NOVEL CED-BASED RHEOLOGICAL TEST TO EVALUATE PULP REACTIVITY

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ABSTRACT

Reactivity is an important quality parameter for some grades of pulp, but its estimation is usually complex and time demanding. The study verified the possibility to utilize an alternative rheological approach to investigate pulp reactivity rapidly and with limited effort. 12.5 ml of pulp at 1.5% consistency was dissolved in 12.5 ml bis(ethylenediamine) copper(II) hydroxide solution (CED) 1 M. The reaction was monitored by a torque rheogram and its two indices: the optimal dissolution time (ODT) and the initial dissolution rate (IDR). The method used to assess pulps either hornified to different extents or subjected to enzymatic hydrolysis. ODT was shown to decrease with increasing pulp swelling, while IDR reported the opposite trend. Both the indices were shown to be sensitive to pulp treatments. However, the ODT showed larger differences between hardwood and softwood pulps. The method had reasonable statistical reliability and required only 1.5 h per measurement.

1 INTRODUCTION

In the past decade, there has been a shift in focus from traditional fiber products to higher value-added applications where the cellulosic fibers are valorized to a greater extent [1]. This includes dissolving pulp, regenerated fibers, nanocellulose, surface functionalized fibers in a wide range of product categories [2].

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In order to facilitate the development of functional cellulosic products, new measurements of pulp fiber quality are required. While a wide range of pulp fiber analysis methods exist already, these are still not adequate to fully characterize pulp performance in systems where it is dissolved, surface modified, ground into nanocellulose or otherwise functionalized. The considerable interest in regenerated cellulose, viscose, and other pulp derivatives highlights the necessity to understand the behavior of pulp under reaction conditions. For this reason, a feature called "pulp reactivity" has been introduced.

The relevance of this feature is generally recognized, especially for dissolving pulps, which are mainly utilized for regenerated cellulose and viscose [3]. For these pulps, the reactivity is probably the most significant quality parameter. Reactivity relates to the accessibility of the hydroxyl groups at C6 and C2/C3 to the reactants, the yield of added substituents, or even the time of pulp pre-aging [4]–[7]. However, a universal definition of pulp reactivity has not yet been established and disagreements about the definition or meaning of pulp reactivity often occur [4], [7].

More generically, pulp reactivity can be considered as the tendency of certain fibers to undergo chemical changes in a specific system. Each fiber component contributes to these changes. Thus, the selection of certain wood types or pulping manufacturing processes leads to different reactivities [8]. For example, the reactivity of dissolving pulps, whose percentage of cellulose accounts for more than 90%, is mainly related to cellulose reactivity, while that of other chemical or mechanical pulps is more affected by hemicelluloses.

In order to be reactive, each fiber component has to be physically accessible to the reactant molecules. Thus, characteristics such as the crystallinity of cellulose, the morphology of the fibers, the fiber pore structure (swelling, pores size, surface area, tortuosity, etc.) and the molecular size of the reagents are all crucial aspects for the success of the reactions. However, accessibility is only one facet of reactivity, and the latter takes into account several other factors, such as the structure of the substituent groups and the reaction temperature [4], [9], [10].

Given that the concept of pulp reactivity is tied to the relationship between the pulp and the conditions under which it reacts, any measurement of this feature depends on both the reactants and the reaction conditions. Despite this limitation, several measuring techniques have attempted to develop a more general measure of reactivity, and several of these focus primarily on dissolving pulps.

The most common approaches to measure pulp reactivity in the viscous process are the gamma number, the viscose filter value and the Fock's test, all which measure the amount of cellulose that remains undissolved in sodium hydroxide [6], [11], [12]. However, these methods are time-consuming. For example, a single Fock's measurement lasts approximately 2 days [11]. Thus, in the last few years, effort has been made to develop alternative measures. These include spectroscopic analyses [6], [13] and microscopic observations [12], [14], [15].

The measurement of pulp reactivity by microscopic analysis monitors the dissolution of individual fibers over time in a certain solvent, which typically is cupriethylenediamine (CED). However, this approach requires a large number of individual measurements to cover the heterogeneity of a typical pulp and achieve statistical reliability [12], [16].

