Rheological insights on the evolution of sonicated cellulose nanocrystal dispersions

Mélanie Girard [a,b], François Bertrand [b], Jason R. Tavares [a], Marie-Claude Heuzey [a,*]

[a] Research Center for High Performance Polymer and Composite Systems (CREPEC), Department of Chemical Engineering, Polytechnique Montreal, Montreal, Quebec H3C 3A7, Canada
[b] Research Center for Industrial Flow Processes (URPEI), Polytechnique Montreal, Montreal, Quebec H3C 3A7, Canada

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ABSTRACT

Cellulose nanocrystals (CNCs) are promising biomaterials, but their tendency to agglomerate when dried limits their use in several applications. Ultrasonication is commonly used to disperse CNCs in water, bringing enough energy to the suspension to break agglomerates. While the optimized parameters for sonication are now well defined for small volumes of low concentration CNC suspensions, a deeper understanding of the influence of the dispersing process is needed to work with larger volumes, at higher concentrations. Herein, rheology is used to define the distribution and dispersion states upon ultrasonication of a 3.2 wt% CNC suspension. After considering the importance of the measurement sampling volume, the behavior of a more concentrated suspension (6.4 wt%) is examined and compared with a never-dried suspension of the same concentration to validate the dispersion state.

1. Introduction

Cellulose nanocrystals (CNCs) are bio-sourced nanoparticles that can be used in various applications such as polymer reinforcement, barrier films or biomedicine [1–3]. Their size and shape, along with their surface chemistry confer upon them beneficial properties for these sectors. For instance, they present a high longitudinal module (around 130 GPa) [4], iridescence [5], and barrier properties [6].

These nanorods are extracted from purified cellulose fibers through acid hydrolysis, either with hydrochloric or sulfuric acid (HCl and H_2SO_4). Amorphous portions are thus removed, leaving only the crystalline part. H_2SO_4 is particularly useful, as it introduces charged sulfate half-ester groups on the CNC surface, facilitating their dispersion in water (contrary to HCl) [7]. However, thermal stability is affected by a high sulfate half-ester group content [8]. The hydrolysis conditions may additionally affect the particle size [9–11].

Following hydrolysis, CNCs are generally neutralized. The choice of the counterion influences the stability or the dispersion ability [12,13]. CNCs may then be dried using either freeze- or spray-drying approaches. Spray-drying is usually favored for industrial synthesis, as it requires less energy. In addition, spray-dried CNCs present higher crystallinity and thermal stability because of a higher cellulose II content than their freeze-

dried counterparts, and lead to a more compact powder [14,15]. However, CNCs tend to agglomerate during drying, either as spherical aggregates when spray-dried or as flakes when freeze-dried. Agglomeration hinders the exploitation of CNC's desirable properties. With the application of appropriate mechanical energy on agglomerated CNC suspensions, it is possible to obtain the same properties and behavior for spray– or freeze–dried systems than for never-dried CNC suspensions [16].

Breaking the agglomerates formed upon drying requires high energy input. Indeed, due to the high surface area of the CNCs (around 155 $m^2 \cdot g^{-1}$ [17]), the agglomerate strength may reach 10^4 to 10^9 Pa depending on the initial particle size [18]. Ultrasonication is typically used in the literature for CNC dispersion, as it can provide energy densities from 10^6 to 10^8 Pa. An alternate solution is to use a high-pressure homogenizer, also based on cavitation generation; this process may be interesting as it makes the suspension flow at high velocities [19], preventing the formation of dead zones identified when using ultrasonication. Due to infrastructure cost, high-pressure homogenization remains rarely used at the lab scale for CNC dispersion.

Ultrasonication probes generate a sinusoidal pressure wave in the medium thanks to piezoelectricity. This induces compression and rarefaction cycles (respectively of negative and positive pressure), creating vacuum bubbles. Bubble sizes are influenced by these pressure variations

by growing and absorbing energy under low pressure and contracting at high pressure. These cycles are repeated until the cavities reach a critical size (~170 μm in diameter at 20 kHz in water), which leads to their implosion at high frequency [20]. This phenomenon called cavitation releases a high amount of energy. However, the active zone in which cavitation takes place is limited to the near-probe region, the size of which is largely dependent on the viscosity of the medium. This limits dispersion in highly concentrated (and therefore viscous) suspensions or in large volumes [21].

