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Highlights

- Determination of complex refractive index of CNCs as a function of wavelength
- The data analysis is based on Beer-Lambert and immersion liquid method equations
- The refractive indexes of CNCs are considerably lower than original cellulose
- The method is independent of the shape or size of a particle
- The accuracy of the refractive index was better than ±0.005 refractive index units

Determining the complex refractive index of cellulose nanocrystals by combination of Beer-Lambert and immersion matching methods

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Abstract

Nanocelluloses have received significant interest due to their unique structural, mechanical, and optical properties. Nanocellulose refractive indices can be used to indicate many crucial characteristics, such as crystallinity, transparency, and purity. Thus, accurate measurement is important. This study describes a new method to determine the wavelength dependent complex refractive index of cellulose nanocrystals (CNCs) by the measurement of light transmittance with a spectrophotometer. The data analysis is based on a combination of the Beer-Lambert and immersion liquid matching equations. The immersion liquid method's main advantage is that it is independent of particle shape and size. Moreover, the measurement is easy and relatively quick to perform. The present procedure is not restricted to the nanocellulose and could potentially be applied to other nanomaterials, such as hyphenate nanoparticle-based, lignin nanoparticles,

nanopigments, biological entities, structural elements of dielectric metamaterials, and nanoparticle-based composites.

Keywords: Cellulose nanocrystals, complex refractive index, Beer-Lambert, immersion matching method, spectroscopy

1. Introduction

Recently, several new biorefinery concepts have been established to produce cellulose nanomaterials at a larger-scale. In 2015, cellulose nanofibrils (CNFs) and CNCs were produced at 5000 and 1800 kg/day, respectively [1]. A set of methodologies, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and dynamic light scattering (DLS) have typically been used for analysis of the features of nanocelluloses [2]. However, effective imaging, characterisation, and fundamental measurement techniques for process control and characterisation of nanocelluloses are still needed [3]. Refractive index is one of a number of potential parameters that can be applied to inspect the nanocellulose quality. Refractive index measurements are widely applied to process control techniques used to verify raw materials and monitor industrial processes. It is also an important parameter for the detection of material concentration, purity, chemical identification of species, density, and even temperature of a liquid [4]. However, it is difficult to measure the refractive index of nanoparticles precisely with current techniques [5]. In general, the refractive index is not only related to the chemical composition, crystal structure, and symmetry of each particle, but it is also affected by the temperature, wavelength of incident light, and internal stresses in the sample [6].

The refractive index of nanoparticles has been investigated using several techniques. Ellipsometry has been used to measure the refractive index of polymer and TiO_2 nanoparticles; it is based on the change in the polarisation state of light reflected from the surface of a sample [7,8]. Interferometry has been used to determine the refractive index of biotic nanoparticles [9]. Both

methods are accurate (0.0001 to 0.00001 refractive index unit), but they are expensive and require samples with very smooth surfaces [10].

Dynamic holography techniques have been used to measure the refractive index of carbon nanoparticles [11]. In-line holographic microscopy techniques have been used for silica nanoparticles with a resolution of 0.002 refractive index unit [12]. Nanoparticle tracking analysis (NTA) is a relatively new technique for determining the refractive index of suspended nanoparticles based on the rate of their Brownian motion [13,14]. Its resolution is 0.021-0.046 refractive index unit. NTA currently works best for particles with diameters between 10 nm and 1000 nm. The lower detection limit depends on the refractive index of the nanoparticles; characterisation is only possible for nanoparticles composed of materials with a high refractive index, such as gold or silver. The upper detection limit is due to the limited Brownian motion of large nanoparticles and is also related to the viscosity and temperature of the liquid [15,16].

Surface plasmon resonance (SPR) has been used to determine the refractive index of nano-size calcium fluoride [17]. The major advantages of a localised SPR sensor compared to other techniques are the sensitivity and the small sample volume (~6 attoliters), while time-consuming measurements are a disadvantage. SPR has achieved an accuracy better than a 0.002 refractive index unit. The critical-angle method has long been applied to Abbe refractometer measurements. The advantages include easy experimental implementation and simple calibration [18]. The critical-angle method is precise to about ±0.002 refractive index units. The disadvantage of this method is that it cannot be applied to a sample with a refractive index greater than the base material upon which it is placed. Moreover, to measure the sample index at other wavelengths, the dispersion of the base or second material must be known [19,20].

