. reported the so-called cross-sectional plots obtained from small-angle X-ray scattering (SAXS) experiments for aqueous suspensions of some CNC samples. The obtained cross-sectional plot for Avicel, which is a commercial CNC sample, resulted from wood pulp via hydrolysis procedure using hydrochloric acid and is believed to possess size and structural characteristics similar to the CNC sample examined in this study, showing that its cross-sectional radius of gyration is ca. 3.8 nm. This observation strongly reveals that the average width of CNC particles of Avicel in aqueous suspensions is estimated to be ca. 7.6 nm by SAXS techniques, which is identical to the $W_n$ value determined above.

**Viscoelastic Behavior.** Modified DLS measurements were carried to obtain dynamic viscoelastic behavior of aqueous suspensions of the CNC sample including a small amount of monodisperse spherical probe particles possessing the diameter of $d = 300$ nm. When the probe particles are dispersed in pure water, they show Brownian motions caused by thermal agitation, feeling only the water viscosity. However, the probe particles dispersed into a viscoelastic medium would demonstrate other types of Brownian motions feeling the viscoelastic properties of the medium even under the same thermal agitation. The aqueous suspensions of the CNC sample examined in this study were not completely transparent by thermal agitation. The aqueous suspensions of the CNC demonstrate other types of Brownian motions feeling the probe particles dispersed into a viscoelastic medium would be directly related to the $t$ dependence of $g_1^2(t)$, which is simply calculated as the number average. On the other hand, the reason for the substantial decrement of 19% found in the $W_n$ from $W_{TEM}$ is not clear at present. Because the transport quantities, $D_w$ and $D_n$, determined in dilute aqueous suspensions strongly assure a high dispersibility of the examined CNC sample into water, uncontrollable processes in the drying and staining procedure during specimen preparation for TEM observation possibly induce some artifacts increasing the $L_{TEM}$ value, such as coagulation of primary CNC particles and excess smearing. Consequently, we might conclude that CNC particles originated from the examined sample well-disperse in dilute aqueous suspension individually, as shown in Figure 1.

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In the case of the dilute aqueous suspensions of the CNC sample, only one retardation process was enough to describe $J(t) - t^{-1}$ data approximately for each concentration sample examined, as seen in Figure 5. The obtained $J(t)$ curves were able to be converted to complex compliance ($J^* = J' - iJ''$; $i$: imaginary unit, $J'$: storage compliance, and $J''$: loss compliance) via Fourier transformation in general. Then, $J'$ and $J''$ are given as functions of the angular frequency ($\omega$) using the determined retardation parameters, $J_1$ and $\lambda_1$, as

$$J' = \frac{J_1}{1 + \omega^2 \lambda_1^2}, \quad J'' = \frac{J_1 \omega \lambda_1}{1 + \omega^2 \lambda_1^2} + \frac{1}{\eta_0 \omega}$$

Finally, the complex modulus ($G^* = G' + iG''$; $G'$: storage modulus, $G''$: loss modulus) can be calculated employing the relationship $G^* = (J^*)^{-1}$. Figure 6a shows the dependencies of the converted $G'$ and $G''$ on $\omega$ for the aqueous system of the CNC sample at $c = 1.0$, 2.0, and 3.0 g L$^{-1}$. All of the obtained

![Figure 5. Dependence of $J(t) - t^{-1}$ data on time, t, for the aqueous suspensions of the CNC sample at $c = 1.0$, 2.0, and 3.0 g L$^{-1}$ obtained by using DLS viscoelastic measurements. Solid lines imply the fit retardation curves to experimental data with one set of retardation parameters, $J_1$ and $\lambda_1$, for each suspension as 2.3 $\times$ 10$^{-3}$ Pa$^{-1}$ and 1.0 $\times$ 10$^{-4}$ s ($c = 1.0$ g L$^{-1}$), 5.6 $\times$ 10$^{-5}$ Pa$^{-1}$ and 1.0 $\times$ 10$^{-4}$ s ($c = 2.0$ g L$^{-1}$), and 9.0 $\times$ 10$^{-5}$ Pa$^{-1}$ and 1.1 $\times$ 10$^{-4}$ s ($c = 3.0$ g L$^{-1}$), respectively.

