Original Article

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Evaluation of the dissolving ability of cellulosic pulps: investigation of a novel method using light scattering follow-up during classical cellulose carbanilation

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Abstract: The aim of the present study is to investigate the dissolving ability of a cellulosic substrate using a derivatization method, i.e. cellulose tricarbanilation and the follow-up by dynamic light scattering (DLS), for particle size measurement. The dissolving behavior of six commercial pulps, selected for their different nature and properties, were compared to the Fock test, and the analysis was completed by other methods for substrate characterization: crystallinity (XRD), DPv (in CuED), sugar analysis, molecular weight distribution (MWD) of cellulose by HPSEC-multidetectors (done on the cellulose tricarbanilates), and solubility in NaOH:urea:water. The proposed carbanilation/DLS method resulted practical and suitable for evaluating the dissolving ability of the different pulps – including hemicelluloses-containing kraft pulps – and allowed to discriminate the samples, contrary to the Fock test. Comparison and assessment of the relevance of the different methods are finally discussed.

Keywords: cellulose carbanilation; cellulosic pulp; dissolution ability; dynamic light scattering.

1 Introduction

In the context of the development of lignocellulosic biorefineries, the market demand for specialty pulps (so-called "dissolving pulps") has raised during the last two decades (Kumar and Christopher 2017; Liu et al. 2016). These pulps are designed for chemical applications, and not cellulosic fibers with high strength for paper and board manufacturing. Dissolving cellulose means to break the strong hydrogen bonds in between the cellulose chains and to replace those by interactions with a solvent or by derivatization of the cellulosic OH-groups (Röder et al. 2013). Low dissolving pulp grades exhibit a cellulose content of approximately 90%, while medium and high grades have a cellulose content of 94–95% and greater than 96% respectively (Liu et al. 2016). Today, 85–88% of the dissolving pulp market are produced from the Prehydrolysis Kraft and Acid Bisulfite pulping processes (Chen et al. 2019). Then, bleaching stages remove lignin whereas cold or hot caustic extraction removes the hemicelluloses (Sixta 2006). However, several studies have been performed to upgrade conventional hardwood kraft pulps (for paper applications) into dissolving pulps by using enzymatic and mechanical treatments (Tian et al. 2014).

In general, high cellulose content is required. Yet, several other parameters should be considered for the quality of a dissolving pulp i.e. in applications like viscose, the desirable intrinsic viscosity should be in the range of 400–600 mL/g (ISO 5351:2010). A uniform molecular weight distribution to ensure homogeneous reactions, as well as high α-cellulose content (>92%) (Sixta 2006). Pulps with high surface area, high porosity, and large pore size often can have high accessibility and reactivity. In summary, the key parameters to monitor in dissolving pulps include high α-cellulose content, alkali solubility, intrinsic viscosity, uniform MWD, and good accessibility, dissolving ability and reactivity.

The Fock test is widely used in research & development (especially in the textile-fibers industry) for the assessment of the reactivity of dissolving pulps. It reproduces the viscose process at lab-scale and gives the measurement of the reacted cellulose during the xanthation reaction. In this method, the pulp is mixed with sodium hydroxide and carbon disulfide, as a result, a solution of cellulose xanthate is produced (Arnoul-Jarriault et al. 2016). Cellulose is later

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regenerated by the addition of sulfuric acid; whose quantity will be used for the determination of the reacted cellulose. Östberg et al. studied some aspects of the reactivity for viscose applications and concluded that, although the Fock test is an established indicator of the reactivity of the pulps, it cannot be used as the sole indicator of it (Östberg et al. 2012). In addition, poor repeatability has been reported as an issue of the Fock test, as variations higher than 50% have been observed (Tian et al. 2013).

The dissolution ability can be also evaluated by gravimetry after cellulose dissolution in a suitable solvent, without cellulose derivatization, where the undissolved fraction is weighted. One well known solvent is the NaOH:urea:water system. This method has been already used to compare pulps, but the result is dependent on the solvent used (Golestani et al. 2017). The advantage of this method is to work in aqueous medium compared to organic solvent and soda is a rather cheap chemical, widely used in the pulp and paper industry. Cellulose dissolution takes place if the cellulose and the solvent share affinity and it has a polar character, due to the OH groups in the substrate. Dissolution proceeds first by swelling, a preliminary step where the solvent penetrates the cellulose structure to significantly alter the volume and physical properties, while at the same time the solid or semi-solid fractions remain practically unchanged. The complete dissolution is expected to fully destroy the supramolecular structure, and the polymer becomes molecularly dispersed (Medronho and Lindman 2015). The effect of alkali on cellulose fibers is mainly swelling, where the natural crystalline structure is relaxed. However, aqueous NaOH alone does not exhibit sufficient penetrating power to fully dissolved cellulose. Adding urea in the system strongly improved cellulose solubility (Kunze and Fink 2005; Zhou and Zhang 2000). Urea accumulates in the hydrophobic region of cellulose via Van der Waals forces, thus improving the solubility and stability by preventing dissolved cellulose molecules from aggregation (Xiong et al. 2014). In this solvent, the solubility increases when the temperature decreases. The more interesting results were observed when the NaOH/urea aqueous solution was pre-cooled to −12.6 °C (Qi et al. 2008). Stirring conditions are also important and experiments suggested that larger stirring blade area, longer stirring time, and higher stirring rate could improve the saturated solubility value of cellulose (Qin et al. 2012).