The morphology and dimensions of CNCs can be described as elongated rod-like (or needle-like) particles in a nearly perfect crystalline structure. CNCs originating from wood and acid hydrolysis have a typical diameter of 2-5 nm and a length of 100 nm-300 nm [21]. Previously, the

refractive index of nanocellulose was not reported as a function of wavelength in the literature, and values from 1.470 [22] to 1.618 [23] can only be found at a single wavelength of 589 nm. The different refractive indices of cellulose are typically attributed to differences in the degree of crystallinity, birefringence (extraordinary and ordinary refractive index), state of purity, source and measurement temperature, and therefore, can also be used as a quality parameter.

Nanocellulose-based materials have been applied in many different fields. Depending on the application, the utility desired of optical properties may vary, however, it is equally important to understand how nanocellulose behaves as an optical medium. Thus, the determination of refractive index as a function of wavelength is an important task. For example, controlling the refractive index of nanocellulose plays a significant role in nano-photonics and bio-photonic applications. In addition, refractive index values are required when calculating the dimension of nanocrystals, for example, by Mie theory or Rayleigh approximation equations.

The aim of this study is to report a method for determining the wavelength dependent complex refractive index of cellulose nanocrystals by a measurement of light transmittance with a spectrophotometer based on Beer-Lambert and immersion matching methods. The immersion matching method relies on the refractive index match between solid particles and the immersion liquid. In this case, transmission through the suspension reaches a maximum as scattering intensity approaches zero [24]. This combined Beer-Lambert liquid immersion method allows the complex refractive index of a nanocellulose to be determined as a function of wavelength relatively quickly and easily by a common a UV-Vis spectrophotometer. The present method is not restricted to the case of nanocellulose and may be applicable across a broad range of applications, such as assessment of the optical properties of nanopigments, biological entities, structural elements of dielectric metamaterials, and nanoparticle-based composites.

2. Experiment

2.1 Preparation of CNC Samples

Cellulose nanocrystals (Blue Goose Biorefineries [BGB] Ultra) were obtained from Blue Goose Biorefineries Inc. (Canada). Acetate-grade dissolving pulp (western hemlock) was used as a raw material. The CNC production process is based on oxidation and does not involve acid hydrolysis. The samples for visualisation of CNC with TEM were prepared by dropping the diluted nanocellulose suspension on a carbon-coated and polylysine-treated copper grid. Filter paper was used to remove excess sample from the edge of the grid. Uranyl acetate (2% w/v) was used in the negative staining of the samples. The TEM images were captured with a Quemesa CCD camera (Japan), using 100 kV as an accelerating voltage. The crystalline structure of nanocrystals was measured using X-ray diffraction with a Rigaku SmartLab 9 kW rotating anode diffractometer (Japan) and determined using the Segal method [25].

As a pre-treatment, crystals were freeze-dried and pressed into tablets of 1 mm thickness. In measurements, a Co Kα radiation source was used (40 kV, 135 mA) (λ = 0.179030), and scans were taken over a 2θ (Bragg angle) range from 5° to 50°, at a scanning speed of 10°/min by a step of 0.05°. The degree of crystallinity was calculated from the peak intensity of the main crystalline plane (200) diffraction (I_{200}) at 26.1° and from the peak intensity at 22.0°, associating the amorphous fraction of crystals (I_{am}). The degree of crystallinity in terms of crystallinity index (*CrI*) is calculated by Equation (1).

$$CrI = (l_{200} - l_{am})/l_{200} \times 100\% \quad (1)$$

Figure 1 shows a TEM image of nanocellulose crystals used in this experiment (1a) and their corresponding X-ray diffraction pattern (1b). According to TEM images, the rod-like individual nanocellulose crystals had an average width of 5 nm and a length of 100 nm-200 nm. The CrI of the crystals was 70%, and from the X-ray diffraction pattern (Fig. 1b), it can be seen that CNC has kept its cellulose I crystalline structure. Depending on the bleaching method, western

hemlock fibres have a degree of crystallinity of 53%-59% [26]. The oxidation of fibres in the production of cellulose nanocrystals degrades hemicelluloses and amorphous parts of cellulose, increasing the degree of crystallinity. The cellulose nanocrystal suspension (1 wt. %) was dried into a thin film at room temperature, with a thickness (d) of 9.6 μm ±2.8 μm (Mach Millitast 1083, resolution of 1 μm).