Rheology is a powerful tool to characterize CNC suspensions [12], especially given the fact that their behavior is concentration dependent. Suspensions go from isotropic at low concentration (below 2 to 4 wt%), to liquid crystal at medium concentration (between 4 wt% and 5 wt%) and finally to a gel at high concentration by forming a percolating network [22] (over 5 and up to 12 wt%) [23–26]. A glassy state has also been defined for high concentrations (over 8 wt%) and very low ionic strength (less than 10^{-2} mol.L^{-1}), with the addition of salt increasing this concentration threshold [22]. In the glassy state, the solid-like behavior is governed by repulsive interactions [27]. The concentration thresholds delimiting the suspension states are not strictly defined as they may depend on the sulfatation degree, ionic strength of the suspending medium and on the CNC aspect ratio [26,28]. Isotropic suspensions exhibit a plateau at low shear rate, shear thinning at intermediate shear rate and another plateau at high shear rate. On the other hand, liquid crystal suspensions lead to a three-region behavior for viscosity in shear rate sweep tests: shear-thinning, plateau, and shear-thinning, respectively for low, intermediate, and high shear rates. For the gel state however, only shear-thinning is observed [23]. CNC gels present a yield stress resulting from the competition between microstructure build-up and destruction. Thus, applying a low shear stress (below the yield stress) results in viscosity build-up over time, or ageing. Conversely, applying a high shear stress (above the yield stress) leads to a viscosity decrease over time, or "rejuvenation" [29,30]. This must be kept in mind for rheological characterization as it induces change in the behavior one is trying to observe.

Rheology can also be used to assess the CNC dispersion state [15,21]. Studies on ultrasonication parameter influence have revealed a decrease in viscosity as the particles become dispersed, i.e. as the agglomerates are broken down due to a thinner electrostatic double layer because of the Na$^+$ counterion release [15,26]. Moreover, for highly concentrated suspensions, the gel behavior can be disrupted to reach a liquid behavior through ultrasonication. The recovery of the initial state, i.e a stable gel, may take more than 6 months [31].

Even if ultrasonication is widely used in the literature, many challenges remain and a deeper understanding is needed to fully benefit from this processing method. In our previous work, a rigorous protocol involving probe position and key metrics accounting for container volume were defined to disperse CNCs efficiently in water [21]. However, that study, as well as most literature articles, focuses almost exclusively on the end-point of dispersion - parameters that lead to a well-distributed and well-dispersed suspension - but neglect the path to achieve this final state. Understanding the sequence of events leading to dispersion may help work around the current limitations of ultrasonication.

Thus, the objective of this paper is to characterize the behavior of CNC liquid-like and gel-like suspension during ultrasonication. In this study, we carefully differentiate distribution and dispersion: while the first refers to the homogeneity of the suspension, the latter qualifies the particle state in the suspension (individual or agglomerated). This paper focuses on the rheology of the CNC suspension during ultrasonication. The effect of the sampling method for rheology measurements is first analyzed. Then, by focusing on sonication at low energy levels (below the previously identified thresholds for dispersion [21]) on a 3.2 wt% CNC suspension (liquid-like behavior), it is possible to better understand the sequence of events to reach a good dispersion state through ultrasonication. Additionally, the comparison of the results given by two rheometer flow geometries further highlights the effect of the sampling

volume. Finally, the behavior of a 6.4 wt% CNC suspension (gel-like behavior) is investigated to confront the previous outcomes to concentrated media.

2. Methodology

2.1. Material

The CNCs used in this work were provided by Celluforce. They present sulfate half ester groups on their surface that result from the hydrolysis step after extracting CNCs from cellulose fiber and removing lignin, hemicellulose, and impurities. There are approximately 3.4 sulfate half ester groups per 100 anhydroglucose rings, giving a sulfur over carbon S/C atomic ratio around 0.0057 [15] or 211 mmol.kg^{-1}. These CNCs were neutralized using sodium hydroxide before either being spray-dried (particle size ~ 127 nm when resuspended), or kept in suspension at 6.4 wt% (never-dried, particle size ~ 90 nm). Note however that both particle size measurements have been carried out by the supplier with 2 wt% suspensions and the results may hide dispersion problems. In both cases, the final crystallinity ratio is around 80 % [32] and the density 1540 kg.m^{-3}. The dried CNCs were used as-received in powder form and have never been sonicated prior to this work.

2.2. CNC suspension preparation

Starting from dried CNCs, suspension preparation followed the same rigorous protocol presented in our previous work [21]. Briefly, 60 mL of either a 3.2 wt% (2.08 vol%) or a 6.4 wt% (4.16 vol%) CNC suspension were prepared by adding half of the water amount, the required CNC amount (respectively 1.91 g or 3.84 g) and the remaining water, in this specific order, to facilitate CNC incorporation, in a 100 mL beaker. A vortexer (Mini Roto S56 – Fischer Scientific – 2800 rpm) was then applied for 30 s to avoid gelation.