In order to tackle this issue, Arnoul-Jarriault and colleagues extended the microscopic analysis to a statistical amount of fibers by utilizing an automated fiber dimension analyzer in the measurement [12]. In their approach, the pulp sample is dissolved in a 1 M CED solution for 2 minutes. Finally, the dimensions of 5000 fibers of the resulting suspension are characterized by a MorFi automatic analyzer, and pulp reactivity is defined as increasing with the increase of the width variation. This gives an indirect way to measure the amount of fiber dissolution under conditions where the pulp is partially dissolved, and the authors showed that their reactivity measures correlated reasonably well to the more traditional Fock's test.

Inspired by the above-mentioned microscopic analyses, this work aimed at measuring pulp reactivity by monitoring the dissolution of sample of pulp exposed to a 1 M CED solution at standard conditions. This specific solvent was chosen because it is safe and has been shown to be suitable in earlier reactivity studies [3], [16]. Additionally, CED effectively dissolves pulp fibers in a low viscosity solution, so it is compatible with the rheology approach we are developing.

The test presented here is called the Dissolution Torque Reactivity test (DTR test). The basic idea in the DTR test is to completely dissolve a suspension of pulp fibers in a CED solvent. When CED is added to a suspension of pulp fibers, the wood polymers begin to dissolve. This causes a change in the solution viscosity as the dissolution proceeds. By monitoring the viscosity over time one can extract information related to the dissolution rate. Essentially, pulp fibers that dissolve faster are considered to be more reactive. The DTR test is fairly quick and simple and well-suited for a laboratory test. 0.25 grams of pulp is used for a measurement, so the statistical problems associated with single fiber tests are avoided.

In this paper, the sensitivity and the consistency of the DTR method were studied for several pulps with differing reactivities. These include hardwood and softwood kraft pulps and hardwood dissolving pulp. The effect of hornification and enzymatic hydrolysis on reactivity is studied with the DTR test.

2 MATERIALS AND METHODS

2.1 Materials

Never-dried bleached kraft hardwood (NDBHW K) and softwood pulps (NDBSW K) were obtained from Finnish mills. The hardwood was birch
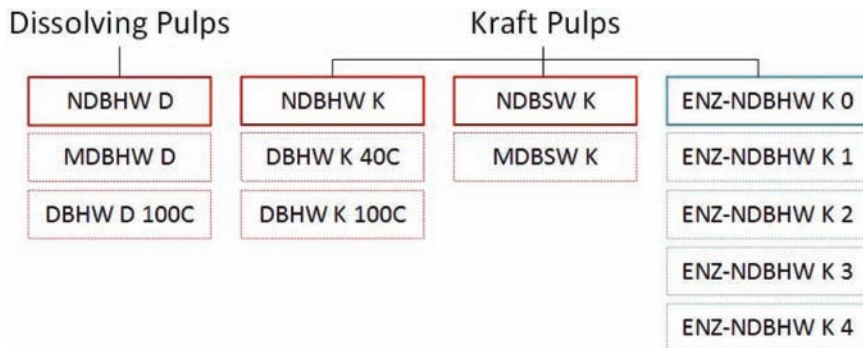
Figure 1. Summary of the reference pulps (solid boxes) and their corresponding treatments (dashed boxes). Each sample is characterized by an acronym as name. This describes both the type of treatment and the origin of the fibers. The drying conditions are represented by ND – never dried, MD – machine dried, D – oven dried. The oven temperature is reported at the end of the acronym. B stands for bleached, while HW for hardwood and SW for softwood. Dissolving pulps are distinguished by a final D, while kraft by a K. The presence of enzymatic hydrolysis is signaled by an initial ENZ, followed by a number representing the duration of the treatment. ENZ-NDBHW K 0 is the untreated reference.

(*Betula spp.*) and a softwood was a mixture of pine and spruce (*Picea abies L.* and *Pinus sylvestris L.*). A never-dried hardwood prehydrolysis kraft dissolving pulp (NDBHW D) was also obtained from a Finnish mill. The NDBHW K pulp was dried at 40 °C for 4 hours (DBHW K 40C). A portion of this sample was exposed to 100C overnight to increase the degree of hornification (DBHW K 100C). For the dissolving pulp a machine dried sample was collected at the mill and a portion of this was exposed to 100 °C overnight. (MDBH D and DBH D 100C, respectively). A machine dried sample of the softwood kraft sample was also collected (MDBSW K). Some of the NDBHW K was enzymatically hydrolyzed to different extents (ENZ-NDBHW K series). The sample matrix is summarized in Figure 1.