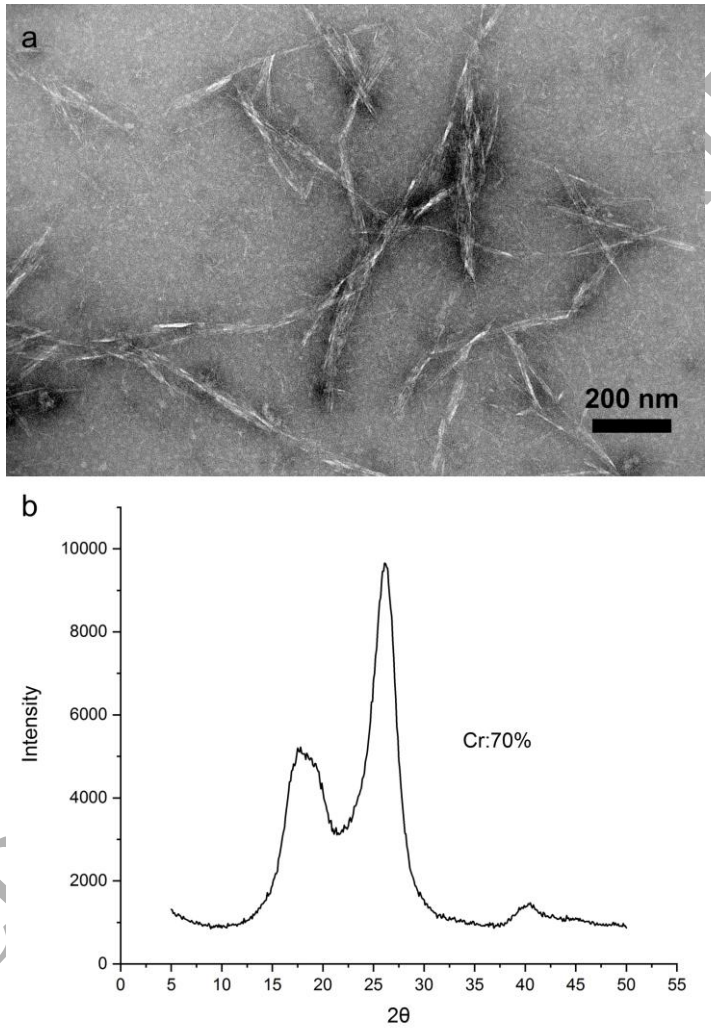

Figure 1. The TEM image (a) and X-ray diffraction pattern (b) of the cellulose nanocrystals, CNC.

The immersion measurement was conducted from a powdered cellulose nanocrystal film. After grinding, the average particle size of the CNC was 286 nm [two peaks: 313 nm (89%) and 68 nm (11%)] as measured by a commercial Malvern Zatasizer Nano ZSP, with an average accuracy of ±0.3 nm. This image is presented in Figure 2.

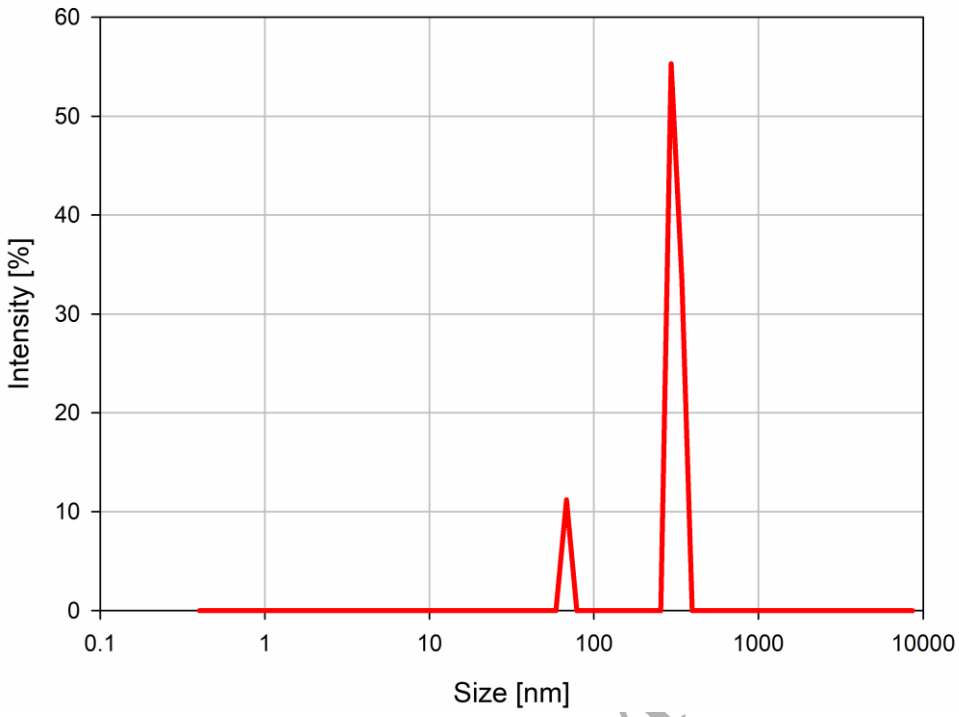

Figure 2. The CNC size analysis by Malvern Zatasizer Nano ZSP.