Considering the above conditions, a testing procedure using NaOH/urea/water solution with the ratio 7:12:81% pre-cooled to −12 °C, done under well controlled stirring conditions, could be envisaged as an interesting method to assess cellulose dissolving ability. Previous studies carried out at LGP2 (Vera-Loor 2022) demonstrated that the NaOH:urea:water system was able to dissolve various cellulosic substrates at 1 wt% concentration using temperature below 0 °C. In these conditions, cellulose solubility exhibited a rather linear correlation with the cellulose DPv. This is also a major drawback of such a test, since other substrate characteristics related to pulp nature (kraft or bisulfite wood pulps, or bleached cotton linters pulp), are much less influencing the results. This makes this test rather poorly discriminating facing other characteristics than cellulose DPv.

As stated above, there are other characteristics that should be reached in order to obtain a dissolving grade pulp, such as the uniform Molecular Weight Distribution (MWD). Size exclusion chromatography (SEC) is the main method to obtain MWD of polymers, widely used for quality and process control in the polymer industry. Since cellulose is not soluble in most organic solvents used for SEC, one possible technique is cellulose derivatization prior to analysis. In this context, the use of cellulose tricarbanilation with phenyl isocyanate, to form cellulose tricarbanilates (CTC), offers non-degrading reaction conditions for cellulose derivatization, and it has been often employed for MWD as it can be carried out without difficulty in laboratory (Danhelka and Kossler 1976; Mortha et al. 2011; Wood et al. 1986). The choice of the solvent during cellulose tricarbanilation is an issue, and previous studies have shown that cellulose can be smoothly reacted with phenyl isocyanate in the presence of pyridine forming the cellulose tricarbanilate. Although the conversion needs a large excess of phenyl isocyanate, only negligible chain degradation occurs, and rather few by-products are formed. After reaction, the excess of phenyl isocyanate is decomposed by addition of dry methanol (Barthel and Heinze 2006; Lapierre et al. 2006), or ethanol (Dupont and Mortha 2004). However, pyridine showed to be less efficient as a carbanilation solvent compared to DMSO (Mortha et al. 2011). DMSO was selected in the present study as solvent for heterogeneous carbanilation due to its reproducibility and the fact that, with good temperature control (not exceeding 65–70 °C), it does not affect the molar mass of the cellulose. The structure of cellulose tricarbanilate is presented in Figure 1.

The aim of the present work was to develop a novel method to assess the dissolving ability of a cellulosic substrate

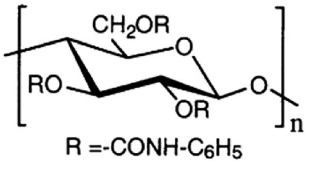

Figure 1: Cellulose tricarbanilate.

in the context of specialty pulp applications, as a complement to the Fock test which is mainly focused on dissolving pulps for textile applications (among them, the dominant viscose process), and recognized as difficult to handle and with a limited accuracy. It is proposed to focus on cellulose carbanilation as a typical and selective reactive-dissolution process (as the Fock test is), widely applied to determine the molar mass of cellulosic substrates. The originality will be to combine the advantage of monitoring cellulose dissolution by Dynamic Light Scattering (DLS) during the reaction, while acquiring the MWD profile of the tricabanilates at the end of the reaction, in the same experiment.

As in the Fock test, cellulose is derivatized during carbanilation to make it soluble. But in the proposed method, cellulose dissolution will be followed kinetically during the full process, and the follow-up will be determined by a physical measurement, i.e. particle size evolution; Also, is to be compared to a procedure that measures the solubility in the NaOH:urea:water system as a testing method. Moreover, it is expected that carbanilation will be less focused on the sole effect of cellulose DPv, but will be more sensitive to substrate nature, composition and microstructure.

In the present study, six commercial bleached pulps have been selected to evaluate and compare the three methods to characterize the dissolving ability (Fock test, solubility in NaOH:urea:water, carbanilation). These substrates come from different pulping processes and wood species. All of them were submitted to the derivatization reaction and the particle size was monitored along derivatization using DLS (a brief recall about DLS principle is given in Appendix A). Further analyses in SEC for the determination of the MWD were performed, as well as other analyses such as X-ray diffraction (XRD) for the crystallinity index, viscosity-average degree of polymerization in CuED (DPv), carbohydrate composition, and morphology analyses in order to have broader information about the cellulosic substrates. Finally, the results were compared to the Fock test, as well as to the direct dissolution in the NaOH:urea:water medium for further evaluation of the relevance of the cellulose carbanilation procedure.

2 Materials and methods

2.1 Cellulosic substrates

Six fully bleached cellulosic pulps from different origins were used: two substrates commonly used for textile applications, i.e. cotton linters fully bleached pulp (CL) and a bisulfite softwood dissolving pulp (SW-S), both supplied by French mills; and four bleached kraft paper grade pulps, supposedly having a low reactivity, referenced in the document as HW-K-1 (France), HW-K-2 (Portugal), SW-K-1 (Finland), and SW-K2 (France), where SW is softwood, and HW is hardwood.

