Simplification of gel point characterization of cellulose nano and microfiber suspensions

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Abstract Nanocellulose is an emerging material that needs to be well characterized to control its performance during industrial applications. Gel point ($\emptyset_g$) is a convenient parameter commonly used to estimate the aspect ratio (AR) of cellulose nano/microfibers (CNFs/CMFs), providing critical information on the nanofiber network. However, its estimation requires many sedimentation experiments, tedious and time consuming. In this study, a simpler and faster technique is presented to estimate $\emptyset_g$, based on one or two sedimentation experiments, reducing the

experiments by a factor of at least 2.5. Here, this new methodology is successfully validated by using the $\emptyset_g$ of different CNF/CMF hydrogels calculated with the traditional methodology, showing an error lower than 7%. The error in the estimation of the AR is lower than 3% in all cases. Furthermore, the two mathematical models currently used to estimate $\emptyset_g$, the smoothing spline and the quadratic fit, are compared and the mathematical assumptions improved.

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Graphical abstract

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Introduction

Gel point (ϕ_g) is defined as the volume concentration of a suspension at the boundary between the semi-dilute and dilute regions. This concentration is considered the lowest at which all flocs are interconnected, forming a self-supporting network (Martinez et al. 2001; Nasser and James 2006; Raj et al. 2016a; Zhang et al. 2012).

In the last few years, ϕ_g has been used to estimate the aspect ratio (AR) of different cellulose materials such as cellulose fibers, fines, microfibrils (CMFs) and nanofibers (CNFs) (Martinez et al. 2001; Sanchez-Salvador et al. 2020a; Varanasi et al. 2013) using two methods: the Effective Medium Theory (EMT) and the Crowding Number (CN) theory (Celzard et al. 2009; Kerekes and Schell 1992).

Performing the ϕ_g methodology requires at least 5 sedimentation experiments, each with a different initial fiber concentration (C_o), which is time consuming and a drawback, especially in industry. Another difficulty is that sedimentation time increases from 2 to 10 days with the fibrillation degree of the fiber sample (Sanchez-Salvador et al. 2020a).

Two mathematical methods have been used to calculate gel point (ϕ_g). In the first, the ϕ_g was estimated from a quadratic fit using Eq. 1 according to Varanasi et al. (2013). In this case, ϕ_g results from the

derivative at the origin of the curve C_o vs H_s/H_o as indicated by Eq. 2 (Martinez et al. 2001).

$$C_o = a \left(\frac{H_s}{H_o} \right)^2 + b \left(\frac{H_s}{H_o} \right) \quad (1)$$

$$\phi_g = \lim_{H_s/H_o \rightarrow 0} \left(\frac{dC_o}{d(H_s/H_o)} \right) = b \quad (2)$$

where H_s/H_o is the sediment height (H_s) normalized by the initial height (H_o) as measured from fiber sedimentation directly in the graduated cylinder.

The second method was developed using the curve fitting tool (CSAPS) in MATLAB. ϕ_g is obtained from the first derivative of each curve in the y-intercept (Raj et al. 2016b). In this case, a smoothing spline is fitted to the data with a smoothing parameter (p) oscillating in the interval [0, 1]. For $p = 0$, the equation solution is the least-squares straight line fit to the data, while, on the other extreme, for $p = 1$, the solution is the variational or natural cubic spline interpolant. As p moves from 0 to 1, the smoothing spline changes as the parameter approaches $p = 1$ the equation is closer to the data than the straight line. Traditionally, a constant “ p ” parameter is used but it must be optimized for each of the different types of nanofibers as explained in Sect. 2.1.

Here, we compare the use of both mathematical methods and their optimization, since in many cases they are used regardless of its mathematical limitations. In addition, we present a simpler and faster technique with mathematical assumptions to characterize ϕ_g and subsequently, the aspect ratio of nano/microfiber suspensions. Besides, these simplifications may be applied to other kinds of suspensions. The

main novelty of this method is the reduction in the number of sedimentation experiments to estimate ϕ_g using only one sedimentation experiment, at an optimal C_o ($C_{o,opt}$), based on a classical approximation of derivatives by a small finite difference close to zero. Thus, the number of experiments and time labour are reduced by at least a factor of 2.5. It is important to adequately select the optimal C_o ($C_{o,opt}$), in order to obtain a sedimentation deposit neither too small to have a high experimental error nor too big to have a disproportionate increment. If this is not achieved, it will be necessary to do a second experiment with a new C_o closer to $C_{o,opt}$. The optimal concentration will depend on the type of fiber source, the pretreatment or the fibrillation degree.

