

DETERMINATION OF LENGTH AND WIDTH OF NANOCELLULOSES FROM THEIR DILUTE DISPERSIONS

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ABSTRACT

Length/width and their distributions of nanocelluloses, prepared from wood pulps with or without chemical pretreatment, are key factors in application to high-strength and light-weight composites, transparent optical films, gas-barrier films, electronic devices, etc. Although microscopy images provide some length/width information, the number of measurable nanocellulose elements is limited. In this paper, three methods to determine nanocellulose lengths and widths are presented. The field-flow-fractionation (FFF) method combined with static light scattering was applied to dilute aqueous TEMPO-oxidized cellulose nanofibril (TOCN) dispersions to obtain average lengths, length distributions, and widths of different TOCNs. Although TOCN elements with lengths >300 nm could not be separated properly according to their lengths by the FFF system, TOCNs with lengths <300 nm were adequately separated, depending on the lengths by the FFF system, and provided length/length distributions and widths, well corresponding to those obtained from microscopy images. Intrinsic viscosities of TOCNs with different lengths and widths were obtained using shear viscosity measurement of dilute aqueous TOCN dispersions. When the obtained intrinsic viscosities $[\eta]$ of TOCN dispersions were compared with aspect ratios p of TOCNs measured from their microscopy images, these two factors had good relationship, when the constant value of TOCN density (ρ) , $\rho[\eta] = 0.15 \times p^{1.9}$ was

used. Compared to length measurement from microscopy images, the viscosity methods provide average lengths of numerous amounts of TOCN elements present in the dispersions. Seven types of nanocelluloses with different average widths and width distributions as well as those with different network structures were prepared via different mechanical and chemical/mechanical processes, and the turbidities of their dilute dispersions were measured. The widths of nanocelluloses were calculated from the respective turbidity plots based on the theory of light scattering for thin and long particles. The turbidity-derived widths of the seven nanocelluloses ranged from 2 to 10 nm, and showed good correlations with the thicknesses of nanocelluloses measured from their microscopy images.

INTRODUCTION

Nanocellulose has attracted increasing attention in the field of materials science such as applications as reinforcing fillers in polymer composites, oxygen-barrier films, electric devices, and heat insulators. The term nanocellulose refers to short cellulose nanocrystals (CNCs) and long cellulose nanofibrils (or cellulose nanofibers: CNFs). Both CNCs and CNFs are characterized by the high strength, high elastic modulus, and low thermal expansion coefficient of the nanoscale elements. For fundamental study, it is particularly important to characterize length/length distribution and width/width distribution of nanocelluloses to produce high-performance nanocellulose-based materials. CNC and CNF are prepared as water dispersions mainly from plant cellulose fibers by mechanical nanofibrillation in water, often including a chemical pretreatment of the cellulose fibers to increase the nanofibrillation efficiency.

The lengths of CNCs are typically 100–150 nm, whereas those of CNFs exceed a micrometer in some cases. Their widths range from dozens of nanometers to a few nanometers. Nanocellulose widths can be estimated using microscopy (e.g., atomic force microscopy (AFM), scanning electron microscopy, or transmission electron microscopy (TEM)), and small-angle X-ray scattering. TEM and AFM, in particular, are often used for width measurements. However, there is no guarantee that the sampled images represent the whole nanocellulose sample.

In this paper, three methods to determine width/width distribution and length/length distribution of nanocelluloses (CNCs and CNFs) with various widths and lengths dispersed in water are reviewed [1–3]. These nanocelluloses dispersed in water were analyzed by the field-flow-fractionation (FFF) combined with static multi-angle laser-light scattering (MALLS), shear viscosity to determine the intrinsic viscosity and the maximum relaxation time, and turbidity.