2.2 Fiber morphology and cellulose crystallinity

Morphological characteristics involve several parameters: fiber length, crystallinity, pore structure and specific surface area. The fiber length and width were measured by MorFi analyses which allowed the monitoring of the physical changes of the fibers. The *crystallinity of cellulose* was estimated by X-ray diffraction, using a diffractometer X'Pert Pro MPD (PANalytical) equipped with a Bragg-Brentano geometry. A copper anode (Kα λ = 1.5419 Å) was used, and 2θ was varied from 6° to 60°. Several methods allow to estimate the crystallinity index, yet the Segal peak height method is the most used (Ahvenainen et al. 2016). For the estimation of the CI by the Segal method, the crystalline part is represented by the height of the highest diffraction peak, and the amorphous by the height of the minimum intensity between the major peaks. The CI is simply the difference between these two intensities, divided by the intensity of the highest (French and Santiago Cintrón 2013; Segal et al. 1959).

2.3 Carbohydrate composition

The carbohydrate composition was determined following the guidelines of *TAPPI T-249 cm-00*. 350 g (oven dried basis) sample was put in a tube, into which 3 mL of 72% H_2SO_2 was added. The tube was then placed in a water bath at 30 °C for 1 h and the sample was mixed often with a stirring rod. When the hour was finished, the solution was transferred into a 100 mL glass resistant flask, and exactly 84 mL of distilled water was added. The flask was closed and then placed in an autoclave for 1 h at 120 °C. At the end of the hydrolysis, and when the flask was cooled down, the solution was filtered and later used for the preparation of dilutions for further analysis in the DIONEX-HPLC.

2.4 Determination of Fock reactivity

The Fock test conditions have been slightly modified over the last years in order to optimize the usage of CS_2 and to correct the high variations in repeatability. The present study is based on the experimental in the improved conditions presented by Tian et al. (2013).

For xanthation and regeneration of cellulose, 0.5 g of pulp sample (oven dried basis) was weighted and introduced in an Erlenmeyer flask with a stopper. 50 mL of 9% (w/w) NaOH solution was added, this flask submerged in a water bath at room temperature with a magnetic stirrer for 10 min. Later, 3 mL of CS_2 were added and immediately the flask was closed with a stopper. The xanthation reaction took place for 3 h under stirring (250 rpm) in the water bath. When the time was up, distilled water was added to complete a total solution weight of 100 g (P_1). The solution was transferred to tubes with stoppers and later centrifuged for 15 min at 3400 rpm to separate the dissolved cellulose from unreacted cellulose. 10 mL of the supernatant was weighted (P_2) and transferred into a 100 mL round bottom flask and neutralized with 3 mL of 20% (w/w) H_2SO_4 solution. The solution was degassed under the fume hood to remove CS_2 and the cellulose was regenerated in 20 h. The

amount of regenerated cellulose (dissolved cellulose during xanthation) was measured as follows:

20 mL of 68% (w/w) H_2SO_4 solution was added to the round bottom flask and stirred for 1 h. Then, 10 mL of 1/6 M $K_2Cr_2O_7$ solution was added, and the mixture refluxed for 1 h where oxidation took place. When the mixture was cooled to room temperature, it was diluted into 100 mL. 20 mL of the late solution were transferred to a 250 mL round bottom Erlenmeyer flask. As soon as 5 mL (v_1) KI (0.1 M) was added, the solution was titrated with $Na_2S_2O_3$ with starch as an indicator. The titration volume value was used to calculate the percentage of cellulose reacted with CS_2, according to the following equation:

$$\text{Fock reactivity} = \frac{\left(c_1 v_1 - \left(c_2 v_2 \times \frac{100}{20}\right) \times \frac{1}{6} \times M_{\text{glucose}} \times \frac{1}{4} \times \frac{P_1}{P_2}\right)}{m} \times 100$$

where, M_{glucose} is the molecular weight of glucose unit (162 g/mol), m is the oven-dried weight of the pulp sample (g), v_1 is the volume of $K_2Cr_2O_7$ added (0.01 L), c_1 is the concentration of $K_2Cr_2O_7$ solution (0.1667 M), v_2 is the volume of consumed $Na_2S_2O_3$ (L), c_2 is the concentration of $Na_2S_2O_3$ solution (0.1 N), (100/20) means 20 mL diluted sample is taken out from 100 mL volumetric flask and titrated, (1/6) means each dichromate ion consumes 6 thiosulfate ions, (1/4) means each glucose unit consumes 4 dichromate ions, P_1 stands for the real mass of the xanthation solution (100 g), and P_2 the mass taken from the supernatant after centrifugation (≈10.5 g).

2.5 Cellulose tricarbanilation

Following the conditions presented in the publication of Mortha et al. (2011), the carbanilation of cellulose performed as follows: 250 mg of oven dried basis grinded cellulosic substrate were weighted in a 250 mL glass bottle with a screw cap and mixed with 25 mL of the reaction solvent, DMSO. Then it was left under stirring at 250 rpm overnight at room temperature. After 18 h, with continuous stirring, the temperature was raised to 70 °C (approximately 1 h). 5 mL of phenyl isocyanate was added slowly under stirring (t_0), followed by 20 mL of DMSO. The reaction proceeded for 48 h.