Theory

Quadratic fit and smoothing spline function

After carrying out the sedimentation experiments with suspensions at different CNF/CMF concentrations, H_s/H_o is measured in the graduated cylinders (See in Supplementary 1, Fig. S1), following the traditional methodology. Then, ϕ_g is estimated using the quadratic fit or the CSAPS method.

When the quadratic fit is used, the conditions to obtain are based on Eqs. 1 and 2. In Eq. 1, the quadratic fit is forced to have an independent term equal to zero. This fact makes the parameter “b” in Eq. 1 slightly lower than both the quadratic fit with the independent term and that calculated with the smoothing spline.

Using the CSAPS smoothing spline function requires to select the value of the “p” parameter based on two criteria:

- The selection of the minimum smoothing parameter (p) to represent the data close to the origin accurately, with the y-intercept very close to zero.
- The first derivative of the function must provide a smooth and gradual increase with no local fluctuations.

The selection of the smoothing parameter (p) in CSAPS smoothing spline function varies for each sample, not being able to use the same “p” value for all CNFs/CMFs. Figure 1 shows the differences between CSAPS smoothing spline functions using

Fig. 1 Selection of the optimum p parameter of CSAPS smoothing spline function. Experimental data are fitted to the traditional quadratic fit; **a** “p” value of 0.99; **b** “p” value of 0.9999; **c** “p” value of 0.99999999

different values of “p” parameter for the results obtained in this study with the same CNF/CMF sample. In Fig. 1a, the “p” parameter is too low, and the curve shows a y-intercept far from zero and a linear trend. In Fig. 1c, the “p” parameter is too high, and the first derivative shows local fluctuations because the curve tries to connect the experimental values without obtaining a curve. However, the y-interception is almost zero. Therefore, the optimal parameter is an

intermediate “ p ” value” as shown in Fig. 1b. As consequence, the $\emptyset_g$ calculated with different “ p ” values that does not adequately represent the gel point curve may have variations even higher than 30%. Further, the “ p ” parameter cannot be a fixed value for all samples as in some instances this value would show local fluctuations and an y-intercept very close to zero (similar to Fig. 1c); the same “ p ” value in other samples would show a line far from the origin in the y-interception as in Fig. 1a. This is the reason why each sample should be selected with an appropriate p-value that adequately represents the $\emptyset_g$ curve. For this, it will be necessary to find a mathematical model that defines a minimum p-value as shown in results, where the smoothing spline curve approaches the curve of the gel point, with a low error in the y-intercept and no local fluctuations of the curve.

Simplifying assumptions

The assumptions to simplify the $\emptyset_g$ calculation are shown in Eq. 3. The derivative is replaced by a classical assumption, an increment between a determined concentration $C_o(i)$ and a theoretical concentration of zero, $C_o(0)$. Therefore, the derivative is approximated as the quotient between the difference of concentrations and the difference in the relation of heights. Both $C_o(0)$ and $(H_s/H_o(0))$ are considered zero.

$$\begin{aligned}\emptyset_g &= \lim_{H_s/H_o \rightarrow 0} \left(\frac{dC_o}{d(H_s/H_o)} \right) \approx \emptyset_{g(est)} \\ &= \frac{C_o(i) - C_o(0)}{(H_s/H_o(i)) - (H_s/H_o(0))} = \frac{C_o(i)}{(H_s/H_o(i))} \quad (3)\end{aligned}$$

$\emptyset_g$ is the experimental gel point, $\emptyset_{g(est)}$ is the estimated gel point for a specific $H_s/H_o(i)$ and $C_o(i)$ the selected initial concentration.

Methods

Determination of the optimal concentration

The selection of the best initial concentration ($C_{o,opt}$) requires a compromise solution. On the one hand, to obtain the minimum difference between $\emptyset_{g(est)}$ and the experimental $\emptyset_g$, the closer the initial concentration to

zero, the better. However, on the other hand, when the H_s/H_o ratio is measured in graduated cylinders, the experimental error is significant at low H_s/H_o (low initial concentration) and decreases at higher values.