The enzymatic treatment was performed using ECOPULP-R (AB Enzymes), a cellulase enzyme derived from *Trichoderma reesei* and whose main activity is endo-1,4-β-d-glucanase [17]. It was used a dosage of 2 mg per gram of never dried bleached hardwood kraft pulp (dried basis), previously adjusted at 4% consistency, pH 6 and 55 °C. The relatively high dosage was chosen in order to maximize the disruptive induced by the hydrolysis. Five different samples were collected respectively after 1, 2, 3, and 4 days of exposure. For each specimen, the hydrolysis was interrupted, increasing both pH and temperature respectively up to 10 °C and 100 °C, followed by cooling a pH decreases to 8.

2.2 Pulp characterization

The pulp samples were characterized in terms of fiber swelling ability, fiber specific surface area, and cellulose degree of polymerization (DP).

Fiber swelling ability was estimated by two methods: water retention value (WRV) according to ISO 23714:2007 standard, and fiber saturation point (FSP). The latter is a method based on solute exclusion, and it was carried out by a modified version of the original test proposed by Stone and Scallan [17], [18].

The internal surface area of the pulps was measured exposing the pulps to a solvent exchange/critical point drying procedure. The BET surface area of the samples was then measured from the N_2 adsorption isotherm. More details of this method can be found elsewhere [18].

Cellulose DP was determined by applying the Mark-Houwink equation in conformity with SCAN-CM 15:99 standard.

2.3 Dissolution-based Torque Reactivity Test (DTR)

The measurement was structured into four phases: sample preparation, homogenization, data acquisition, and data analysis.

In order to ensure reasonable precision and allow the comparison of different pulps, the samples needed to be prepared in a consistent manner. First, the pulps were cold disintegrated in water and concentrated to a solids content of $10 \pm 1\%$ for storage. Then, before the reactivity test, the pulp suspensions were adjusted to 1.5% solid content. Deionized water was used in all dilutions.

The DTR test was carried out by a Physica MCR 300 Rheometer equipped with a 4-blades-vane and basket geometry. The inner diameter of the cylindrical cup measured 28.913 mm, while the vane was 40 mm long and with a diameter of 22 mm. The use of this geometry allowed the decrease of both slip effects and sample disturbances [20].

For each dissolution, 12.5 ml of pulp suspension at 23 °C was placed in the rheometer cell. The sample was mixed for 10 min at a constant shear rate of 200 s^{-1} with the vane set at 0.5 mm from the bottom of the cup and. Without interrupting the mixing, 12.5 ml of CED 1 M were quickly injected into the system, initiating the dissolution process.

From the moment of the injection, the torque was recorded over time. The duration of the experiment was constant and long enough for almost all the fibers to dissolve. Data were recorded at 5 s intervals for a total of 650 acquisitions. The resulting rheograms typically showed four consecutive phases: decreasing torque, linear increase of torque, nonlinear torque increase and plateau (Figure 2).

The first phase lasted in the order of a few seconds and was caused by the dilution as a result of the CED injection. For this reason, its duration was named
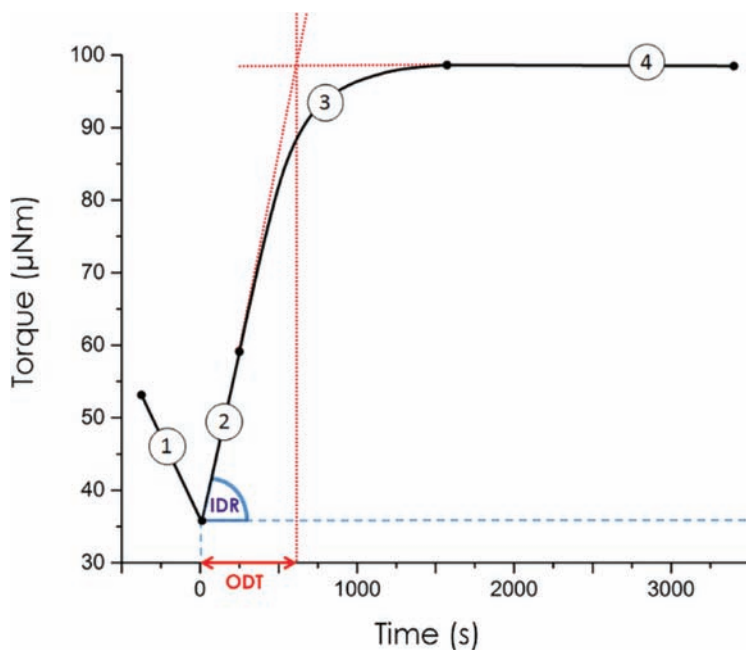
Figure 2. Schematic representation of the four phases that characterize the evolution of torque from the injection of CED till the end of the dissolution: decreasing torque, linear increase of torque, nonlinear torque increase and plateau.