For the DLS analyses, 1 mL of the sample was collected and diluted 10 times as follows: 5 mL of DMSO and 1 mL of acetone were introduced into a 10 mL volumetric flask, followed by 1 mL of the cellulosic substrate undergoing dissolution was sampled, and the 10 mL volume was completed with DMSO. This diluted sample is later analyzed by DLS. This sampling procedure is repeated several times during the tricarbanilation reaction to monitor the particle size evolution. The repeatability of the described method was evaluated by triplicate. As for the DLS information input, a DMSO reflective index of 1.4772 and a viscosity of 1.99 mPa-s were considered at 25 °C.

2.6 Size-exclusion chromatography

For the remaining sample, 42 mL, when 8 samples were taken, 16 mL of acetone were added carefully in the hot reactional mixture. The sample was cooled down slowly while stirring. 1 mL of this solution was diluted in 10 mL of THF, and 100 µL of the diluted solution was injected in the SEC system for MWD analyses. A multi-detector HPSEC system was used for the analyses (Malvern 302 TDA (Di-angle (7°, 90°) light-scattering system operating with a 3 mW laser diode at 670 nm, 10 µL scattering cuvette, coupled to a GPCmax auto-injector), and the MWD profiles were obtained using the software OmniSEC 4.5 (Malvern Co.). Some of the parameters studied (and adjusted) include peak integration limits (based on RI signal), and molecular weight M versus elution volume fit; both influenced in a significant manner the shape of the MWD curves, the dispersity index value ($Đ_M$), and average molecular weight calculations (Mortha et al. 2011). The SEC column system used was 3 PLGEL mixed-D with a PLGEL precolumn, detectors and columns were at 35 °C, eluent was stabilised THF at a flowrate of 1 mL/min. All diluted samples were filtered through a 0.45 µm PTFE filter (Whatman) before injection in the SEC system.

2.7 Data treatment in DLS

The instrument used was a VASCO™ particle size analyzer with a light source from a diode laser emitting 657 nm. A *correlator*, which is a signal comparator, measures the degree of similarity between two signals, or one signal with itself at varying time intervals. The time at which the correlation starts to significantly decay is an indication of the mean size of the sample (Hassan et al. 2015). The DLS analyses the intensity fluctuations in the time domain. The average decay rate is estimated from the intensity autocorrelation function by means of the *cumulants* analysis method (Braun et al. 2011). The size distribution given by the DLS software is a plot of the relative intensity of light scattered by particles in several size classes and is known as an intensity size distribution. Three mathematical algorithms are used to obtain the size distribution in the DLS software. The *cumulants* method assumes that there is only one main population in the sample whose sizes respect a Gaussian distribution. The second *Pade Laplace* assumes that there are a discrete number of different sizes in the sample. The last one, *SBL* (sparse Bayesian learning), looks for a multimodal distribution and multi-disperse nanoparticle sizes (Cordouan 2019). However, *Z-average and PDI from the cumulants method* are the only parameters recommended by ISO 22412:2017, and the ones used for this study.

2.8 Dissolution test in the NaOH:urea:water system – protocol

0.25 g (1 wt%) of cellulosic substrates were dispersed in 24.75 g pre-cooled (–12 °C) solvent made of NaOH:urea:water with a ratio of 7:12:81 wt%. The liquid portion was pre-cooled in the system under agitation at 400 rpm for 15 min before adding the cellulose substrate. After the pre-cooling time, the bottle was opened and the sample transferred in with the help of a tweezer, very slowly and for exactly 5 min, while maintaining 400 rpm agitation. After the addition of the substrate, it was verified that there was no sample on the walls of the bottle. The system was closed and allowed to dissolve for 15 min. Afterwards, the solution was transferred to centrifuge tubes and sent for centrifugation for 30 min at 4000 rpm. The supernatant was removed with a pipette and the undissolved fraction was washed with distilled water until reaching neutral pH (~600 mL). The pre-weighted sintered-glass crucible (pore No. 2) used for washing, was then placed in the oven at 105 °C for 24 h. Before measuring the final weight, the hot crucible was placed in a desiccator for 15 min. The cellulose solubility (S_a) in NaOH:urea:water solution was calculated as presented in the equation below, where w_0 is the weight of the sample and w_i the undissolved fraction.

$$S_a\,(\%) = \frac{w_0 - w_i}{w_0} * 100$$

3 Results and discussion

3.1 General characterizations of the cellulosic pulps

Several analyses were performed in order to characterize the industrial bleached pulps. Table 1 lists the physical/morphological characteristics, DPv values and cellulose crystallinity. Table 2 presents the carbohydrate composition of the samples. These values will be taken into consideration in the discussion when evaluating the dissolving ability of the substrates using the three proposed methods.

3.2 Assessment of dissolution ability by carbanilation-DLS analysis

In Figure 2, the average particle diameter of colloidal particles, as measured by DLS, is followed during the carbanilation reaction of the pulp samples. The curves presented are average results from at least three repeated trials on the same sample.