Therefore, the determination of a relation between $C_{o,opt}$, to calculate $\emptyset_{g(est)}$, and $\emptyset_g$ should be analyzed. For that, 25 gel point curves were studied from multiple CNFs/CMFs, most of them from published studies (Ang et al. 2020; Raj et al. 2016a; Sanchez-Salvador et al. 2020a) and others not published, and used to evaluate their relation and the best correlation as a function of $\emptyset_g$. From them, the points of the curves C_o vs H_s/H_o were used to obtain H_s for each point, the quadratic fit and also the smoothing spline fit calculated without local fluctuations nor y-intercept far from zero, as Fig. 1 indicates.

An example to determine the $C_{o,opt}$, from a gel point curve previously graphed, is shown in Fig. 2. The orange line shows $\emptyset_{g(est)}$ of a sample curve for each H_s/H_o (Eq. 4), assuming Eq. 1 to calculate C_o . On the other hand, $\emptyset_{g(est)}$ obtained from experimental points are shown with the orange bullets, observing, as expected, a greater deviation at low H_s/H_o .

$$\begin{aligned}\emptyset_{g(est)} &= \frac{C_o(i)}{(H_s/H_o(i))} = \frac{a(H_s/H_o(i))^2 + b(H_s/H_o(i))}{(H_s/H_o(i))} \\ &= a(H_s/H_o(i)) + b \quad (4)\end{aligned}$$

$\emptyset_{g(est)}$ increases with C_o and moves away from the $\emptyset_g$ calculated by the quadratic fit (grey line, Fig. 2). As previously mentioned, the $\emptyset_g$ quadratic fit is forced to

Fig. 2 Estimated gel point ($\emptyset_{g(est)}$) vs. Initial concentration (C_o). Obtention of the optimal initial concentration to simplify gel point method

have an independent term equal to zero. Therefore, the “b” parameter is slightly lower than the quadratic fit with independent term and the smoothing spline fit. However, the quadratic fit is useful to describe the $\emptyset_g$ curve as in Eq. 4. On the other side, $\emptyset_g$ calculated with the smoothing spline of MATLAB (green line), this line crosses the $\emptyset_{g(est)}$. The exact interception depends on the “p” parameter selected that gives a different $\emptyset_g$ value, as mentioned in Sect. 2.1.

To consider the experimental error due to the visualization of the H_s using the common 250 mL graduated cylinders, we assumed an estimated error of $H_s \pm 1$ mL. H_s/H_o and $\emptyset_{g(est)}$ were recalculated for each sample using Eq. 4, substituting H_s/H_o by $((H_s \pm 1)/H_o)$. The experimental error effect is shown in Fig. 2 by the dashed blue lines indicating the maximum lower and upper error.

Comparing $\emptyset_{g(est)}$ with the possible experimental error, the upper blue line shows a minimum error value at the concentration indicated by the red line. Reading the initial concentration in the red line it is possible to obtain the $C_{o,opt}$ and $\emptyset_{g(est)}$ with the minimum deviation. At this point, the difference between $\emptyset_{g(est)}$ and $\emptyset_g$ calculated with the smoothing spline and a correct estimation of the “p” parameter is minimum.

Experimental validation

To validate the simplifications of the new methodology, sedimentation experiments of 8 different types of CNFs and CMFs were carried out preparing suspensions at different initial concentrations. Three cellulose sources (cotton, eucalyptus and recycled paper) were tested to validate the simplifications with a wide range of morphologies and chemical compositions in order to try the method for all kinds of CNFs/CMFs. All samples were treated in a PANDA PLUS 2000 laboratory homogenizer (GEA Niro Soavi, Parma, Italy) at different passes and pre-treated with mechanical or chemical processes or not pre-treated. The characterization of the different samples, according to Sanchez-Salvador et al. (2020b), is summarized in Table 1.

The CNF/CMF suspensions at different C_o were prepared using deionized water and stirred. 200 μ L of crystal violet 0.1 wt. % was added to dye the fibers. 250 mL of each suspension were settled into graduated cylinders until the sediment reached a steady

value to obtain the complete deposition of fibrils. H_s/H_o values were used to build the gel point curves.