This pre-mixed suspension was then sonicated for a specific time at power P = 65 W, placing the probe off-center near the liquid surface. This power level has been chosen to find a balance between ultrasonication efficiency and time needed to achieve dispersion. This value is the one shown on the device and correspond to an actual delivered power of 15 W [21]. The beaker was put in an ice bath to avoid overheating. Under these conditions, the required sonication energy is around 167 kJ.g^{-1}.L^{-1} to achieve a well-dispersed suspension (refers to kilojoules per gram of CNCs and liter of suspension) [21]. We will refer to this value as "optimal energy level" henceforth in the text. Ultrasonication was used at different energy levels, ranging from very low (2 kJ.g^{-1}.L^{-1} or ~ 3 s of ultrasonication for a 3.2 wt% suspension), low (15 kJ.g^{-1}.L^{-1} or ~ 10 s at 3.2 wt%) or optimal (167 kJ.g^{-1}.L^{-1} or ~ 320 s at 3.2 wt%).

The never-dried CNC suspension was either characterized as received, or after applying the equivalent optimal energy level (167 kJ.g^{-1}.L^{-1} or ~ 640 s), following the same protocols outlined above. This energy level leads to a minimum viscosity and longer ultrasonication does not decrease the viscosity any further (Figure S1)

2.3. Rheology

Rheology measurements were carried out using an Anton-Paar rotational rheometer (MCR501). Either a concentric cylinder (CC) or a Couette double gap (DG) flow geometry was used. The required volume for each geometry (20 mL for CC or 8 mL for DG) was sampled using a syringe unless specified otherwise. Shear rate sweep tests were carried out from 1000 s^{-1} to 1 s^{-1} (high to low shear rate, unless specified otherwise). These tests were preceded by a pre-shear at 10 s^{-1} for 120 s to prevent the presence of air in the sample and ensure of a similar starting microstructure, followed by a 180 s rest time. All tests were performed at 25 ℃.

2.4. Particle size analysis

Particle sizes were determined using a laser obscuration time technique (EyeTech, Ankersmid). This method was chosen as no dilution is needed prior to analysis, avoiding any change in the particle dispersion. It can measure particles as small as 0.1 μm.

2.5. UV–vis spectroscopy

One way to evaluate the dispersion state is by analyzing suspension turbidity. This was carried out with UV–vis spectroscopy (USB4000-XR1-ES, Ocean Insight). The absorbance was measured between 200 and 850 nm using 1-cm quartz cell. However, results must be interpreted carefully as other physical phenomena could influence the optical properties.

2.6. Ageing tests

The behavior of a never-dried CNC suspension was compared to that of a suspension of the same concentration, i.e 6.4 wt%, prepared with spray–dried CNCs. Shear rate sweeps from 1000 s^{-1} to 1 s^{-1} (high to low) were done on those suspensions within 5 min following ultrasonication and were then repeated after a specific time to follow the evolution (ageing) over time. This specific time, specified in the corresponding discussion as DX for "day X", was the same for every suspension. Meanwhile, the suspensions were stored at room temperature.

Because of the fast-evolving behavior over time, a repeatability study was carried out by analyzing one sample of three suspensions obtained with the same parameters, instead of several samples of the same suspension. This allowed us to keep the study time constant.

3. Results and discussion

3.1. Sampling method

As explained in Section 2.3, suspensions are usually sampled with a syringe. However, this may filter out the largest agglomerates (larger than 2 mm) and bias the rheological assessments. Thus, two additional sampling methods were compared to study their effect: a truncated syringe allowing agglomerates up to 15 mm to be sampled, and pouring the sample directly from the beaker into the flow geometry.

To highlight the effect of the sampling method, the applied ultrasonication energy was 2 kJ.g^{-1}.L^{-1}, as inhomogeneity in the distribution and poor dispersion are expected at this very low energy level. The DG flow geometry was used to carry out a shear rate sweep study. The three sampling methods were compared by analyzing six to seven samples for each, and repeated three times. Then, the standard deviation normalized by the average viscosity value was calculated for all samples and averaged for all three repetitions to compare the variation caused by each sampling method (Fig. 1).

Note that, at this energy level, the initial state influences the measured viscosity. Indeed, even if the suspension preparation protocol was rigorously followed, a great deal of variability was introduced by the very low-energy dispersion approach. Agglomerates were formed randomly, and the ultrasonic probe could not be placed at the same position relative to each of them, leading to variations between each repetition.