In this study, the cellulose nanocrystal powder was suspended in acetone (VWR Chemicals) and immersion oil (Type A Cargille) mixtures. The wavelength dependent refractive index of acetone and immersion oil were obtained from the literature [27,28,29]. The idea of the immersion method is to prepare immersion liquid pairs with refractive indices higher and lower than the refractive index of the CNC being studied, whereby, the inflection point of transmission can be determined. The inflection point of transmission is crucial because for that particular wavelength and that particular liquid mixture, maximum light transmittance of the suspension is achieved.

For such a purpose in this study, we chose six acetone-immersion mixtures [acetone/immersion oil ratios: 0% (0 ml and 1.750 ml), 4.2% (0.072 ml and 1.750 ml), 8.7% (0.154 ml and 1.750 ml), 13.9% (0.244 ml and 1.750 ml,), 19.8% (0.345 and 1.750 ml), and 26.3% (0.461

ml and 1.750 ml)], which had the refractive indices of 1.515, 1.507, 1.499, 1.492, 1.484, and 1.476, respectively, at the wavelength of 589 nm and at 22^{o} C. The pairs of immersion liquids were prepared by weighing each liquid component on a laboratory balance (Mettler Toledo AG204, accuracy of +/- 0.1 mg), using density data to determine the volume of the components. The density of immersion oil and acetone were obtained from the producers, and at room temperature, they are 0.928 g/ml and 0.790 g/ml, respectively. The concentration of CNC was 1.2 wt. % in each immersion liquid pair.

2.2 Complex Refractive Index

The optical properties of any material may be described by the complex refractive index,

$$N(\lambda) = n(\lambda) - ik(\lambda), \quad (2)$$

where λ is the wavelength, i is unit imaginary number, k is the extinction coefficient, and n is the real refractive index. The refractive index is determined by the phase velocity of the light propagating through the homogeneous medium [30].

2.2.1 Calculation of the Imaginary Portion of the Complex Refractive Index

The absorption coefficient can be calculated using the Beer-Lambert law:

$$\alpha(\lambda) = -ln(I/I_0)/d = -\ln(T)/d = A/d \quad (3)$$

where I_o is the initial light intensity, I is the light intensity after it passes through the sample, d is the thickness of the medium, T is transmission, and A is absorbance [31]. The imaginary portion of the complex refractive index, k, is the extinction coefficient, which gives the attenuation of light as a function of wavelength as it passes through the medium. The absorption coefficient is related to the extinction coefficient by the following formula:

$$k(\lambda) = \frac{\lambda\alpha(\lambda)}{4\pi} \quad (4)$$

2.2.2 Calculation of the Real Portion of the Complex Refractive Index

The definition of the real portion of the complex refractive index, *n*, of the immersion liquid is based on measurement of the volumes V_a and V_b of two liquids, *a* and *b*, with measurements of the refractive indices n_a and n_b and the use of the formula [32].

$$n(\lambda) = \frac{V_a n_a(\lambda) + V_b n_b(\lambda)}{V_a + V_b}. \quad (5)$$

The accuracy of the assessment of the refractive index of the particle from the transmission signal (*T*) can be improved using, for example, the Lorentzian-fitting procedure, which is assumed to hold for particles that have a Lorentzian size distribution:

$$T = y_0 + \frac{a}{1 + \left(\frac{(n_{liquid} - n_{cellulose})}{b}\right)^2}, \quad (6)$$

where y_o is a baseline, *a* is an amplitude, and *b* is related to the width of the normal distribution at the half maximum.