Results

Comparison of the two mathematical methods to select the optimal initial concentration

$C_{o,opt}$ vs. $\emptyset_g$ was calculated from 25 gel point curves from CNFs/CMFs with different raw materials and treatments. The quadratic fit and the smoothing spline method were used to calculate $\emptyset_g$ and to compare both methods in the estimation of $C_{o,opt}$. In a first approximation to compare both fits, the “p” parameter of the smoothing spline function was selected to obtain a y-intercept less than 0.01. A MATLAB script to determine a suitable p value for each sample is shown in Supplementary 2, which inputs are the experimental points of the curve C_o vs. H_s/H_o , and the outputs are the $\emptyset_g$, the p value calculated and the value in the y-interception. $C_{o,opt}$ was calculated as shown in Fig. 2; it does not depend on the $\emptyset_g$ methodology, just to calculate the error regarding them. For further details, Supplementary 3 presents an example calculating $C_{o,opt}$.

The relationship between $C_{o,opt}$ and $\emptyset_g$ is observed in Fig. 3, which represents the errors between the $\emptyset_{g(est)}$ calculated from Eq. 3 with $C_{o,opt}$ as initial concentration and the experimental $\emptyset_g$ for each methodology. Figure 3 shows that in both cases, the relationship between the $C_{o,opt}$ and the experimental gel point is almost linear without significant differences in the residual sum of squares.

However, as Fig. 4 indicates, the error between the experimental $\emptyset_g$ and $\emptyset_{g(est)}$ is different when using the smoothing spline or the quadratic fit methods. When the quadratic fit method is used, the average error for all samples shows that $\emptyset_{g(est)}$ is higher than $\emptyset_g$ in $12.2\% \pm 8.1$, whereas when using the smoothing spline fit, the average error is inferior with a value of $-7.8\% \pm 6.4$. In both cases, the error is biased and depends on the value of $\emptyset_g$.

As Fig. 4 indicates, the quadratic fit is not the best tool to estimate adequately the gel point due to the large deviations between $\emptyset_{g(est)}$ and $\emptyset_g$. However, the smoothing spline option with a “p” value according to a fix y-interception is not adequate either because, for low gel point values, the errors are higher than for high

Table 1 Characterization of CNF/CMF hydrogels used to validate the methodology

Source	1	2	3	4	5	6	7	8
	Cotton			Recycled paper			Eucalyptus	
Pretreatment	Commercial cellulose powder from cotton linters No pretreated			Refining 5000 revolutions	TEMPO-mediated oxidation, 10 mmol/g pulp of NaClO		Refining 5000 revolutions	TEMPO-mediated oxidation, 5 mmol/g pulp of NaClO
Treatment	Homogenization 2 steps, 300 bars	Homogenization 2 steps, 300 bars 2 steps, 600 bars 2 steps, 900 bars	Homogenization 2 steps, 300 bars 2 steps, 600 bars 2 steps, 900 bars	Homogenization 6 steps, 600 bars	Homogenization 4 steps, 600 bars		Homogenization 2 steps, 300 bars	Homogenization 6 steps, 600 bars
Preparation ϕ_g sample	Low agitation, Magnetic stirring	Low agitation, Magnetic stirring	Low agitation, Magnetic stirring	High agitation, Overhead stirrer	Low agitation, Magnetic stirring	High agitation, Overhead stirrer	Low agitation, Magnetic stirring	Low agitation, Magnetic stirring
CNF/CMF Characterization								
Nanofibrillation yield (%)	< 5	< 5	39		78		5	>95
Transmittance 400 nm	7.1	2.1	1.8		15.4		17.5	83.5
Transmittance 800 nm	11.7	9.2	8.7		35.7		29.4	94.8
Polymerization degree (Monomeric units)	232	229	703		201		930	440
Carboxylic groups (mmol/g)	0.06	0.06	0.07		0.81		0.13	0.59

Fig. 3 Relation between the optimal initial concentration ($C_{o,opt}$) and the experimental gel point ($\varnothing_g$)

Fig. 4 Errors between the estimated gel point and the experimental gel point

gel point values. Therefore, an alternative is developed to calculate the gel point using the smoothing spline tool but optimizing the “p” parameter for each case.