MATERIALS

Three cellulose samples were used as starting materials to prepare aqueous TOCN and CNC dispersions: cotton linters, softwood bleached kraft pulp, and algal cellulose (*Cladophora* sp.). The TEMPO-oxidized celluloses were prepared from native celluloses by the TEMPO/NaBr/NaClO with 3.8–10 mmol/g NaClO in water at pH 10 or TEMPO/NaClO/NaClO₂ system in water at pH 5 according to a previously reported method [1]. Aqueous TOCN dispersions were prepared by sonication of the TEMPO-oxidized celluloses in water. Aqueous CNC dispersions were prepared from cotton linters, softwood bleached kraft pulp, and algal cellulose by TEMPO-mediated oxidation and subsequent hydrolysis with 2.5 M HCl at 105 °C for 4 h, dialysis, and sonication [1]. The concentrations of CNC and TOCN dispersions were controlled by either dilution with water or evaporation. Softwood powder was prepared from Japanese cypress. The softwood powder and commercial microcrystalline cellulose powder were partially esterified with maleic anhydride. The maleic anhydride-treated samples were mechanically disintegrated in water using a high pressure homogenizer to prepare maleic anhydride-treated lignin-containing CNF and maleic anhydride-treated CNF, respectively [2].

ANALYTICAL METHODS

The lengths of isolated ~200 nanocellulose elements were measured using a TEM (JEOL JEM 2000-EXII). The widths of isolated ~30 nanocellulose elements were measured from their AFM height images (Veeco Nanoscope III operating in the tapping mode, with a Bruker MPP-11100-10 tip). Shear viscosity measurements of dilute CNC and TOCN dispersions were conducted at 25 °C using a rheometer (MCR 302, Anton Paar GmbH). The shear viscosities were measured using a cone-plate jig at a shear rate from 1 to 1000/s. The experimental maximum relaxation time τ_c of the dispersions was determined as the inverse of the critical shear rate or the shear rate at the beginning of shear-thinning. The optical densities, representing the turbidity, of the dispersions were measured using a quartz cell with a 1-cm path length in the wavelength range 250–800 nm using a UV–Vis–NIR spectrophotometer (V-670, JASCO). The dn/dc values of the dispersions were determined using a refractive index detector (Optilab T-rEX, Wyatt Technology) at 685 nm and 25 °C [2]. The FFF/MALLS system consisted of a FFF separation channel (Eclipse AF4, Wyatt Technologies) and MALLS detector (DOWN HELEOS-II, $\lambda = 658$ nm, Wyatt Technologies). Aqueous dispersions of TOCNs and acid-hydrolyzed TOCN in 5mM NaCl were subjected to the FFF/MALLS system using a polyethylene sulfonate membrane at an elution flow rate 1 mL/min, a cross flow rate 0.4 mL/min, and a gradient time of 40 min.

RESULTS AND DISCUSSION

Length determination of TOCNs from their intrinsic viscosities

Nanocelluloses with different lengths and widths were prepared from cotton, wood, and algal celluloses by TEMPO-mediated oxidations with or without dilute acid hydrolysis and 64% sulfuric acid hydrolysis to prepare CNCs [1]. All nanocelluloses were individually dispersed at the nano-element level without agglomeration, which fulfills the necessary conditions for determination of nanocellulose lengths from their intrinsic viscosities. The intrinsic viscosities of the dilute nanocellulose/water dispersions were then obtained through shear viscosity measurements using a viscometer [1]. The original celluloses, their average lengths and widths measured from their TEM images are summarized in Table 1.

The experimental maximum relaxation time (τ_c) of the nanocellulose dispersions was determined by shear viscosity measurement [4,5]. The experimental intrinsic viscosities $[\eta]_e$ were determined by applying their relative viscosity to solvent viscosity according to the Fedors plots given by the following Equation 1:

$$\frac{1}{2(\eta_{rel}^{1/2} - 1)} = \frac{1}{[\eta]_e} \left(\frac{1}{c} - \frac{1}{c_m} \right) \quad (1)$$

where η_{rel} is the relative viscosity, c is the solid concentration and c_m is the maximum packing density [6,7]. The theoretical maximum relaxation time (τ_t) was calculated by applying the average length L and width d values of the