$$J(t) = \sum \left\{1 - \exp\left(-\frac{t}{\lambda_j}\right)\right\} + \frac{t}{\eta_0}$$

(3)
viscoelastic spectra, \(G'\) and \(G''\) versus \(\omega\), for the system were well-described with a Maxwell model with a set of relaxation strength \((G)\) and time \((\tau)\) and the high frequency limiting viscosity \((\eta_\infty)\) as given by

\[
G' = \frac{G_0 \tau_0^2}{1 + \omega^2 \tau_0^2}, \quad G'' = \frac{G_0 \tau_0}{1 + \omega^2 \tau_0^2} + \eta_\infty \omega
\]

The concentration, \(c\), dependencies of \(G\), \(\eta_0\) and \(\eta_\infty\) from viscoelastic spectra seen in Figure 6a are shown in Figure 6b. The \(G\) value clearly increases with increasing \(c\) in proportion to \(c\) with the slope of ca 0.2 Pa L g\(^{-1}\), whereas the \(\tau\) seemed to be approaching the constant value of 1.0 \(\times\) 10\(^{-1}\) s with decreasing \(c\). Moreover, the values of \(\eta_0\) and \(\eta_\infty\) slightly increase with increasing \(c\).

Theoretical consideration has been established for a viscoelastic behavior of suspensions of rodlike particles dispersed into viscous media.\(^{33,34}\) The theory for monodisperse particle suspensions predicts the relationship between the relaxation strength \((G)\) and time \((\tau)\) and the high frequency limiting viscosity \((\eta_\infty)\) as given by

\[
G' = \frac{G_0 \tau_0^2}{1 + \omega^2 \tau_0^2}, \quad G'' = \frac{G_0 \tau_0}{1 + \omega^2 \tau_0^2} + \eta_\infty \omega
\]

We consequently might conclude that CNC particles of the examined CNC sample disperse well into water and behave as individually isolated rodlike particles possessing the dimension with \(L \approx 170\) nm and \(W \approx 7.6\) nm also from the viewpoint of viscoelastic behavior of aqueous suspensions of the CNC sample, as clearly demonstrated in the TEM observation described above. The reason why the CNC sample has such a high dispersibility into water should be effective electrostatic repulsive interaction between the CNC particles because of the presence of anionically charged sulfate groups in water, which are introduced on the surface of CNC particles during the hydrolysis reaction using sulfuric acid. It looks similar to the fact that the electrostatic repulsive interaction between sulfate groups effectively prevents from hydrogen bond (re)formation between hydroxy groups on the surface of different CNC particles in the sample. At last, we conclude that the commercial prototype CNC sample examined in this study has morphological characteristics, that is, highly extended rodlike structure with approximately monodisperse length and width of 170 and 7.6 nm, respectively, which would be a promising feature as industrial materials to provide anisotropic mechanical and/or optical properties with low density of carbohydrates.

Mao et al.\(^{18}\) very recently reported that the rotational and translational diffusion coefficients were determined to be \(D_r = 4.0 \times 10^{-13}\) s\(^{-1}\) and \(D_t = 4.4 \times 10^{-12}\) m\(^2\) s\(^{-1}\), respectively, for CNC particles contained in the same sample as examined in this study. Because the reported \(D_t\) value was miscalculated by the authors and the correct value can be calculated to be \(D_t \approx 670\) s\(^{-1}\) from the data shown in the literature,\(^{18}\) their (correct) \(D_t\) and \(D_r\) are substantially smaller than the values determined in this study and give much longer \(L\) values than the \(L_\text{TEM}\) and \(L_w\) as seen in Figure 2a. However, the reason for the observed disagreement between their \(D_t\) and \(D_r\) values and that determined in this study is not clear at present. Because the TEM image of CNC particles shown in the literature\(^{18}\) looks quite similar to that in Figure 1 in this study, the \(D_t\) and \(D_r\) determined in this study seem to be more reliable than their values.
CONCLUSIONS