3. Results and Discussion

3.1 The Imaginary Portion of Complex Refractive Index

The transmission spectra (400 nm-700 nm) were measured at 1 nm intervals from cellulose nanocrystal film (9.6 μm) using a Simadzu UV-1800 spectrophotometer at room temperature (22° C). Reporting absorbance to ±0.004 is quite a large uncertainty if *n* and *k* are reported to ±0.001. Thus, the absorbance and extinction coefficient of the cellulose nanocrystal film were calculated

from measured data using Equations 3 and 4, respectively. The absorbance spectrum of the CNC is shown in Figure 3. Figure 5 shows the calculated results for the imaginary component of the complex refractive index of CNC. The imaginary portion of the complex refractive index was k = 0.0019 at 400 nm and k = 0.002 at 700 nm, without major wavelength dependence. Bergström et al. [33] determined the extinction coefficient of cellulose at wavelength 466 nm, 633 nm, and 763 nm, which resulted in values of 0, 0, and 0.005, respectively. Generally, extinction coefficients below 0.001 were considered negligible. Low values of the imaginary component of the complex refractive index correspond to high optical transparency. The scattering intensity depends upon, among other things, the real refractive index difference between nanocellulose and the surrounding medium.

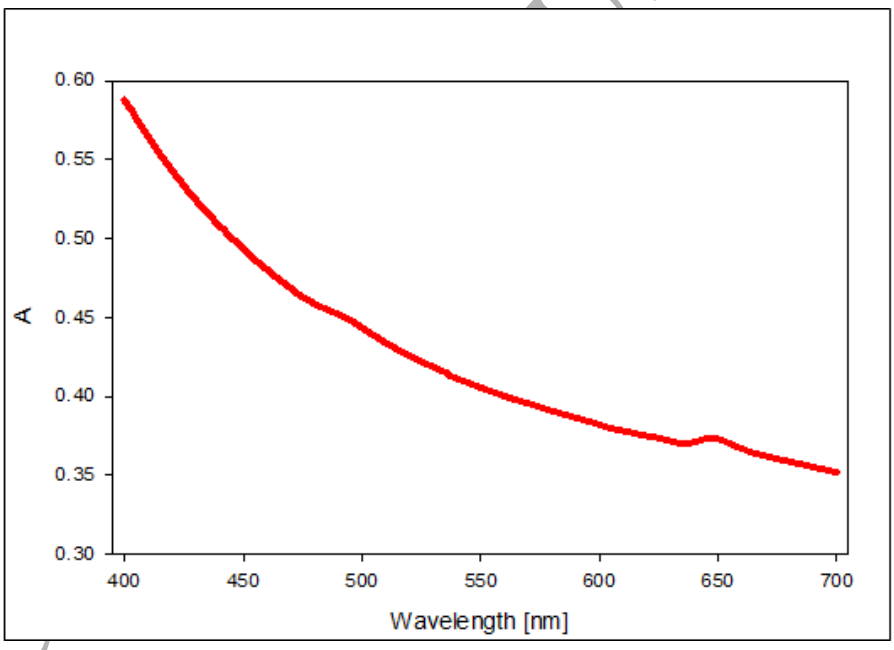

Figure 3. Absorbance results for CNC as a function of wavelength.

3.2 The Real Portion of the Complex Refractive Index

The motivation for this study was to determine the refractive index of CNC as a function of wavelength. This information is valuable for calculating the optical properties of that material. Transmittance intensity of CNC suspended in the acetone-immersion oil mixtures were done in the same standard 10 mm UV fused quartz cuvette with lid. The transmission spectra (400 nm-700 nm)

of the suspensions were determined at a regulated constant room temperature using the Shimadzu UV-1800 spectrophotometer (the baseline was measured with deionised water). In Figure 4(a), the obtained transmittance curves of CNC are presented as three-dimensional plots, both as a function of the wavelength and the refractive index of the six immersion liquid mixtures. In Figure 4(b), the transmittance is shown for a single fixed wavelength of 590 nm.

We observe in Figure 4 that the acetone-immersion mixture of 8.78% gives the highest transmittance values (inflection point) as a function of wavelength for the CNC sample.