This variation between samples obtained with the same sampling method is significant, showing that the initial state influence prevails over the effect of the sampling method itself. Indeed, by considering this variation, the value of the standard deviation is approximately the same whatever the method. The higher values observed for the beaker sampling method are inherent to the fact that all agglomerates are considered with this method whereas only a few agglomerates are collected with both syringe sampling methods. It also confirms that despite the rigorous preparation protocol meant to avoid manipulation error, there is some variability that cannot be controlled.
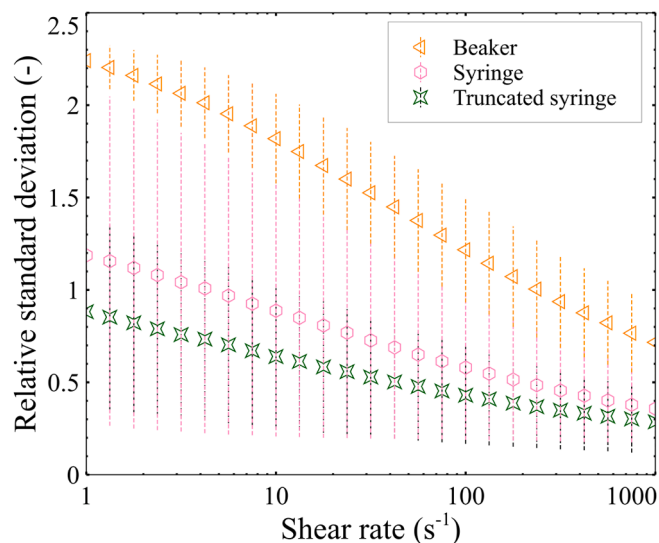

Fig. 1. Relative standard deviation of 3.2 wt% CNC ultrasonicated suspensions as function of shear rate (V = 60 mL, P = 65 W, E = 2 kJ.g^{-1}.L^{-1}) using either the syringe, the truncated syringe or the beaker sampling method.

For the following analyses, the syringe sampling method was retained, and the whole suspension was analyzed unless stated otherwise. While the truncated syringe is moderately better (Fig. 1), the plain syringe approach is much easier to implement.

3.2. Ultrasonication timeline

The suspension must be well-distributed and well-dispersed to give optimal results. To understand how these conditions can be reached, the ultrasonication process was decomposed into several steps and the suspensions were then analyzed using rheology. The DG flow geometry was used again for this study. Starting from an initial state consisting of an inhomogeneous medium with many large agglomerates, ultrasonication was applied either at 2 kJ.g^{-1}.L^{-1} (purple data in Fig. 2), 20 kJ.g^{-1}.L^{-1} (green data) or 167 kJ.g^{-1}.L^{-1} (red data).

Applying the lowest amount of energy led to large variations between samples. Although the average of the measurements may indicate that a fair dispersion was achieved, the overall variations show
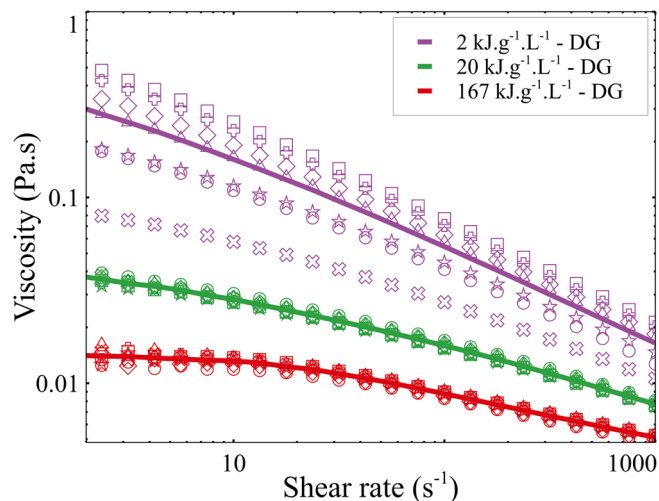

Fig. 2. Viscosities of 3.2 wt% CNC ultrasonicated suspensions obtained for E = 2, 20 or 167 kJ.g^{-1}.L^{-1} as function of shear rate (V = 60 mL, P = 65 W, DG flow geometry). Solid lines represent the average values of all corresponding measurements.

that the suspensions were in fact inhomogeneous. This confirms that, at this very low energy level, the distribution and the dispersion are both unsatisfactory.

Increasing the sonication energy to 20 kJ.g^{-1}.L^{-1} resulted in a significant reduction of the data spread: all samples have similar viscosity values, meaning that a good distribution state must have been reached (i.e. all samples measured are similar, and thus there is better homogeneity). However, when these values are compared to those of a well-dispersed suspension (Fig. 2) at 167 kJ.g^{-1}.L^{-1}, it becomes clear that the dispersion had not yet reached its optimal state (as the viscosity values at 20 kJ.g^{-1}.L^{-1} are significantly higher).

In summary, three states can be observed during ultrasonication, as illustrated in Fig. 3. Upon increasing the energy level, the suspension goes from a not-well distributed and not-well dispersed state to a distributed but not well-dispersed state before finally reaching a well-distributed and well-dispersed state. Indeed, by increasing the time of ultrasonication, more mixing cycles may be achieved, increasing the process efficiency. This confirms the findings from numerical simulations presented in our previous work [21]. Photos taken right after ultrasonication validate this sequence. While photos on the left show the suspension as is, increasing the contrast and decreasing the brightness (photos on the right) helps to better visualize the presence of agglomerates at t = 0 and t_1. In addition, an opaquer suspension is observed for t_2 compared to t_f, confirming a worse dispersion. This last point has also been proved using UV–Vis spectroscopy (Figure S2).