"pre-dissolution time" (PDT). The dissolution was assumed to begin at the end of the pre-dissolution period, named "time-zero".

Given that shear rate and temperature were constant throughout the measurement, the increase in torque was related primarily to the dissolution of the pulp fibers in the CED solvent. The "initial dissolution rate" (IDR) was the slope of the early fast part of the dissolution process. In phase 3 the dissolution rate slowed down until the plateau was reached (phases 3 and 4, respectively in Figure 2). The final torque plateau corresponded to the end of the reaction, and it was quantified by averaging the last ten recorded values.

The DTR test assumed that the pulps that dissolved the fastest were the most reactive. Thus, by measuring the total dissolution time, it was possible to obtain an empirical value that allowed ranking and comparison of different pulps. However, the gradual leveling-off of the torque curve made the end-point of the dissolution process difficult to define. A preferred way to estimate dissolution time was to consider the intercept of a line drawn tangent to the plateau and the slope of the initial dissolution rate (Figure 2). The quantity was called "optimal dissolution time" (ODT), and it

represented the minimum theoretical time necessary to complete pulp dissolution, had the initial dissolution rate stayed constant. Thus, IDR and ODT gave independent measures of pulp reactivity in CED under constant conditions.

The results were obtained from non-smoothened curves, which were usually stable enough to carry out the measurement. However, in some cases, there were several minima after the CED injection. In these cases, it was difficult to define "time zero". For this reason, the latter was defined as the minimum torque followed by at least five progressively increasing values. Thus, the zero-time did not necessarily correspond to the lowest available torque value.

A few rheograms showed sudden torque jumps, which could be easily distinguished from the ordinary fluctuations. These anomalies were attributed to the abrupt disentanglement of residual fiber agglomerates. In each case, these plots were discarded.

Each sample was measured in triplicate, and the average recorded.

2.4 Imaging analysis

The solutions resulting at the end of the measurements were first filtered using Supor® Membrane Disc Filters (Pall Corporation), and then observed at the optical microscope (Leica ICC50 HD).

Although the main part of the filtrations confirmed that most of the sample dissolved, in some cases, a small amount of undissolved fibers remained. These residuals were critical point dried, coated with a thin layer of gold, and further studied by scanning electron microscope (Zeiss Sigma VP SEM).

The procedure used for critical point drying is described by Lovikka *et al.* [18], but in this case the samples were placed in a metallic sample holder instead of a dialysis membrane. Apart from an initial gentle shaking to avoid the presence of air bubbles, no stirring was applied. The Leica EM CPD300 was utilized to exchange acetone to liquid carbon dioxide, which was then evaporated above its critical point.

3 RESULTS AND DISCUSSION

3.1 Effects of hornification on pulp features

When pulp fibers are first dried and rewetted, their physical properties change. This process is called hornification. Hornification involves the closure of large pores in the cell wall and the loss of swelling [21]. The underlying mechanism of hornification involves the irreversible aggregation of elementary microfibrils when water is removed from the cell wall. Besides water removal, exposing pulps to high temperature increases the amount of hornification. Hornification is one of the main factors affecting pulp reactivity since it affects the accessibility to the internal regions of the

cell wall and the amount of internal surface area available for reactants [21], [22]. Dissolving pulps that are over-dried are well-known to have reactivity problems.

3.1.1 *Effects of hornification on pulp reactivity*

The rheograms of the hornified pulps (Figure 3) were analyzed in terms of the three torque-based indices: plateau, initial dissolution rate, and optimal dissolution time. The results are summarized in Figures 4, 5, and 6.