Optimization of “p” parameter in smoothing spline as a function of gel point to select the optimal initial concentration

To avoid a biased error that depends on the value of $\varnothing_g$, the y-interception error was set as a function of $\varnothing_g$ using 7 conditions: (a) $< 0.0005 \cdot \varnothing_g$; (b) $< 0.001 \cdot \varnothing_g$; (c) $< 0.0015 \cdot \varnothing_g$; (d) $< 0.0017 \cdot \varnothing_g$; (e) $< 0.002 \cdot \varnothing_g$; (f) $< 0.0025 \cdot \varnothing_g$; (g) $< 0.005 \cdot \varnothing_g$. A new MATLAB script (Supplementary 4) that replace the condition of a y-interception under 0.01 by the conditions a–g, in function of the $\varnothing_g$. Figure 5 relates the $C_{o,opt}$ and the experimental gel point with different y-intercept as function of $\varnothing_g$. The curves can be linearly adjusted in the same way as in Fig. 3 without significant

differences. Figure 6 shows the error between the experimental and estimated $\varnothing_g$ from these gel point estimations. The best results are obtained with a y-intercept error under $0.0015 \cdot \varnothing_g$ although the lower sum of squared residuals is obtained with a y-intercept error $< 0.002 \cdot \varnothing_g$. When the y-intercept error is under $0.001 \cdot \varnothing_g$, some samples have local fluctuations in the MATLAB curve. A high y-intercept error (under $0.005 \cdot \varnothing_g$) also shows a bad estimation with a high sum of squared residuals.

Validation of the assumptions to simplify gel point method

In order to validate the simplified gel point methodology, the results of full sedimentation experiments from 8 different CNF/CMF samples (presented in Table 1) are considered (Fig. 7).

From Fig. 7, the experimental gel point, using both the quadratic fit and the best smoothing spline fit (y-intercept under $0.0015 \cdot \emptyset_g$), were calculated (Table 2). In most of the cases a higher $\emptyset_g$ using the smoothing spline fit is observed. From the $\emptyset_g$ calculated by this last method, the $C_{o,opt}$ for a single experiment is calculated with Eq. 5 (obtained from Fig. 5). Calculation of $C_{o,opt}$ is not possible for the sample 1 as the $\emptyset_g$ range in Eq. 5 is up to around 30, since the nanocellulose is more in the form of nanocrystals instead of nanofibers. Therefore, $\emptyset_g$ reaches a value of 317 which indicates a very low AR of around 10, usually corresponding to nanocrystals. For sample 2, the proximity of $\emptyset_g$ with the range limit allows the calculation of $C_{o,opt}$. The differences between both mathematical methods are due to the forced fit without the independent term of the quadratic fit. Therefore, while the quadratic fit is a good tool to estimate a value in the curve C_o vs. H_s/H_o , it is not the best method to obtain $\emptyset_g$.

$$C_{o,opt} \left(\frac{kg}{m^3} \right) = 0.0572 \cdot \emptyset_g \left(\frac{kg}{m^3} \right) - 0.0127 \quad (5)$$

Table 3 shows the $\emptyset_g$ (est) for several experimental points (red zone), calculated for the different types of CNFs/CMFs and C_o from Fig. 7 and Eq. 3. In addition, $\emptyset_g$ (est) was calculated for $C_{o,opt}$ (green zone). In this case, H_s/H_o was obtained from the resolution of the quadratic fit of the data in Fig. 7 at $C_{o,opt}$ and using Eq. 3.

The results show that comparing $\emptyset_g$ (est) at the $C_{o,opt}$ with the smoothing spline fit $\emptyset_g$ the errors are under 7%. $\emptyset_g$ (est) in the experimental points at C_o similar to the $C_{o,opt}$ are also closer to the $\emptyset_g$ obtained with the sedimentation curve and the smoothing spline fit. Concretely, bold marked results in Table 3 show the results with an error under 7% respect to the smoothing spline fit. This fact indicates a certain versatility in the selection of C_o which would allow the use of a C_o in the same order of magnitude of $C_{o,opt}$ with a tolerable error without affecting the result to a greater extent. Some clarifications could be done in sample 4, whose $C_{o,opt}$ is 0.074 kg/m^3 , half of minimum C_o studied (0.15 kg/m^3), and would show an error slightly higher, around 12% at this concentration. On the other hand, sample 8 shows a low error during a wide

Fig. 5 Relation between the optimal initial concentration and the experimental gel point using the difference with the y-intercept as function of $\emptyset_g$

Fig. 6 Errors and statistics between the estimated gel point and the experimental gel point using the difference with the y-intercept as function of $\bar{O}_g$