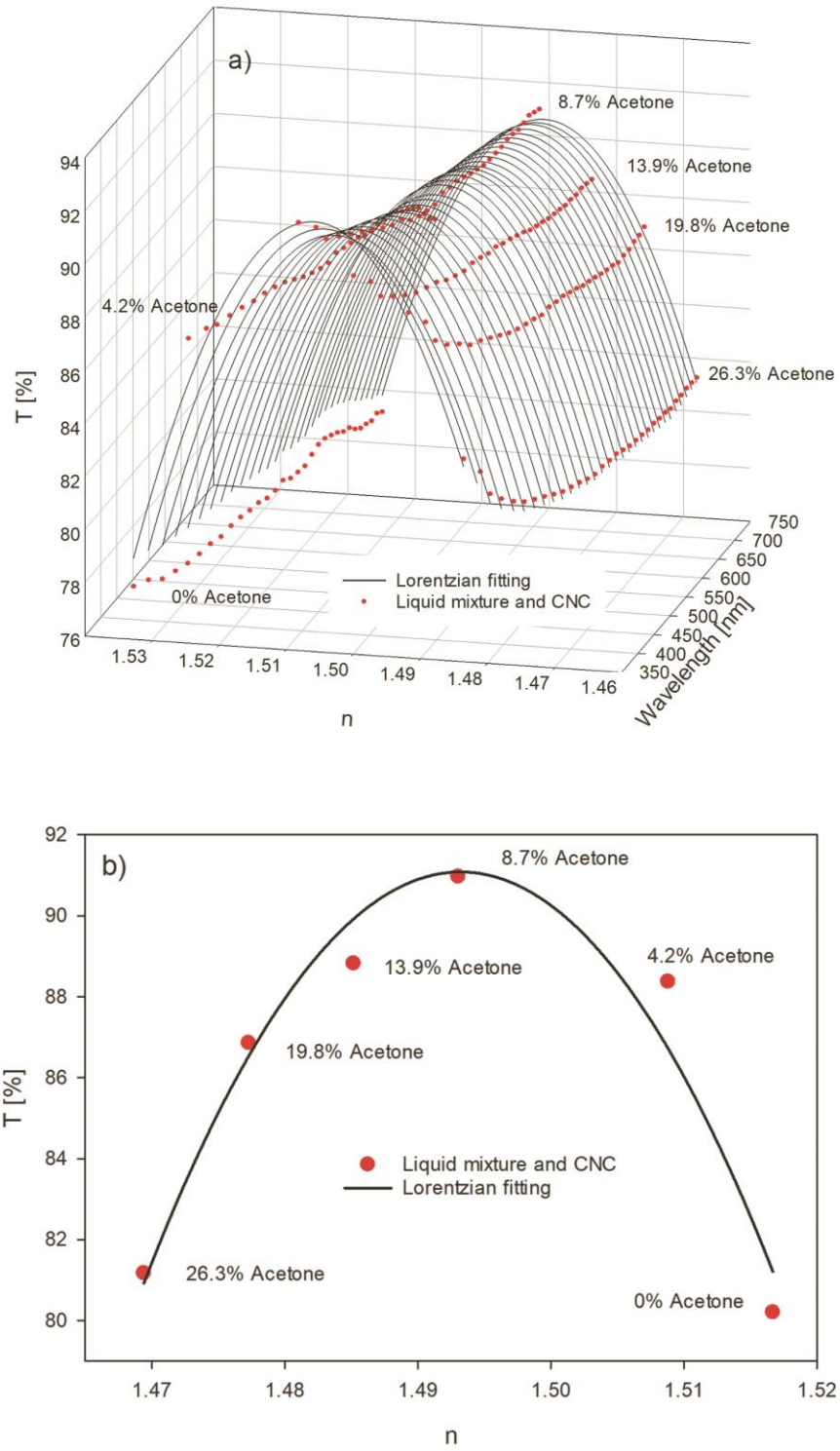

Figure 4. Transmission spectra of cellulose nanocrystals measured by spectrophotometer (dotted line) (a) as a function of wavelength, and (b) at 590 nm. The solid line is a Lorentzian fit of the experimental transmittance data.

The transmittance curves (T) for the CNC samples can be approximated by fitting a Lorentzian functional form (Eq. 6) to the data to determine the maximum point of transmission (the inflection point) at 10 nm intervals. The refractive index of the liquid pair is wavelength dependent. We calculated the wavelength dependence of refractive indices for each acetone/immersion oil mixture using values found in the literature [27,28,29].

In addition, we can see from Figure 4 that the maximum point of transmission is about 92%. The transmission curves did not achieve an ideal maximum value of transmission (100%) because of a small refractive index mismatch between the immersion liquid pair and the cellulose nanocrystals. This is due to the cellulose nanocrystals containing constituents that have different refractive indices (birefringence) and/or impurities. In other words, the scattering and absorption are increased, causing a decrease of the maximum transmittance. However, this is not an issue in the immersion matching method because the intention was to find the tipping point at a wavelength that shows refractive index. Moreover, the maximum point of transmission may be used to estimate the impurity and birefringence of CNCs. The maximum point of transmission may be utilised to estimate the purity of the material or/and birefringence. The cellulose nanocrystal has several different refractive indexes, and the immersion method gives an average value. Therefore, we use the term "effective refractive index, n_{eff}". The effective refractive index is the sum of the refractive indices of the material.