3.3. Geometry comparison and sampling volume

The previous section has underlined that variations in the viscosity values provide information on a suspension's distribution state. This suggests that the sampling volume is critical when analyzing a suspension. To validate this hypothesis, the concentric cylinder (CC) and the Couette double gap (DG) flow geometries were compared as these require sample sizes of either 20 mL or 8 mL, respectively. Several levels of energy were studied: either 2, 10, 15 or 20 kJ.g^{-1}.L^{-1} to reach progressively the well-distributed state (minimum of 20 kJ.g^{-1}.L^{-1}).

To account for variations between samples, the standard deviation may be more relevant than the viscosity value itself. As discussed in Section 3.1, the average obtained from all the samples analyzed with the same geometry may differ from a suspension to another because of a

different initial state (CNC agglomerates being formed in an uncontrolled manner in the beaker). Thus, the standard deviation is normalized by the average viscosity for each sample, giving a relative standard deviation, to minimize the effect of the initial state. Fig. 4 present thus the relative standard deviation as a function of the shear rate for the different energy levels, for the DG case (empty symbols) and the CC case (filled symbols). The relative standard deviation is larger for the DG case than the CC case at all energy levels. The DG flow geometry volume being smaller, the distribution effect is more visible. As the ultrasonication energy increases, the difference between the two geometries is reduced. This indicates that the sampling volume is less influential. In addition, as the distribution state improves when increasing the ultrasonication energy, the relative standard deviation decreases. Both points imply an improving distribution state.

Thus, relative standard deviation of the viscosity value serves as an indicator for distribution. However, the absolute value of viscosity needs to be considered to assess the dispersion state as explained in Section 3.2.
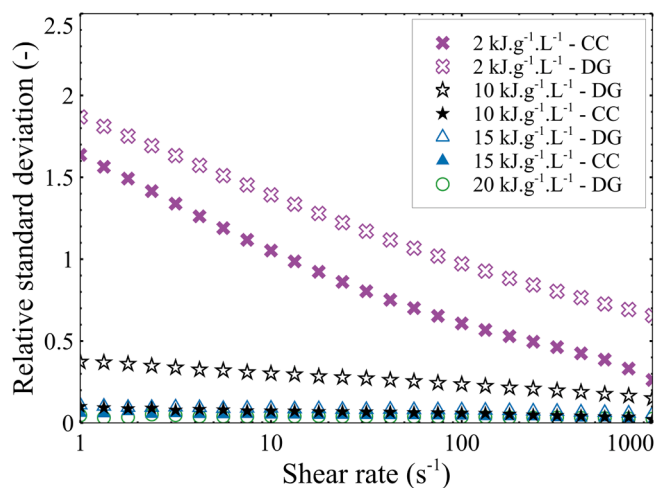
Fig. 4. Relative standard deviation of 3.2 wt% CNC ultrasonicated suspensions obtained either with a concentric cylinder (CC – filled symbols) or a double gap (DG – empty symbols) geometry for E = 2, 10, 15 or 20 kJ.g^{-1}.L^{-1} as function of shear rate (V = 60 mL, P = 65 W).
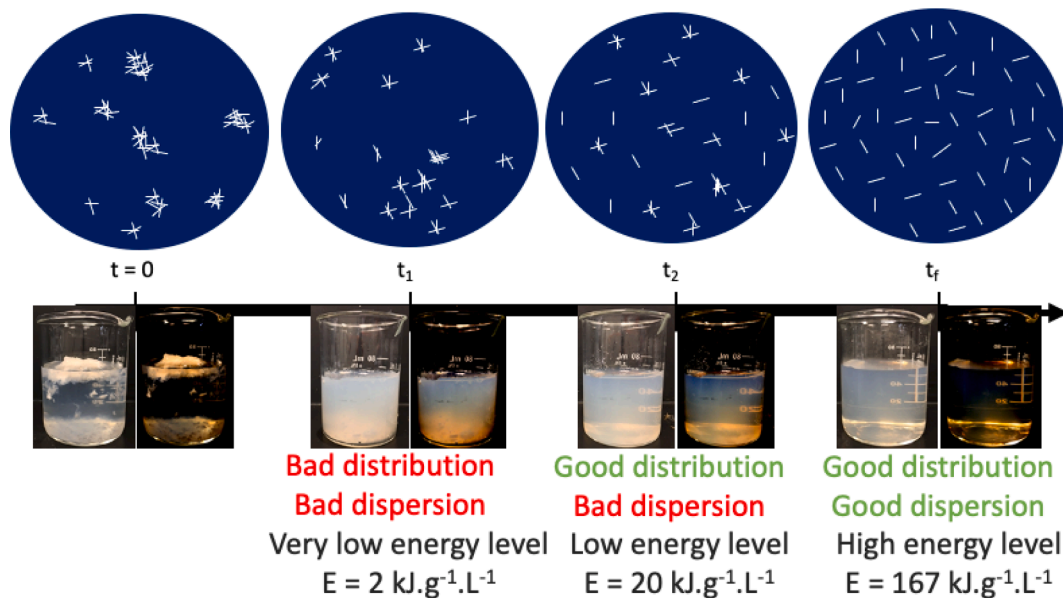
Fig. 3. Suggested ultrasonication mechanism over time. Original (left) and modified (right) photos are shown for each time. The same modifications have been applied for every case.