During the first hours of reaction, DLS results were highly dispersed, which can be easily explained by the heterogeneity of the initial particle population (Forplex hammer-grinded fibers were used). After about 8 h, all the pulps achieved particle sizes lower than 100 nm, which stabilized during the next 40 h of the experiment (results not shown). Kinetic behaviors differ markedly in the early time of dissolution, each typically related to the type of pulp. SW-S was the faster pulp to reach particle size lower than 100 nm, in less than 4 h. It is closely followed by HW-K-1 and HW-K-2. SW-K-1 and SW-K-2 are slower to dissolve, and still, CL pulp is the slowest one in the early time of dissolution, but in the end, SW kraft pulps become slower to reach the final particle size plateau below 100 nm (where it can be noticed that CL and SW kraft pulps reached higher final particle sizes, around 70–80 nm, than HW kraft and SW-S pulps, around 50 nm).

Table 1: Main characteristics of the industrial pulp samples.

Samples	Brightness (% ISO)	DPv	Fiber length (µm)	Fiber width (µm)	Crystallinity index
CL	90	1005	909	21	89
HW-K-1	86	876	683	20	71
HW-K-2	88	692	646	16	78
SW-K-1	87	1086	1311	28	73
SW-K-2	88	797	1246	28	73
SW-S	85	1600	1346	29	73

Table 2: Carbohydrate composition (except for CL sample, which is pure cellulose).

	HW-K-1	HW-K-2	SW-K-1	SW-K-2	SW-S
Cellulose (%)	74	79	82	77	91
Hemicelluloses (%)	26	21	18	23	9
Glucomannans (%)	0	0	12	15	5
Xylans (%)	26	21	6	8	4

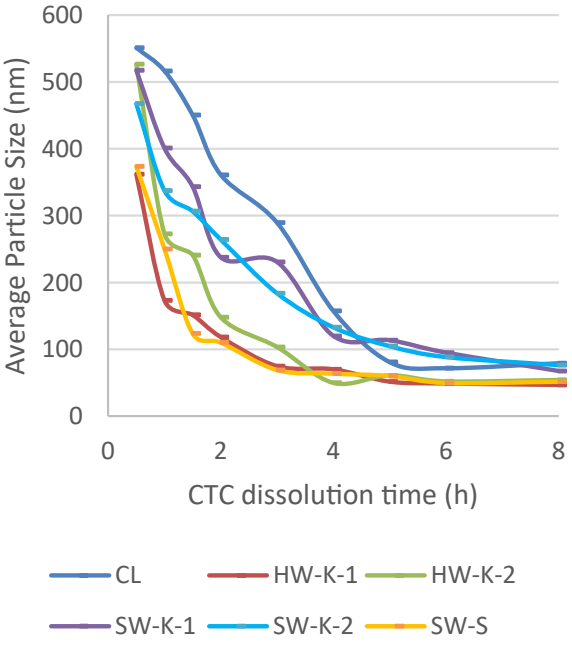

Figure 2: Average particle size 'Z' of the samples, CTC dissolution in DMSO-phenyl isocyanate.

The HW kraft pulps appeared easier to dissolve than SW kraft pulps, without any correlation with the cellulose DPv, nor with the hemicelluloses content. The different nature of hemicelluloses, mainly xylans in hardwood and glucomannans in softwood may be the reason, i.e. the derivatization efficiency or disturbances in cellulose accessibility may be linked to the hemicelluloses type.

In Table 3, a ranking of the "slowest-to-dissolve" to "fastest-to-dissolve" pulp was established based on the measured average particle size obtained at different dissolution times during the 48 h of the tricabanilation reaction. Such ranking could be used as an *index of dissolving ability*, as it is a convenient representation of what can be observed in Table 3.

Therefore, from Table 3 it is shown that the different samples exhibit well-distinguished tendencies in terms of dissolution ability. Furthermore, it seemed difficult to

Table 3: Average particle size (nm) estimated during 4 h and 8 h of the dissolution reaction.

	4 h	8 h	Ranking
Slowest	331 ± 60	251 ± 38	CL
	247 ± 33	201 ± 27	SW-K-1
	230 ± 12	187 ± 15	SW-K-2
	143 ± 35	123 ± 30	HW-K-2
	123 ± 12	97 ± 80	SW-S
Fastest	109 ± 10	92 ± 80	HW-K-1

establish some correlation with other measured properties such as the cellulose degree of polymerization, crystallinity index or cellulose content. At the same time, it was observed that the ranking of dissolution remained the same when sampling for 4 h or 8 h.

3.3 Molecular weight distribution (MWD) analysis of the derivatized samples

The derivatized samples were further analyzed by SEC, using THF as solvent, as described in the experimental section. The results obtained after a reaction time of 48 h of derivatization, are presented in Table 4 and Figure 3.

CL and SW-S samples were the least dispersed ones in comparison to the kraft pulps. The mean hydrodynamic radius (R_h) values confirmed that the particle size of all the samples were below 100 nm at the end of the reaction. Colloidal particle size values in a similar order of magnitude were observed by DLS after 8 h of derivatization. Other interesting information is presented in Table 4 such as intrinsic viscosity (IV), and the dispersity index ($Đ_M = M_w/M_n$), which expresses the narrowness of the MWD profile.

The bottom part of Figure 3 presents the MWD profiles. CL exhibited a regular monomodal profile which is generally observed in the case of well-dissolved, pure cellulose.