At increasing drying temperatures, both plateaus and IDR values decreased, while less hornified samples were characterized by shorter ODTs (Figures 4, 5, and 6). The only inconsistency was reported for DBHW K-samples, which resulted barely influenced by the thermal treatment.

According to these results and the statements reported by the literature, both optimal dissolution times and initial dissolution rate could be considered as representative of pulp reactivity. When the latter is higher, ODT increases and IDR decreases, and vice versa.

Dissolving pulps, whose main application is the production of regenerated cellulose, are necessarily more easily dissolved than kraft pulps, and in agreement with this, the optimal dissolution times ranked them as the most reactive. However, on the other hand, the highest initial dissolution rates corresponded to hardwood kraft pulp.

This incongruence was interpreted as due to the different nature of the two indices. The initial dissolution rates represented only the beginning of the dissolution, while the optimal dissolution times summarized the information of the whole reaction.

According to the results, IDR variations were mainly induced by the treatments, while plateau values were principally influenced by the type of pulp.
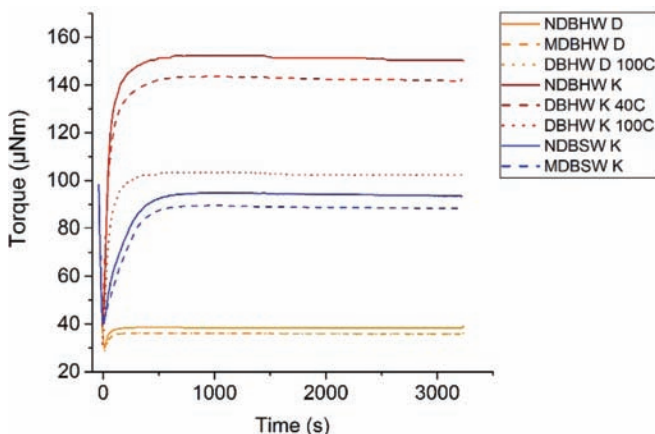

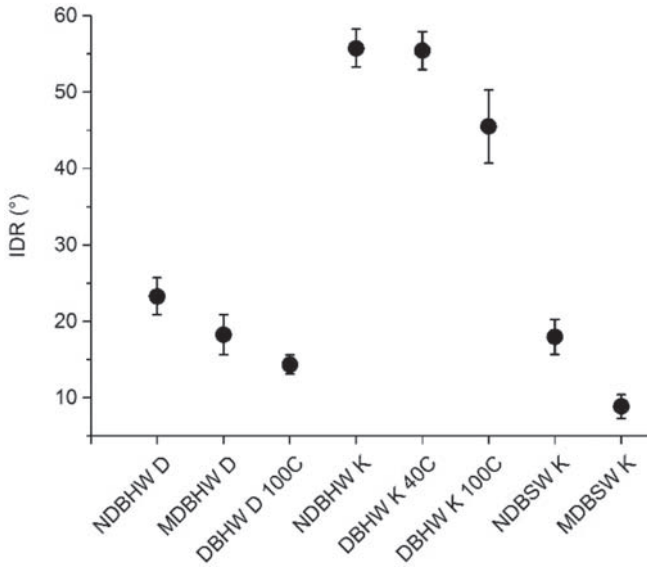**Figure 3.** Torque rheograms of the thermally treated samples.

Figure 4. Summary of the variations of the initial dissolution rate induced by drying. The bars illustrate ±1 SD.
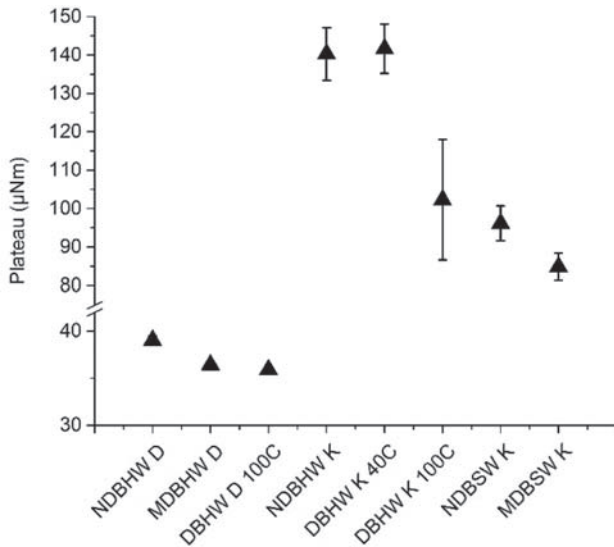