3.4. Challenges at higher concentrations

At higher concentration, CNC suspensions present a gel-like behavior. In this case, the previous conclusions may not be easily extrapolated, which warrants studying a 6.4 wt% CNC suspension.

One of the main concerns at higher concentration is to validate that a good dispersion can still be achieved as the formed agglomerates present a much higher local concentration than those of the suspension, multiplying the interparticle interactions. Thus, an ultrasonicated never-dried CNC suspension (UND) was compared with a spray-dried CNC suspension (USD) at the same 6.4 wt% concentration. Both have been ultrasonicated by applying the same energy level ($167 \text{ kJ.g}^{-1}.\text{L}^{-1}$) to study the viscosity buildup after ultrasonication. Fig. 5 depicts the viscosity values of each suspension as functions of shear rate followed over time after ultrasonication. The unsonicated, never-dried CNC suspension (ND) behavior is reported as a reference. ND and UND suspensions are supposed to present a well-dispersed state, as the CNC agglomeration is mainly induced from the drying process. At day 0 (D0), the viscosity measurements are essentially the same for USD and UND suspensions. This suggests that the dispersion state of the USD suspension is the same as the UND suspension, meaning that CNCs have been well-dispersed and well-distributed. The usual gel behavior at high concentration is replaced by a two–region curve: a shear–thinning behavior below 100 s^{-1} and a zone with a higher slope at higher shear rate. Though we do not observe a plateau at intermediate shear rates, a similar behavior has been reported in the literature [23] and a shear thinning region with a high slope is expected at lower shear rate: this is a liquid crystal behavior. To ease the comparison, the viscosity value at 5.62 s^{-1} is followed over time (Table 1). This value has been chosen to be in the mid-range of the lower shear rate values, where the interparticle contribution is visible [33]. After 11 days (D11), the final state seems to have been reached, as there is no significant difference with the behavior at day 20 (D20). The original ND values ($1.4 \text{ Pa.s} \pm 0.1$ at 5.62 s^{-1}) have been reached for the D20 USD suspension, but the D20 UND suspension remains at a lower viscosity level. However, the behavior for all suspensions is similar for shear rates above 40 s^{-1}. Indeed, only the hydrodynamic contribution plays a role on viscosity values at high shear rate [33]. The absence of complete recovery of the viscosity for the UND suspension has already been reported for ultrasonicated commercial concentrated suspension, even over longer time scales [31]. Two zones can be distinguished on the viscosity curve, which may suggest a biphasic structure with isotropic and anisotropic regions. This observation is also valid for the USD suspension even if this is much slighter.

Table 1
Sample viscosity values at 5.62 s^{-1} of 6.4 wt% never-dried (A) or spray-dried (B) CNC ultrasonicated suspensions, respectively noted UND or USD (E = 167 kJ.g^{-1}.L^{-1},V = 60 mL, P = 65 W) after 0, 1, 4 11 and 20 days (D0, D1, D4, D11, D20). The value for the 6.4 wt% never–dried CNC suspension is indicated as a reference.

	D0 (Pa.s)	D1 (Pa.s)	D4 (Pa.s)	D11 (Pa.s)	D20 (Pa.s)
UND (A)	0.09 ± 0.02	0.41 ± 0.06	0.63 ± 0.04	0.9 ± 0.1	0.89 ± 0.05
USD (B)	0.067 ± 0.001	0.570 ± 0.001	0.95 ± 0.05	1.29 ± 0.02	1.4 ± 0.3

To complement this study, a shear rate sweep has been carried out from low to high shear rates (Fig. 6A). In this case, both UND and USD suspensions behave the same as the ND suspension. In addition, the comparison between both tests for the ND suspension (Fig. 6B) shows a hysteresis phenomenon below 10 s^{-1}. This behavior has been already observed in the literature for thixotropic yielding materials [29], implying different dynamic and static particle network structures [34]. Thus, as differences from USD/UND and ND are visible only from high to low shear rates, it implies that the dynamic particle network structure is not the same. This point was confirmed by measuring a larger light absorbance for USD and UND compared to ND suspensions aged by 1 and 8 days, increasing with time (Figure S3). The ultrasonication step allows CNCs to re-arrange themselves while the gelation phenomenon is not instantaneous. It has been reported that CNC suspensions present a larger anisotropic volume fraction with increasing ultrasonication time [35], which would lead to a larger absorbance.