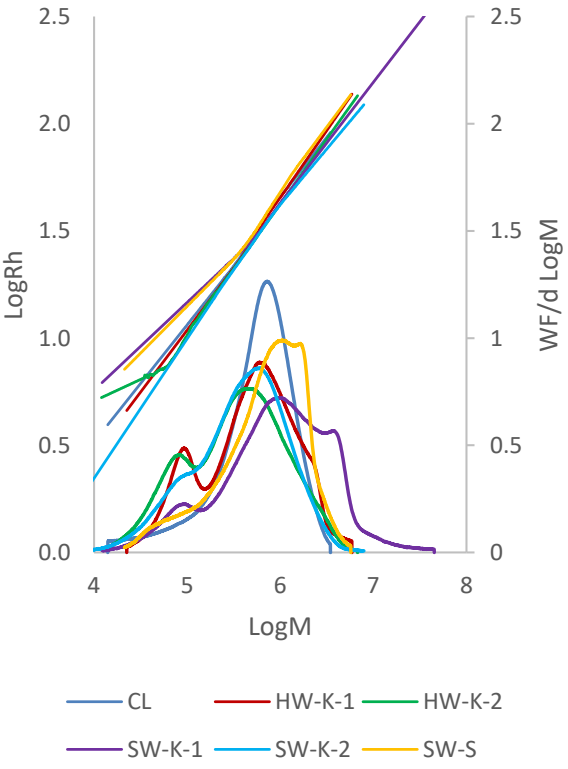

Figure 3: Log R_h versus Log M (up) and MWD profiles (bottom) of the cellulosic substrates.

A rather similar case was observed for the softwood bisulfite dissolving pulp (SW-S), which contains a low amount of hemicelluloses (<10%). But despite apparent good dissolution shown by DLS, the MWD profile presented shoulders in the high mass range, which can be attributed to persistent aggregates in the injected sample solution. This fact reveals imperfect CTC dissolution in the injection solvent in which THF, with low polarity, predominates (it also contains DMSO and acetone with higher polarities). Traces of polar groups in CTCs are likely due to incomplete derivatization and cause re-aggregation of the cellulosic chains. This was not observed by DLS since the solvent was DMSO/acetone

Table 4: SEC-multidetectors mean data of the derivatized cellulosic substrates.

Samples	Weight-average degree of polymerization (DP_w)	Dispersity index (M_w/M_n)	Intrinsic viscosity (IV, mL/g)	Weight-average hydrodynamic radius (R_h, nm)
CL	1509 ± 15	2.5 ± 0.3	445 ± 18	35.7 ± 0.6
HW-K-1	1502 ± 7	5.1 ± 0.4	426 ± 8	33.8 ± 0.4
HW-K-2	1237 ± 22	4.5 ± 0.5	282 ± 8	27.8 ± 0.5
SW-K-1	(–)	4.2 ± 0.3	637 ± 2	52.0 ± 0.2
SW-K-2	1192 ± 26	3.7 ± 0.3	303 ± 15	27.8 ± 0.4
SW-S	1869 ± 10	2.6 ± 0.4	695 ± 12	44.4 ± 0.6

Indications: DP_w measured by LALS-DRI detectors coupling; (IV, R_h) measured by viscometer-DRI detectors coupling; (–) non-reported DP_w value, affected by the presence of aggregates (*) the sulfite pulp value might also be slightly affected by the presence of aggregates, see Figure 4 curve.

(without THF). In the past, it has been often observed such re-aggregation in THF prior to SEC injection for some samples; this can be minimized by applying a suitable mild ultrasonic treatment on the diluted samples just before their injection in SEC (Lapierre et al. 2006). Therefore, SEC results in Table 4 for the SW-S pulp are affected by the presence of aggregates, leading to imperfect quantification for R_h and DPw. But in the context of this study focused on dissolving ability of cellulosic substrates, SEC curves analysis also provides some indication on the reactive dissolution behavior, facing the carbanilation reaction. Such information is complementary to the DLS profiles examination. Indeed, in this case, CL, although exhibiting slow dissolution rate by DLS, yields a more complete derivatization at final reaction time than the SW-S substrate, although the latter is more rapid by DLS. The slowness of CL dissolution is related to high cell wall compacity, high level of cellulose chains interlinkages and crystallinity degree.

For all the kraft pulps, contrary to the dissolving pulps, a second peak was observed in the lower mass range. The bimodal profile is well-known to be due to the presence of hemicelluloses or degraded cellulose. In the high mass range, it can also be seen that SW-K-1, and HW-K-1 to a smaller extent, exhibited typical aggregates-containing curve patterns. These two kraft pulps had also an incomplete reactivity with phenyl isocyanate, leaving some free –OH groups at the end of the reaction, contrary to the two others, SW-K-2 and HW-K-2. On the DLS curves, both hardwood pulps exhibited a rather fast dissolution, but SW-K-1 was significantly slower than SW-K-2.