Fig. 7 Initial concentration of CNFs/CMFs vs. H_s/H_o

Table 2 Gel point and optimal initial concentration for the CNF/CMF samples using the quadratic fit and the smoothing spline function

Sample	Quadratic fit	Smoothing spline ($< 0.015 \cdot \emptyset_g$)	
	($\emptyset_g$)	($\emptyset_g$)	($C_{o,opt}$)
1	281	317	Out of range
2	28.4	31.2	1.77
3	2.12	2.31	0.119
4	1.39	1.52	0.074
5	2.71	2.84	0.150
6	3.63	4.00	0.216
7	2.08	2.02	0.101
8	25.0	25.5	1.44

interval of C_o . This fact is associated to a more linear trend in the curve C_o vs. H_s/H_o in this sample, compared to a more pronounced curvature in the others.

Since $\emptyset_g$ is used as a tool to estimate AR of CNF/CMF samples, AR was calculated in Table 3 according to the Eq. 6, employing the Crowding number theory (CN) and assuming a cellulose density of 1500 kg/m^3 (Varanasi et al. 2013).

$$\text{AspectRatio} = 5.98 \cdot \left(\frac{\emptyset_g \left(\frac{\text{kg}}{\text{m}^3} \right)}{1000} \right)^{-0.5} \quad (6)$$

As Eq. 6 indicates, AR is inversely proportional to the square root of $\emptyset_g$. Therefore, the error between the AR using smoothing spline and AR with the $C_{o,opt}$ decrease with respect to the $\emptyset_g$ error, reaching always values under 3%.

Considerations to apply the simplify gel point methodology

The application of this simplification to measure $\emptyset_g$ in CNFs and CMFs does not require the previous preparation of the $\emptyset_g$ curve with more than 5 graduated cylinders. However, the selection of the C_o is a key factor to obtain an adequate $\emptyset_{g(est)}$, so a second additional experiment may be required in case of not obtaining a favourable result in the first one, using the Eq. 5 to recalculate a new C_o according to the $\emptyset_{g(est)}$ obtained in the first sample.

To select C_o in the first experiment, the recommendation would be to obtain a sedimentation height around 4–12% of the total height, since a lower value would be difficult to measure with precision, and a higher H_s would cause a great deviation in the substitution of the derivative for an increment (Eq. 3), moving away from the limit H_s/H_o close to zero. The selection of C_o depends on several factors as the raw material, the pretreatments or the intensity of the mechanical treatment.

A first approximation to select the value of C_o for the first graduated cylinder could be carried out according to the pretreatment process:

- Refining: from $0.05\text{--}0.5 \text{ kg/m}^3$, using lower C_o values as refining intensity increases.
- Enzymatic pretreatments: around $0.2\text{--}0.5 \text{ kg/m}^3$ due to the ratio length/diameter is very similar after pretreatment and mechanical treatments.
- Samples in a powder state: The decrease in length produces a lower AR and higher $\emptyset_g$ as commercial cellulose powder from cotton linters, so the C_o should be higher, $> 1 \text{ kg/m}^3$.
- TEMPO-mediated oxidation: from 0.5 to 3 kg/m^3 , using higher C_o values as the oxidant dose increases.

In addition, the intensity of the mechanical treatment, as high-pressure homogenization, also produces a variation in the selection of C_o . In general terms, a high intensity in the mechanical treatment requires a low C_o within the established ranges due to an increase of AR except in TEMPO-mediated oxidation, in which the intense mechanical treatment promotes not only the separation of the fibers, but also helps in the shortening of the fibers affected by the previous TEMPO-mediated pretreatment, increasing probably the $\emptyset_g$ and, therefore, C_o .

After completing the first experiment $\emptyset_{g(est)}$ is calculated and the $C_{o,opt}$ is obtained from Eq. 5. If the values of C_o and $C_{o,opt}$ are too different, a second experiment should be carried out using a new C_o close to $C_{o,opt}$. The results of the CNF/CMF samples studied in Table 3 show that at least when C_o is in the interval $(0.5 \cdot C_{o,opt}, 1.5 \cdot C_{o,opt})$, the $\emptyset_{g(est)}$ error is under 7% in all cases. This approach cannot be used for micro or nanocrystals, since the AR must be higher than 30.