Figure 5. Summary of the variations of the torque plateau induced by drying. The bars illustrate ±1 SD.
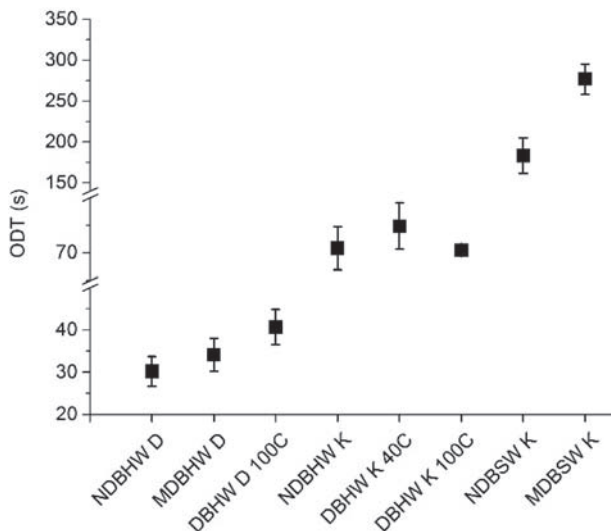
Figure 6. Summary of the variations of the optimal dissolution time induced by drying. The bars illustrate ±1 SD.

Consequently, ODTs were sensitive to the variations of pulp reactivity related to both pulp type and treatment, whereas the sensitivity of IDRs was limited.

Despite this, the value of the initial dissolution rates should not be minimized, because in several occasions the target of a pulp reactivity measures is to estimate the effects of certain treatments only. For this purpose, IDRs would be even more convenient than ODTs. In fact, they were characterized by a smaller standard deviation.

3.1.2 Pulp reactivity as a function of BET Surface Area, FSP Porosity, and WRV

Pulp accessibility and reactivity are strictly related to pulp surface area and porosity. When these values are high, solvents and reactants have larger access to the reactive groups. Thus, high surface areas and large porosities contribute actively to the increase of pulp reactivity. On the other hand, the water retention value is an empirical test that estimates the swelling ability of fibers as a function of the water retained by their cell wall [23]. Higher swelling leads to higher surface areas. Thus, also this value is representative of pulp accessibility [4].

Drying treatments are known to reduce pulp accessibility and reactivity by a phenomenon called "hornification", which consists in the tight cohesion of the

Table 1. BET Specific Surface Area (black stars), FSP (red triangles), and WRV (blue squares) of the drying series. Data extracted from Lovikka *et al.* [18]

Sample	BET Specific Surface Area (m²/g)	FSP (ml/g)	WRV (g/g)
NDBHW-D	199	0.99	1.50
MDBHW-D	104	0.54	0.91
DBHW-D100	85	0.50	0.85
NDBHW-K	225	1.33	1.67
DBHW-K40	173	1.00	1.30
DBHW-K100	150	0.87	1.15
NDBSW-K	282	1.20	1.53
MDBSW-K	–	–	1.09

fibrillar elements [21]. Consequently, dried samples are generally characterized by the decrease of pulp specific surface area, porosity, and degree of swelling. These trends were confirmed for the samples under analysis (Table 1).

The trend of pulp accessibility described by BET surface area, FSP porosity, and WRV was close, but not entirely corresponding to that estimated for pulp reactivity. Both the features decreased with the increasing drying temperatures (Figures 7 and 8). However, except for softwood kraft pulps, IDR and ODT variations resulted less incisive than those reported by the BET surface area, the FSP porosity, and the WRV. Compared to the large drop of pulp accessibility, the reactivity of hardwood dissolving pulps reported only a modest decrease, while that of hardwood kraft pulps revealed just a barely noticeable reduction.

According to these results, pulp accessibility represented only one of the several facets of pulp reactivity, and this concept was further corroborated by the comparison of the ranking of the accessibilities and reactivities of kraft and dissolving pulps. If the accessibility were equivalent to the reactivity, the latter should be less reactive than kraft pulps. Conversely, dissolving pulps measured the lowest ODT of this set of samples.