The upper part of Figure 3 represents the relationship between the carbohydrate size (hydrodynamic radius, R_h) and the molar mass (M) which is a good indicator of the structural conformation of the substrates (Das 2012). Curves are superimposed, showing that all the derivatized cellulosic samples presented similar polymer conformations. The log R_h versus log M curve slope is related to "a", the slope of the Mark–Houwink–Sakurada (MHS) power-law relationship, by the relation: slope $= \frac{a+1}{3}$ (see explanations in Appendix B). Since the readable value of the graph slope in Figure 3 is approximately 0.57 ± 0.03, this leads to "a" exponent value in the range of 0.62–0.8, which is a normal range for well-dissolved CTCs in THF (Mortha et al. 2011).

3.4 Dissolution ability by the Fock test

Pulp dissolution ability could be assessed by commonly used method, the Fock test (Figure 4). As already mentioned, this is a reactive dissolution test using xanthation, and suited for dissolving pulps testing for viscose and other textile applications. It is shown that the CL sample did not have a good dissolution ability, compared to the other samples. This is probably due to the high crystallinity of cellulose in the CL, interfering with derivatization, as already seen by the carbanilation test followed by DLS. Nevertheless, comparing all pulps, it seems that there is a small sensitivity to discriminate the substrates from their origin. Surprisingly the Fock reactivity of the sulfite pulp does not exceed 60%, as it is a dissolving-grade pulp. This can be related to the incomplete derivatization observed during the carbanilation test. All kraft pulps exhibited Fock reactivity values in the same range, around 55%–60%, except HW-K-2 with a Fock reactivity above 75%. Again, this is rather coincident with the result of carbanilation, since HW-K-2 both exhibited fast dissolution followed by DLS, and full derivatization observed by SEC/THF. The presence of significant amounts of hemicelluloses in the kraft pulp samples (see Table 2) is certainly affecting the derivatization and consequently the measured dissolution ability by the Fock Test. The Fock test is thus not adequate for the characterization of hemicellulose-containing pulps, and therefore not suitable to discriminate pulps from different origins/processes. This highlights the need for an alternative method to evaluate the dissolution ability of hemicellulose-containing substrates.

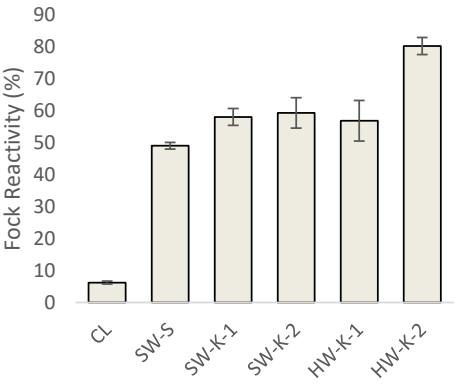

Figure 4: Fock test reactivity (%).

3.5 Dissolution in the NaOH:urea:water system

Contrary to the two methods already discussed, no derivatization occurs in this method, the dissolution is direct. In this case, the cellulosic substrates are not chemically modified, dissolution is due to the full solvation of the polymer chains after hydrogen bonds break up. The results are presented in Figure 5.

For all the samples, the cellulose solubility in this aqueous system was very low, less than 35%. A correlation between cellulose DPv and solubility was observed for wood pulps, whatever the pulping process (sulfite or kraft), or the wood specie: the

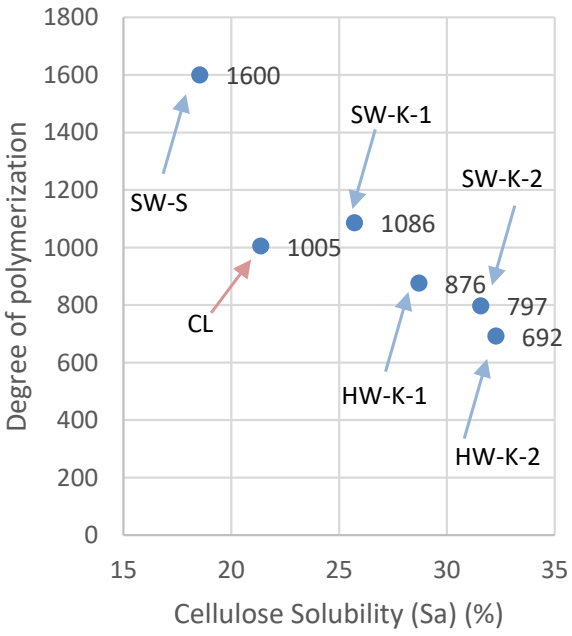

Figure 5: Solubility of the cellulosic substrates in the NaOH:urea:water system.

lower the cellulose DPv value, the higher the cellulose solubility. In this system, the solvent diffuses between the molecular chains and the reaction starts from the end-groups of the polymer chain (Xiong et al. 2014). If the chains are shorter, dissolution is faster. A rather linear relation is observed in Figure 5, except for CL, with DPv 1005, which did not follow the same tendency, and reached only 21% of solubility despite the low DPv value. SW-K-1, with a similar DPv value of 1086, reached a higher solubility, 26%, compared to CL. Two differences between CL and the wood substrates may explain the behavior: CL does not contain hemicelluloses, and exhibit a higher crystallinity, compared to the other substrates (Table 1). As soon as the substrate exhibits crystallinity of similar value, the solubility is affected mainly by the polymer chain length since the substrate accessibility is the same.