To conclude on the dispersion state of the USD and UND suspensions, the particle sizes were compared, and the results are reported on Fig. 7 just after ultrasonication (D0) and after 1 day (D1). At D0, the USD suspension presents larger particles than the UND suspension - these differences are of the same range than the initial particle size measured by the supplier Celluforce. Thus, a well-dispersed state must have been reached for the USD. After one day, the particle sizes increase for both suspensions, with a higher increase for the USD suspension. This is consistent with the faster ageing over time that was observed in the rheology measurements. Particle size increase over time illustrates that a percolating network of particles is forming, as expected for a gel.

Compared to the study at 3.2 wt% CNC suspension (Section 3.3), the dispersion and distribution state of a 6.4 wt% CNC suspension cannot be determined as easily. Indeed, the method presented needs to be adapted as the concentrated suspension viscosity evolves quickly over time. The
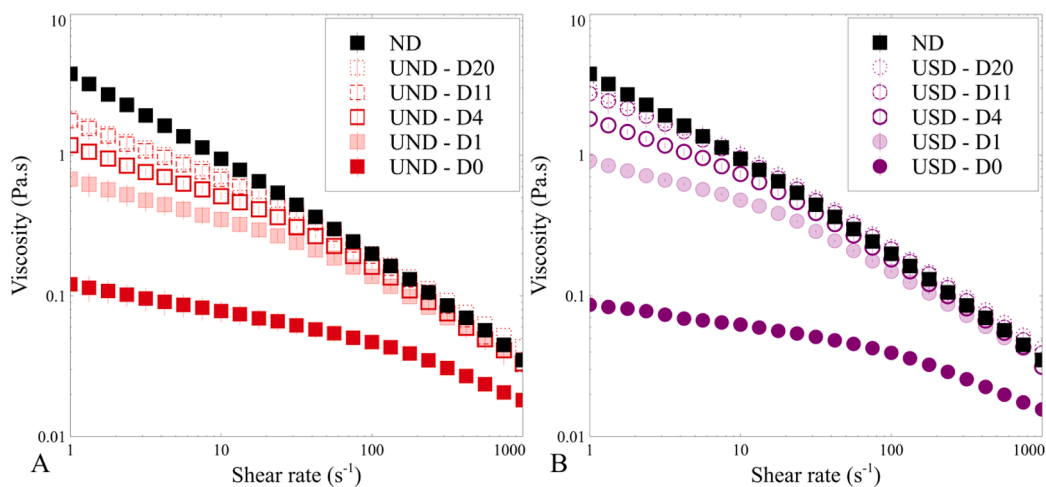