Table 1. Average length and width of nanocellulose samples [1]

Nanocellulose sample	Starting cellulose	Weight-average length (nm)	Weight-average width (nm)
A	Cotton	138	6.1
B	Softwood kraft pulp	168	3.8
C	Algal cellulose	1105	14.4
D	Softwood kraft pulp	267	2.6
E	Softwood kraft pulp	333	2.6
F	Softwood kraft pulp	551	2.6
G	Softwood kraft pulp	977	2.6

nanocellulose elements to the following Equation 2 for rotational motions of rigid rod-like polymers in dilute region [8].

$$\tau_t = \frac{1}{6D_r} = \frac{\pi\eta_s L^3}{18k_B T \left[\ln\left(\frac{L}{d}\right) - \gamma \right]} \quad (2)$$

where D_r is the rotational diffusion constant, T is the absolute temperature, η_s is the solvent viscosity and k_B is the Boltzmann constant. The value γ is derived from the hydrodynamic interaction assuming rotational motions of rigid rods in dilute region and defined as the following Equation 3.

$$\gamma = 1.57 - 7 \left(\frac{1}{\ln\left(\frac{L}{R}\right)} - 0.28 \right)^2 \quad (3)$$

The theoretical intrinsic viscosity $[\eta]_e$ was calculated by applying L and d values of a nanocellulose to the following Equation 4 for rotational motions of rigid rods in dilute region [4, 8]:

$$[\eta]_t = \frac{2\pi L^3}{45 \left(\ln\left(\frac{L}{d}\right) - \gamma \right)} \frac{1}{\rho \pi R^2 L} \quad (4)$$

where ρ is the density of the nanocellulose fibril (1.6 g/cm³), and R is the radius ($d/2$). The volume of rod ($\pi R^2 L$) is taken into account, which is a significant difference from Equation 2.

To take the flexibility of the nanocellulose into account for the intrinsic viscosity [9–12], the $[\eta]_e$ values were plotted as a function of their aspect ratio p (Figure 1). The $[\eta]_e$ values are exponentially proportional to the p values, and the linear relationship in the log-log plot Equation 5 was obtained:

$$\rho[\eta]_e = 0.15 \times p^{1.9} \quad (5)$$

where the density ρ of fibril was involved for making the intrinsic viscosity $[\eta]_e$ dimensionless. In this empirical equation, the flexibility of nanocellulose fibrils should correspond to the exponent 1.9, considering the following general Equation 6 of intrinsic viscosity $[\eta]$ for polymer solutions:

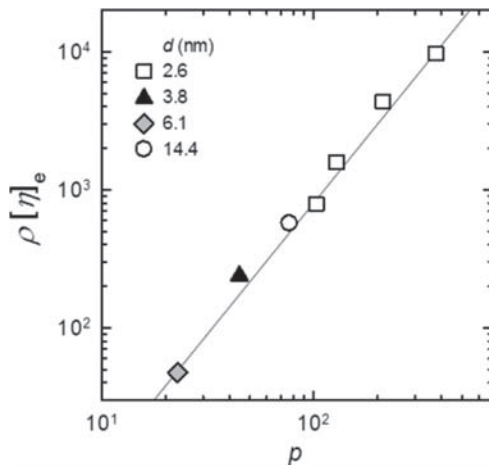


Figure 1. Intrinsic viscosity $[\eta]_e$ of the nanocellulose dispersions as a function of aspect ratio p . ρ is the density of the nanocellulose: 1.5 g/cm³ [1].

$$[\eta] = KM^a \quad (6)$$

where M is the molecular weight, K is a constant, and a is a parameter that reflects chain expansion. This is well-known as the Mark–Houwink–Sakurada equation. The exponent a for semi-flexible polymers appears to be greater than 1.2, and asymptotically approaches 2 with increasing rigidity of the polymers [13].

Compared to length measurement from TEM images, the viscosity methods provide average lengths of numerous amounts of nanocellulose elements present in the dispersions. Thus, the average lengths of nanocelluloses, including cellulose nanocrystals with small aspect ratios and TOCNs with large aspect ratios, can be simply determined using this empirical equation by measuring the $[\eta]$ values of their dispersions.