Dispersion data obtained by this method for the effective real part of the complex refractive index of cellulose nanocrystals are shown in Figure 5. It is observed that n = 1.508 ±0.005 at 400 nm and decreases to 1.489 ±0.005 at 700 nm. The refractive index dispersion of materials can be described by the Cauchy equation [34]. The empirical coefficients of the Cauchy dispersion equation may be calculated by fitting to the recorded complex effective refractive index curve (Fig. 4), which results in Equation (7) at a wavelength range of 400 nm-700 nm.

$$N_{eff}(\lambda) = 1.4767 + \frac{0.0063}{\lambda^2} - \frac{0.0002}{\lambda^4} + 0.002i \quad (7)$$

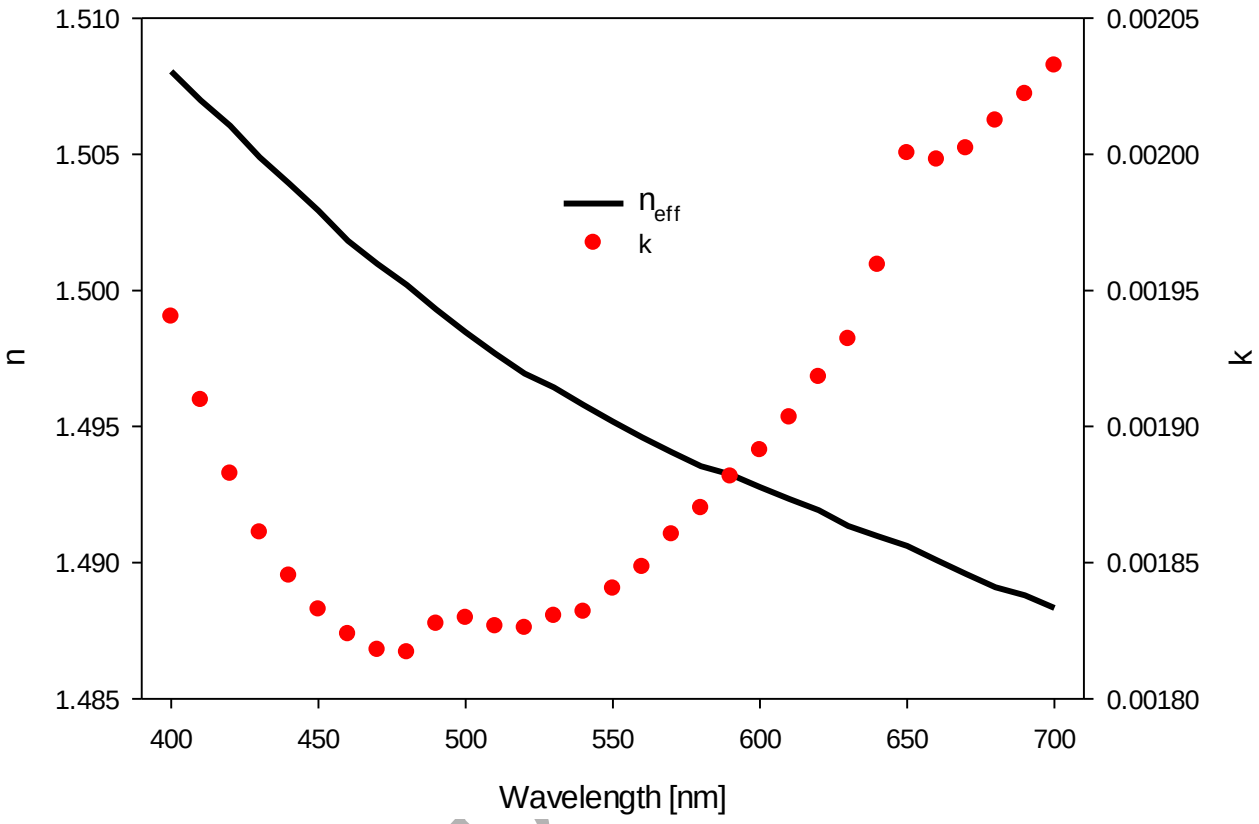

Figure 5. Complex effective refractive index of cellulose nanocrystals as a function of wavelength.