In this study, transport properties for a CNC sample in the white dry powder shape resulted from chemical pulp via hydrolysis procedure by sulfuric acid, supplied by InnoTech Alberta Inc. as a commercial prototype sample, were determined using dynamic light scattering techniques in aqueous suspensions at room temperature of 25 °C. The obtained average rotational, translational diffusion coefficients and viscoelastic relaxation times for the CNC sample at dilute conditions reveal without contradiction that CNC particles contained in the sample possess almost a monodisperse length and width of 170 and 7.6 nm, respectively. These structural quantities well-correspond to that evaluated TEM images, which demonstrated a vast number of thin needle- or spindle-like shape objects recognized as primary CNC particles, obtained from a highly dilute aqueous suspension of the CNC sample. Then, the CNC particles in the sample keep high dispersibility into water even after the (complete) drying out process necessary as a producing one.

EXPERIMENTAL SECTION

Materials. A CNC sample made from the hardwood chemical pulp sourced from *Populus tremuloides* Michx. was kindly supplied by InnoTech Alberta Inc. (Edmonton) in the shape of white dry powder. Highly deionized water with the specific resistance higher than 1.8 × 10⁸ Ω m, which was generated by a Direct-Q UV3 (Merck Millipore, Darmstadt), was used as a medium to prepare aqueous suspensions of the CNC sample. Poly(styrene) spherical latex particles (PL3) possessing the mean diameter of 300 nm with a sharp narrow distribution was purchased from Sigma-Aldrich Co. LLC (St. Louis) in the shape of an aqueous suspension at the concentration of 10 vol % and was added into aqueous CNC suspension as probe particles to measure viscoelastic behavior using DLS techniques.

The concentration of the CNC sample in aqueous suspension used for TEM observation was ranged from *c* = 0.1 to 0.01 g L⁻¹ and chose a suspension sample at *c* = 0.05 g L⁻¹ as an adequate one for the purpose and also the statistical analysis of the obtained TEM images. Dilute aqueous suspensions of the CNC sample were prepared at concentrations of *c* = 1.0 and 5.0 g L⁻¹ for depolarized and usual DLS measurements to determine *D*<sub>1</sub> and *D*<sub>i</sub> values. These concentrations were much lower than the previously reported critical concentrations for usual CNC samples prepared from chemical pulp to show liquid crystalline phases. The prepared aqueous suspensions were sonicated for longer than 1 min using a usual sonicator bath to disperse CNC particles effectively and were filtrated through a hydrophilic membrane filter with the pore size of 5 μm to remove coarse dust and CNC particle aggregates. The probe PL3 particles were added to aqueous CNC suspensions at a low concentration of 1.5 × 10⁻² g L⁻¹.

Methods. A JEM-1400 Plus transmission electron microscope (JEOL Co. Ltd., Tokyo, Japan) was operated to observe CNC particle specimens at the acceleration voltage of 80 kV. The prepared aqueous suspension of the CNC sample was dropped on lacey film-coated copper grids (SPI Supplies/Structure Probe Inc., West Chester) supported by carbon films. For negative staining, 2% aqueous uranyl acetate solution was dropped on the grid containing CNC particles, and the excess solution was removed using a filter paper followed by air drying.

DLS experiments for *D*<sub>1</sub> and *D*<sub>i</sub> measurements were carried out using an ALV/CGS-3 compact goniometer system equipped with a 7004/UBS correlator (ALV-Laser, Langen) and an Nd:YAG laser (λ = 532 nm) as a light source. Because the incident laser source was vertically polarized, the depolarized and usual measuring conditions were obtained by inserting a horizontally polarizing optical device or not. Then, the usual DLS condition detects all of the scattered light from the vertically polarized incident laser source. Auto correlation functions of scattered light intensities were recorded at 25 °C as functions of time at several scattering angles ranged from 30 to 150°.

DLS experiments for viscoelastic measurements were carried out using a DLS-7000HL DLS photometer (Otsuka Electronics Ltd., Hirakata) equipped with an R9880U-01 photomultiplier tube (Hamamatsu Photonics K.K., Hamamatsu), an LSI correlator (LS Instruments AG, Fribourg), and a He–Ne laser (λ = 632.8 nm) as a light source. All of the measurements were carried out at 25 °C at the fixed scattering angle of 60°.

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Notes
The authors declare no competing financial interest.

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