There are some challenges in the length determination method of nanocelluloses using the intrinsic viscosities of their aqueous dispersions. Although the length distribution of nanocelluloses is large, only one average length is obtained for each nanocellulose by this method. An advanced and reliable method to determine length distribution of nanocelluloses should be, therefore, developed for further scientific investigation and applications of nanocelluloses. Most nanocelluloses, prepared from celluloses simply by mechanical disintegration in water without any chemical pretreatment, have more complicated network structures with heterogeneous widths. The average lengths of these nanocelluloses cannot be determined by the simple shear viscosity method.

Width determination of various nanocelluloses from their turbidities

Nanocellulose widths can be estimated using microscopy such as AFM, TEM and small-angle X-ray scattering. The widths of various nanocelluloses not only consisting of individually dispersed elements but also forming network structures in water were prepared and estimated based on their water dispersion turbidities [2]. The results were compared with the AFM-derived thicknesses of individual nanocellulose elements. The cross sections of the nanocelluloses were assumed to be square. Seven types of nanocelluloses with different average widths and width distributions were prepared from various cellulose resources through different processes (Table 2), and their turbidities of dilute dispersions were measured according to Equation 7 [14–17]:

$$\tau = \left(\frac{88\pi^3 nc}{15\lambda^3 N} \right) \left(\frac{dn}{dc} \right)^2 \mu \tag{7}$$

where λ is wavelength (cm), N is Avogadro’s number, n is the refractive index of the dispersing medium, and c and dn/dc are the concentration (g/mL) and specific refractive index increment (mL/g) of the dispersions, respectively. The mass-length ratio μ of a nanocellulose is described using its width d (nm) as $\mu = 9.85 \times 10^9 \times d^2$, assuming that the nanocellulose elements are individual cellulose crystallites, irrespective of the dimensions and surface chemical compositions of the elements.

Table 2. AFM-measured thicknesses and turbidity-derived widths of nanocelluloses and refractive index increments (dn/dc) of the dispersions [2]

<i>Nanocellulose sample</i>		<i>Thickness by AFM (nm)</i>		<i>Width from turbidity (nm)</i>	<i>dn/dc (mL/g)</i>
		<i>Arithmetic mean</i>	<i>Cross-section weighted mean</i>		
H	Cellulose nanocrystal	3.5	5.5	3.8	0.17
I	Cellulose nanocrystal	4.5	5.9	3.3	0.15
J	TOCN	2.0	2.4	2.7	0.15
K	TOCN	2.2	2.7	2.0	0.16
L	TOCN	2.9	3.4	2.1	0.15
M	Ligno-nanocellulose (L-CNF)	3.7	6.6	10.9	0.17
N	Nanocellulose (CNF)	6.4	9.5	10.5	0.16

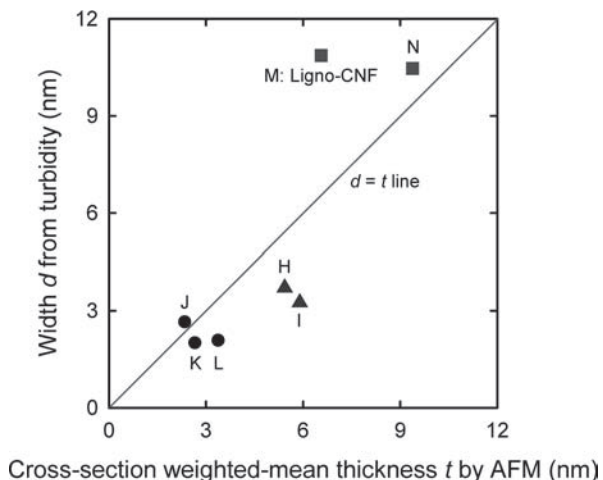


Figure 2. Relationship between turbidity-derived widths d and cross-section-weighted mean thicknesses t measured using AFM. A-G correspond to those in Table 2 [2].