4 Conclusions

The method widely used in literature, the Fock test, which reproduces the viscose process for textile applications of dissolving-grade pulps, is affected by the presence of hemicelluloses. For this reason, in this study, the Fock test demonstrated to be not suitable for the characterization of the dissolving ability of kraft pulps. Moreover, the Fock reactivity is disturbed by high crystallinity, which may interfere with the derivatization.

A novel procedure to assess the dissolving ability of cellulosic substrates has been investigated: cellulose carbanilation, accompanied by the monitoring of particle size (by DLS) along the dissolution during the derivatization reaction. It is an indirect dissolution method, as the Fock test is, since it involves substrate derivatization to allow dissolution. The proposed dissolution test exhibited a good ability to differentiate the reactivity of various cellulosic substrates from different processes and wood species, contrary to the Fock test. An advantage of the proposed method is that, at the end of the derivatization reaction, the sample could be diluted in THF, to be later analyzed by HPSEC with multi-detectors, for the obtention of MWD profiles, as well as for other additional information such as the R_h, IV, PDI.

In conclusion, the proposed carbanilation procedure and the dissolution in NaOH:urea:water allowed to obtain valuable information regarding the dissolution ability of the studied substrates. These can be useful to deepen analyses on the dissolution ability of cellulosic substrates of various origins, before and after chemical treatments, and providing additional information for the choice of pulps for textile applications, complementing the results of the Fock test which was found poorly discriminating in the case of kraft pulps.

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Appendix A: The dynamic light scattering (DLS) principle

Particles in suspension undergo Brownian motion caused by thermally induced collisions between the suspended particles and solvent molecules (Takeo 2000). DLS is a non-invasive technique that measures particles in a dispersed medium (Boluk and Danumah 2014). The rate at which the

scattered signal changes will depend on the speed of the motion of the suspended particles, with large particles leading to slow fluctuations, and small particles leading to fast fluctuations (Braun et al. 2011). The speed of the Brownian motion is defined by the *translational diffusion coefficient*, and the size is calculated using the Stokes–Einstein equation below. The translational diffusion coefficient will depend not only on the size of the particle but also on the surface structure, as well as the concentration and type of ions in the medium.

$$d_{\mathrm{H}} = \frac{kT}{3\pi\eta D}$$

where d_{H} is the hydrodynamic diameter, D is the translational diffusion coefficient, k is Boltzmann's constant, T is the absolute temperature and η is dynamic viscosity. The diameter measured in DLS is referred to as a *hydrodynamic diameter* and it is defined by the manufacturers as the size of a hypothetical hard sphere that diffuses in the same fashion as that of the particle being measured (Niskanen et al. 2019).

In the present study, six commercial bleached pulps have been selected to evaluate and compare the three methods to characterize the dissolving ability. These substrates come from various pulping processes and wood species. All of them were submitted to the derivatization reaction and the particle size was monitored along derivatization using DLS. Further analyses in SEC for the determination of the MWD were performed, as well as other analyses such as X-ray diffraction (XRD) for the crystallinity index, the cellulose degree of polymerization (DPv), and morphology analyses in order to have broader information about the cellulosic substrates. Finally, the results were compared to the Fock test, as well as to the direct dissolution in the NaOH:urea:water medium for further evaluation of the relevance of the proposed derivatization method: carbanilation.

Appendix B: the relationship between the "*a*" exponent of the MHS power-law relationship and the slope of the log R_{h} versus log M curve representation

The MHS power-law relationship is expressed as:

$$[\eta] = KM^{a} \tag{1}$$

The Einstein law for viscosity, which defines the hydrodynamic R_{h} of a dissolved polymer pellet as a function of the intrinsic viscosity and molar mass of the chain is expressed as:

$$R_{\mathrm{h}} = \left(\frac{3\,[\eta]\,M}{10\pi N_{\mathrm{av}}}\right)^{1/3} \tag{2}$$

where: M is the molar mass; N_{av} is the Avogadro number (6.023×10^{23}); $[\eta]$ is the intrinsic viscosity; K is the MHS law pre-exponential factor; a is the MHS law exponent; R_{h} is the hydrodynamic radius.

Arranging Equation (2): $\log(R_{\mathrm{h}}) = \frac{1}{3}[\log(C) + \log([\eta]) + \log M)]$ where: $C = \left(\frac{3}{10\pi N_{\mathrm{av}}}\right)$

Then, substituting Equation (1) in Equation (2):

$$\log(R_{\mathrm{h}}) = \frac{1}{3}[\log(C) + \log(KM^{a} + \log M)]$$
$$= \frac{1}{3}[\log(C') + (a+1)\log M]$$

$$\text{where: } C' = \left(\frac{3K}{10\pi N_{\mathrm{av}}}\right) \tag{3}$$

After a final rearrangement: $\log(R_{\mathrm{h}}) = C'' + \frac{a+1}{3}\log M$

$$\text{where: } C'' = \frac{1}{3}\log\left(\frac{3K}{10\pi N_{\mathrm{av}}}\right) \tag{4}$$

The curve representation of Equation (4), as $\log(R_{\mathrm{h}})$ versus $\log M$, displays a straight line with a slope equal to $\left(\frac{a+1}{3}\right)$, where a is the MHS power-law exponent.

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