Table 3 Estimation of $\emptyset_g$ and AR using different initial concentrations

$\emptyset_g$ sample	$\emptyset_g$ using smoothing spline	$\emptyset_g$ (est) at different C_o (kg/m ³)—Experimental points						$\emptyset_g$ (est) at the $C_{o,opt}$ (according Eq. 5)		
		~ 0.15	0.2–0.25	0.5–0.75	~ 1	~ 1.5	~ 3	$C_{o,opt}$	$\emptyset_g$ (est)	Error with smoothing spline
1	317	–	157		295	311	308	Out of range		
2	31.2	–	21.6	28.1	–	30.7	31.5	1.77	30.3	2.8%
3	2.31	2.33	2.50	3.23	3.44	–	–	0.121	2.36	2.0%
4	1.52	1.69	1.97	2.68	2.94	–	–	0.074	1.60	5.5%
5	2.84	2.78	2.99	3.54	3.74	–	–	0.154	2.91	2.4%
6	4.00	3.95	4.17	5.28	5.68	–	–	0.217	4.22	5.5%
7	2.02	2.03	2.36	2.51	2.83	–	–	0.101	2.14	6.2%
8	25.5	26.7	25.5	25.0	25.4	25.7	–	1.45	25.6	0.6%
AR sample	AR using smoothing spline	Estimation AR at different initial concentrations (kg/m ³)						Aspect ratio using the $C_{o,opt}$		
		~ 0.15	0.2–0.25	0.5–0.75	~ 1	~ 1.5	~ 3	$C_{o,opt}$	$\emptyset_g$ (est)	Error with smoothing spline
1	10.6	–	15.1	–	11.0	10.7	10.8	Out of range		
2	33.9	–	40.7	35.7		34.1	33.7	1.77	34.3	1.4%
3	124	124	120	105	102	–	–	0.121	123	1.0%
4	153	145	135	116	110	–	–	0.074	149	2.6%
5	112	113	109	101	98	–	–	0.154	111	1.2%
6	95	95	93	82	79	–	–	0.217	92	2.6%
7	133	133	123	119	112	–	–	0.101	129	3.0%
8	37.4	36.6	37.4	37.8	37.5	37.3	–	1.45	37.3	0.3%

Conclusion

Nanocellulose is arguably the emerging nanomaterial of the last two decades. However, its full industrial deployment depends on the ability to conveniently characterize and control its quality during manufacturing. The gel point methodology is commonly used to calculate its aspect ratio (L/D) and could also be used to optimize its dispersion degree. However, sedimentation experiments are most tedious to perform which difficult its implementation in industrial environments and are certainly incompatible with industry environment and practice.

This study shows that the gel point can be estimated using one or two sedimentation experiments and selecting an optimal initial concentration ($C_{o,opt}$), based on the minimal experimental error and on a simplification of the gel point equations. The main simplification is that the derivative is replaced in a classical interpretation by an increment between a determined concentration and a theoretical

concentration of zero. Therefore, the derivative is approximated as the quotient between C_o and H_s/H_o .

The two usual methods to calculate $\emptyset_g$, the smoothing spline and the quadratic fit, were compared. We conclude that the smoothing spline is generally the most reliable method, provided that the smooth spline fitting parameter is chosen correctly. Here, for the first time, an objective criterion for determining the appropriate smoothing spline parameter is presented.

The results obtained with the fitting procedures were validated with independent full studies of eight CNF/CMF samples. It was possible to estimate the gel point from a single sedimentation experiment at the $C_{o,opt}$. The difference between the experimental $\emptyset_g$ obtained by the $\emptyset_g$ curve and the $\emptyset_{g(est)}$ from the simplification was under 7% for all samples and under 3% in the case of the aspect ratio estimation. This was achieved with the smooth spline fitting parameter calculated using a MATLAB script in which y-interception in the curves C_o vs. H_s/H_o was $< 0.0015 \emptyset_g$. The main drawback of this simplification is the a priori

selection of the $C_{o,opt}$, so in some occasions if the selected C_o is too far from the $C_{o,opt}$, the selected C_o is not adequate and a new sedimentation experiment is required using the equation that relates ϕ_g and $C_{o,opt}$.

This new method shows that the sedimentation experiments can be reduced by a factor of 2.5–5 and is a promising tool to easily control nanocellulose quality and effectiveness during the different applications, compatible with industrial environments.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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