The widths of nanocelluloses were calculated from the respective turbidity plots based on the theory of light scattering for thin and long elements [2]. The turbidity-derived widths of the nanocelluloses ranged from 2 to 10 nm, and showed good correlations with the thicknesses of nanocelluloses measured from their AFM images (Figure 2). Ligno-CNF (M in Table 2) was clearly out of line, with the turbidity giving a higher estimate than that obtained using AFM. The wavelengths used in the calculations for this sample were longer than those used for the other samples, probably because of the UV absorbance tail of lignin overlapping the short wavelengths. Moreover, the AFM-measured thickness t of ligno-CNF can be underestimated because of its heterogeneous and locally flat cross-sections.

As a consequence, a fast and robust method for estimating the widths of nanocelluloses from the turbidities of their water dispersions has been established. The widths of seven nanocelluloses with different widths, lengths, chemical compositions, and network structures were calculated from turbidity plots using Equation 7. The calculated width values of the nanocelluloses showed good correlations with the AFM-measured thicknesses except the lignin-containing nanocellulose.

Field-flow-fractionation/multi-angle light scattering analysis

The FFF/MALLS was applied to dilute aqueous TOCN dispersions to obtain average lengths, length distributions, and widths of TOCNs. TOCNs with different

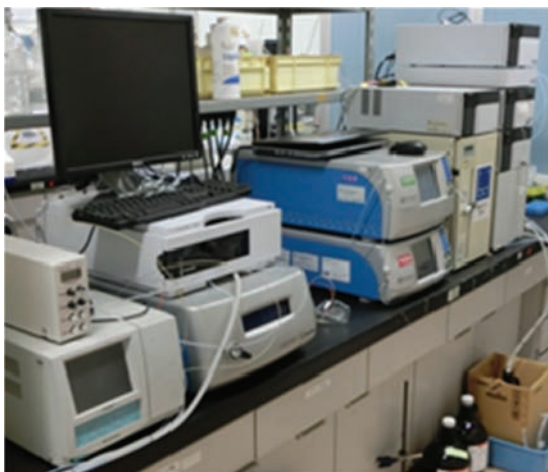


Figure 3. FFF-MALLS system.

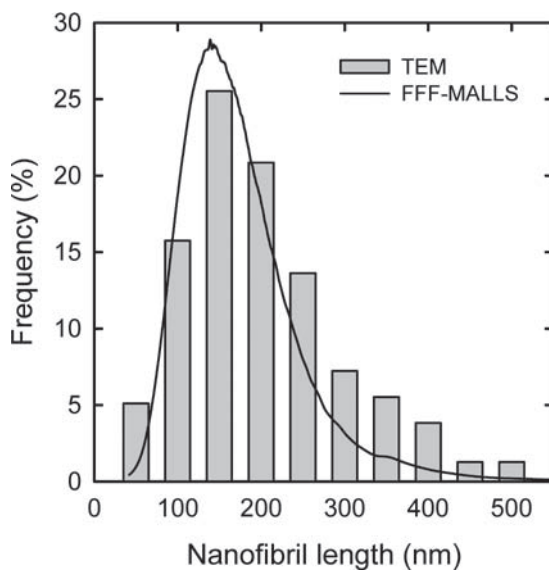


Figure 4. Length distribution of TOCN with number average length of 208 nm.

lengths and widths were prepared by controlling oxidation conditions with different amounts of NaClO and acid hydrolysis of once-prepared TOCN from softwood bleached kraft pulp. The FFF/MALLS system used is shown in Figure 3.

The experimental conditions to obtain reliable data were studied in terms of eluents with different salt concentrations, flow rates, cross-flow rates, gradient times, filters, and injection volumes. As a result, although TOCN elements with lengths >300 nm could not be separated properly according to their lengths by the FFF system, TOCNs with lengths <300 nm were adequately separated, depending on the lengths by the FFF system, and provided length/length distributions and widths, well corresponding to those obtained from TEM images (Figure 4). Moreover, dilute acid hydrolysis of TOCNs caused a binding of two or more TOCN elements parallel to the longitudinal direction probably because of partial removal of the surface carboxy-rich molecules on TOCNs, resulting in an increase in the average width from ~3 nm to ~6 nm.