Previously, Reid et al. [35] used the SPR technique to simultaneously determine the refractive index and thickness of a CNF film. The SPR method resulted in a thickness of 39.7 ±0.6 nm and a refractive index of 1.458 ±0.008 at 785 nm [35]. Angle-dependent optical reflectometry and ellipsometry have been used to measure the refractive index of CNC at 633 nm, resulting in values of 1.51 ±0.01 and 1.516 ± 0.001, respectively [36]. Landry et al. [37] determined the refractive index of CNCs both by the ellipsometer and a critical-angle method principle at 589 nm. In the critical-angle principle, the refractive index of CNC was measured to be 1.499 at 589 nm. The ellipsometer technique gave the refractive index of CNC film as 1.5 at 589 nm. From Landry

and colleagues' result, it can be concluded that the nanocellulose form (suspension or solid) does not affect the value of the refractive index. The best refractive index estimates obtained by our method are n_{589}=1.493 and n_{633}=1.490, matching very well with the literature.

However, the complex refractive index of CNC has not been reported previously as a function of wavelength. The refractive indices of cellulose nanocrystals are considerably lower than ideally oriented cellulose crystal structures, which have extraordinary and the ordinary refractive indices of 1.618 and 1.544, respectively. Thus, the birefringence is +0.074 at the sodium D-line wavelength, 589 nm [23].

Our results indicate that the cellulose nanocrystals give lower refractive indices than the original cellulose. The decrease in the refractive index of cellulose nanocrystals is likely due to the combination of imperfect chain orientations and the existence of amorphous regions. An ideal cellulose crystal does not contain amorphous elements [38]. Granston et al. [36] proposed that refractive index differences are due to various packing densities of cellulose nanocrystals in the film. The inaccuracy of the extinction coefficient will be approximately a ±0.00045 unit considering the uncertainty caused by the thickness of the film is about 0.00043 (9.6 μm+ 2.4 μm) units, and the inaccuracy of the UV-Visible spectrophotometry is about 0.00001 units.

The accuracy of the detection of the refractive index is estimated to be better than ±0.005 by the immersion matching technique [24]. Temperature control is important because the refractive index of immersion oil and acetone changes by approximately 0.00033 and 0.0005 per 1° C, respectively. In addition, the density of acetone and immersion oil depend on temperature. For example, temperature changes from 20° C to 22° C, corresponding to the variation in the density of acetone of 0.0023 g/ml. The volume fraction determination accuracies (weighing method) affect 0.001 refractive index units. Refined procedures for the application of the immersion method are estimated to give an error of 0.005-0.001 refractive index units, however, involve the temperature control, a monochromator source, the use of a graduated series of calibrated liquids, inhomogeneity

of particles, and a skilled analyst. In addition, the method of refractive index calculation is based on an average estimate, which increases the accuracy and reliability of the method compared to measuring individual particles in microscopy.

4. Conclusion

We have introduced a method for the determination of an averaged complex refractive index of cellulose nanocrystals based on transmission spectra using the Beer-Lambert immersion matching method. In this study, an immersion oil-acetone mixture served as an immersion liquid, and the complex refractive index of CNCs was determined at discrete wavelengths in the spectral range of 400 nm-700 nm. The accuracy could be improved by using the Lorentzian-fitting procedure mathematically to find the maximum transmittance. The accuracy for the real portion of the refractive index was 0.005 refractive units and for the imaginary portion of the refractive index 0.001 units. Our results suggest that the refractive index is decreased by the influence of the birefringence of cellulose nanocrystals.

The major advantages of the Beer-Lambert immersion matching method are that it is independent of the shape or size of a particle, the measurement is relatively easy to conduct, data analysis is uncomplicated, and methods are applicable to various media. Furthermore, the method does not require the use of special devices, only a spectrophotometer, which is a standard measurement device typically found in laboratories.

This work suggests that the introduced approach may lead to a variety of applications and models for the identification of unknown nanomaterial dispersion properties. The immersion techniques open a new window in the process of tailoring and manipulating the optical properties of nano-sized particles in various fields, such as cosmetics, paint, printing inks, paper, and plastic products.

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Supplementary material

Supplementary material associated with this article can be found, in the online version,

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Graphical abstract

Determining the complex refractive index of cellulose nanocrystals (CNC) by Beer-Lambert-Immersion method