Fig. 5. Sample viscosities of 6.4 wt% never-dried (A) or spray-dried (B) CNC ultrasonicated suspensions, respectively noted UND or USD (E = 167 kJ.g^{-1}.L^{-1},V = 60 mL, P = 65 W) after 0, 1, 4, 11 and 20 days (D0, D1, D4, D11, D20) compared with a 6.4 wt% never-dried CNC suspension, noted ND (no ultrasonication) as function of shear rate (high to low).
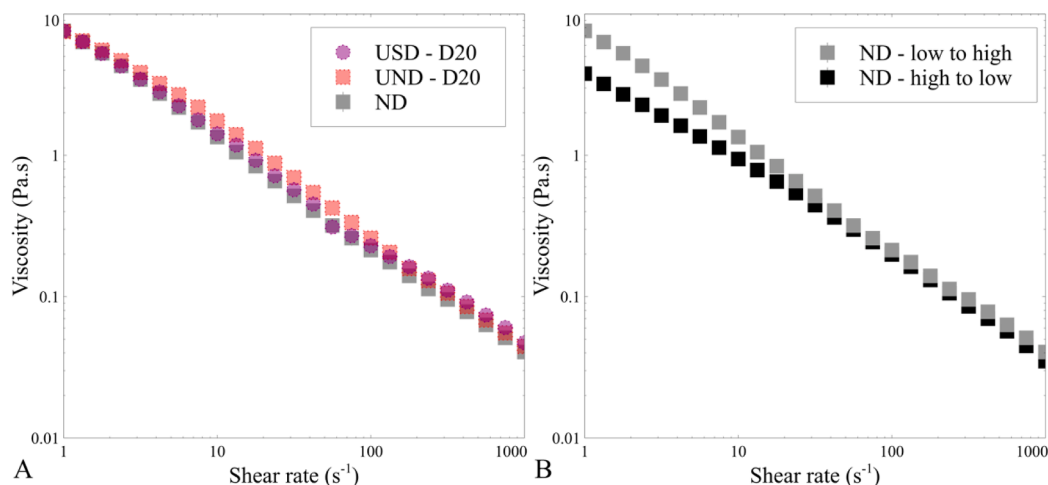
Fig. 6. A: Sample viscosities of 6.4 wt% never-dried and spray-dried CNC ultrasonicated suspensions, respectively noted UND or USD (E = 167 kJ.g^{-1}.L^{-1},V = 60 mL, P = 65 W) after 20 days (D20) compared with a 6.4 wt% never-dried CNC suspension, noted ND (no ultrasonication) as function of shear rate (low to high). B: Sample viscosities of a 6.4 wt% never-dried CNC suspension (ND) from low to high and high to low shear rate.
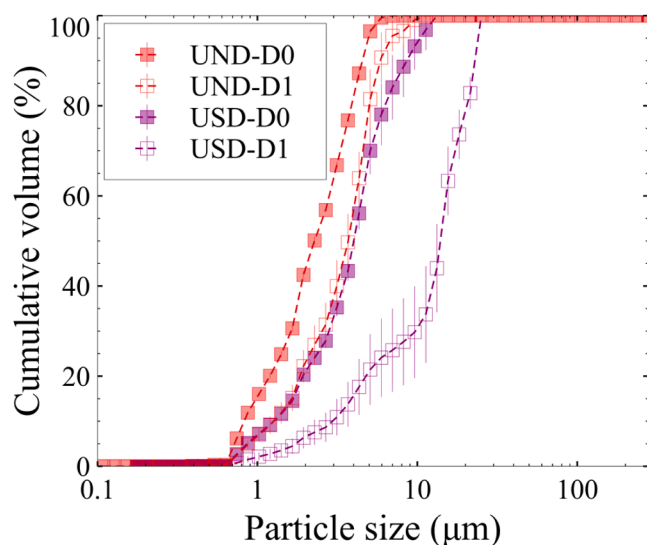

Fig. 7. Cumulative volume distribution of 6.4 wt% never-dried and spray-dried CNC ultrasonicated suspensions, respectively noted UND or USD (E = 167 kJ.g^{-1}.L^{-1},V = 60 mL, P = 65 W) after 0 and 1 day (D0 and D1 respectively).

distribution state needs to be analyzed at the same time by comparing the behavior of similar suspensions. Fig. 5 shows very small standard deviation with three samples of three different suspensions obtained with the same parameters, implying a good distribution state. In addition, as explained above, the dispersion is established by comparing the measurements with a never-dried suspension which had undergone the same ultrasonic energy level. The initial behavior (at D0) must be sufficient to conclude that the spray-dried CNC suspension is as well-dispersed as the never-dried CNC suspension.

4. Conclusion and further recommendations

Using ultrasonication to disperse nanoparticles can be challenging, especially when assessing the distribution and dispersion states. In this work, it has been demonstrated that rheology was a powerful tool for characterizing CNC suspensions at low concentration, if used properly. Studying the viscosity homogeneity in a suspension provides information on the distribution state. However, the sample volume is an important limitation for further conclusions. The viscosity value itself

can be used to assess the dispersion state as it decreases until a minimal value as the dispersion improves.

One must keep in mind the sampling volume influence when carrying analyses, such as density measurement or even microscopy observations. It could mask the true state of the suspension, leading the researcher to an incorrect interpretation.

The sampling volume issue also hints at greater issues when attempting to disperse larger volumes. The volume which can be handled is indeed a strong limitation for using sonication as a dispersion tool. One possible solution is to use a continuous setup that would gradually treat the suspension. The knowledge developed in the present work on ascertaining how both the dispersion and distribution states evolve during ultrasonication will facilitate implementation of an online measurement technique in larger-scale systems. This work is on-going in our team.

Finally, for higher CNC concentrations, the fast evolution of the microstructure complicates its study. However, a comparison with a never-dried suspensions provides insight on the distribution and dispersion state. The rigorous protocol developed in our previous work was successfully applied to produce a 6.4 wt% suspension, and similar properties as never-dried CNC suspensions could be obtained from spray–dried CNCs.

Because other nanoparticles share the same issue related to their dispersion, this study could eventually be broadened to them as well.

CRediT authorship contribution statement

Mélanie Girard: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Visualization. **François Bertrand:** Writing - review & editing, Supervision. **Jason R. Tavares:** Writing - review & editing, Supervision. **Marie-Claude Heuzey:** Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

nanocrystals. Additionally, we would like to thank CREPEC for the expertise and infrastructure access, as well as the Simulation-based Engineering Science (Génie Par la Simulation) group for scholarship support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2021.105747.

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