CONCLUSION

The influence of the flexibility and dimensions of nanocelluloses on the flow properties of their dilute dispersions was investigated by experimental and theoretical approaches using various nanocelluloses. The maximum relaxation time τ of the nanocellulose dispersions was strongly influenced by their dimensions, such as widths and length distributions. When the $[\eta]$ values were plotted against aspect ratio p of the nanocelluloses to take into account the flexibility, the relationship between $[\eta]$ and p values was $\rho[\eta] = 0.15 \times p^{1.9}$ irrespective of the flexibility and dimensions of the nanocelluloses. Thus, the average lengths of nanocelluloses can be simply determined using this empirical equation by measuring the $[\eta]$ values of their dispersions. On the other hand, we developed a fast and robust method for estimating the widths of nanocelluloses from the turbidities τ of their water dispersions. The calculated width values of the nanocelluloses showed good correlations with the AFM-measured thicknesses.

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Transcription of Discussion

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Daniel Söderberg KTH Royal Institute of Technology

Thank you for a very interesting presentation and I think that your idea that 20 years from now we will be able to characterize nanocellulose properly, is not only good for research but also for industrial applications. I have a question regarding your exponent 1.9 and, before asking the question, I have two checks. What is the concentration when you do the measurement of viscosity?

Akira Isogai The University of Tokyo

You have to use the concentrations lower than the critical point each CNF, from which network formation of nanocellulose elements starts in water. Therefore, before measuring the intrinsic viscosities, you have to measure the viscosities to see the concentrations are lower than the critical point, which depends on the length of CNFs. The CNF with longer length has to be diluted much more. In the case of CNCs with shorter lengths, higher concentrations are available. Again, the intrinsic viscosity should be measured at concentrations below the critical point.

Daniel Söderberg

And when you have the upper right side, we have different lengths. Are there different charts from this?

Discussion

Akira Isogai

These upper-right four samples are the same TEMPO-CNFs with different lengths. The acid-hydrolysed samples have different positions, because they have carboxyl contents different from TEMPO-CNFs. However, because all samples can be plotted on the same line, the different surface charges have no influence on the plot as long as the samples are individually dispersed without agglomeration. When samples have low charges, they sometimes form aggregates. When nanocelluloses form aggregates in water, this equation cannot be applied to the nanocellulose dispersions. However, this equation was obtained empirically based on the obtained results. I cannot explain the meaning of the values of the front factor 0.15 and the number power of 1.9. I hope that someone can consider this empirical equation from theoretical point. I am not so familiar with such theoretical approach, and again I hope that someone would figure out the meanings of the values of 1.9 and 0.15 in the equation some day in future.

Daniel Söderberg

Maybe it's 2.0. You could expect if you look at sort of the basic of interaction between fibres.

Akira Isogai

Yes. But it's not readily available to the equation because nanocelluloses are new materials, and so far no such nanofibre models have been investigated from theoretical points. I hope you do manage to figure out this equation.

Jonathan Phipps FiberLean Technology

Could you explain how you derived the length of the fibres from the MALLS data? Did you use the same algorithms and assumptions that you would for a polymer solution or did you use a different analysis?

Akira Isogai

As long as using the accurate DN/DC values of nanocellulose/water dispersions, the same analytical procedure of MALLS is applicable to nanocelluloses in the Field-Flow-Fractionation analysis. In this study, we used nanocelluloses with different lengths or widths, which were controlled by controlling the TEMPO-oxidation conditions or the following sonication conditions. When you extend the sonication time, the lengths of nanocelluloses become smaller and smaller. When

you apply a smaller amount of NaClO in TEMPO-oxidation, you would have nanocelluloses with longer lengths. Of course, in this case, a relatively large amount of unfibrillated fraction, which can be removed from the dispersion by centrifugation, is formed.

Jonathan Phipps

Did you obtain the length data directly from the light scattering or did you have to use a fitting procedure?

Akira Isogai

We obtained the length data directly from MALLS data using the software attached the MALLS system.

Kit Dodson School of Materials, University of Manchester

Could we go back to the slide which you showed before, I believe it was number 23. Just looking at these distributions and the variety of them, I would suggest that they are very close to gamma distributions and if you plot the standard deviation against the mean, you will find a straight line and the slope of that will give you a pretty good measure of the distribution given the mean length. I have a question also relating to where the viscosity was found to be proportional to what would be the mean length. How does that fit with the data that you have found? Is there a conflict with this empirical equation in some way? I could not see easily how to make the two results correspond?

Akira Isogai

Thank you for your suggestion. I would consider the length distributions in terms of gamma distributions. We fortunately had a good empirical relationship between the mean length of nanocelluloses and intrinsic viscosity of the nanocellulose/water dispersions. The traditional Doi-Edward equation applicable to polymer solutions was not applicable to nanocellulose/water dispersions. Because the equation was obtained empirically, we do not know why the mean length of nanocelluloses can be expressed as a factor of their intrinsic viscosities. We have to accumulate much more data.

Kit Dodson

Are the diameters constant?

Discussion

Akira Isogai

These TEMPO-CNFs have the constant widths of ~ 3 nm. However, the acid-hydrolyzed CNFs have much larger widths, and especially this acid-hydrolyzed algal cellulose CNC had the largest width of ~ 14.4 nm.

Kit Dodson

Well, if the diameters differ very much, then it is quite likely that the mechanisms giving rise to the viscosity will alter. You reflected that in your pictures, where you have bendy ones at the top.

Akira Isogai

In the case of these samples used in this study, we had a good relationship between the aspect ratio of CNFs and intrinsic viscosity of the CNF/water dispersions, irrespective of their different widths. However, the relationship was obtained as preliminary data. We have to use many more samples to see whether the equation is applicable to most of the nanocelluloses.

Gil Garnier Monash University

Thank you for an excellent and authoritative presentation. I would like to continue on the question of Professor Dodson. Can you give us a good strategy to obtain long nanofibres all of the same narrow diameter distribution?

Akira Isogai

In the case of TEMPO-CNFs prepared from plant celluloses, they have almost the same widths of ~ 3 nm, and only lengths and length distributions are variables. As long as the TEMPO-CNFs were used, the equation is applicable irrespective of the large or small length distributions. However, we have to accumulate much more data.

Gil Garnier

Would there be a benefit in going to a higher DS than 1?

Akira Isogai

No, I don't think so because if you use a large amount of chemicals like sodium hypochlorite in TEMPO-oxidation, remarkable depolymerization is unavoidable,

resulting in low CNF yields and short CNF lengths. Therefore, the TEMPO-oxidation conditions should be carefully controlled to introduce carboxyl groups just on the surface of crystalline cellulose microfibril surfaces.

Gil Garnier

Here, basically, the way we understand it, is that we rely on the TEMPO oxidation of cellulose to increase the electrostatic repulsion between carboxyl groups, which facilitates nanocellulose chain fibrillation upon shear/mechanical action. Would it be interesting to combine TEMPO with the addition of a surfactant to decrease the friction or to combine with some esterification of cellulose with long alkyl chains to facilitate individual cellulose chain fibrillation/release?

Akira Isogai

I am not sure. Usually we use TEMPO-CNFs with maximum carboxyl content to get completely nanofibrillated cellulose/water dispersions. In the case of wood cellulose, the carboxyl content >1 mmol/g is required to prepare completely nano-dispersed TEMPO-CNF/water dispersions. As Dr Konno of Nippon Paper presented this afternoon, general carboxyl contents of TEMPO-CNFs are ~ 1.5 mmol/g, which give high nanofibrillation yields.