3.1.3 Pulp reactivity as a function of the degree of polymerization

The DP analysis reported lower values for dissolving pulps than for kraft pulps, but also lower values in case of more severe drying conditions. The latter trend confirmed the statements of previous studies [21], [24], [25], and it was explained as a result induced by the thermal degradation [21].

This slight decrease of cellulose degree of polymerization nicely correlated to the decrease of pulp reactivity (Figure 9 and 10). Although apparently anomalous,
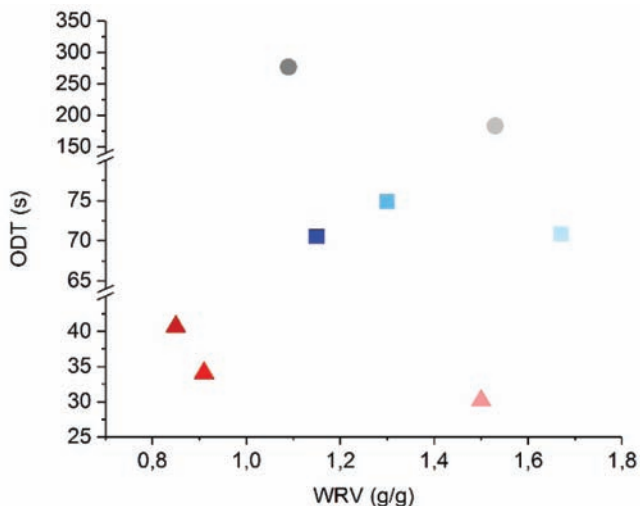
Figure 7. Optimal dissolution time as function of water retention value. The forms represent different types of pulps: circles – softwood kraft pulps, squares – hardwood kraft pulps, and triangle – hardwood dissolving pulps. The color tone becomes darker with the drying temperature.
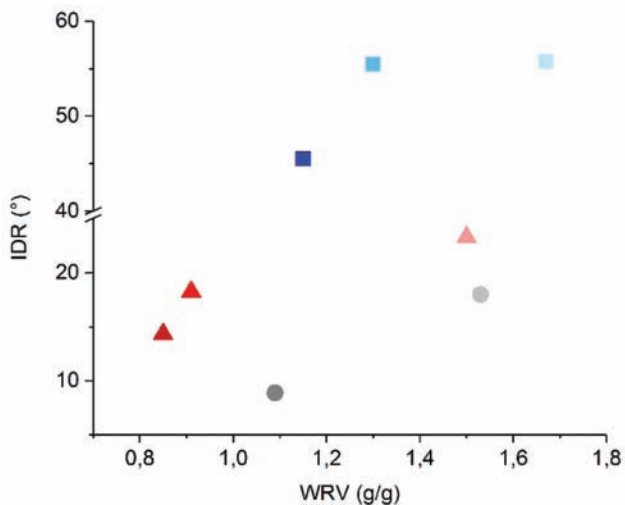

Figure 8. Initial dissolution rate as function of water retention value. The forms represent different types of pulps: circles – softwood kraft pulps, squares – hardwood kraft pulps, and triangle – hardwood dissolving pulps. The color tone becomes darker with the drying temperature.
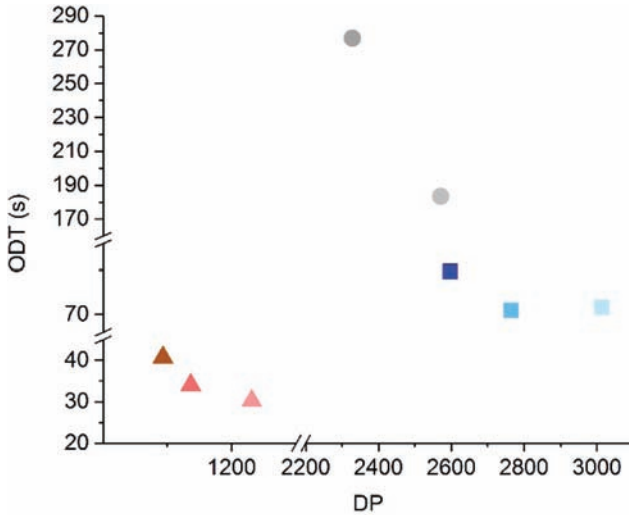
Figure 9. Initial dissolution rate as function of DP. The forms represent different types of pulps: circles – softwood kraft pulps, squares – hardwood kraft pulps, and triangle – hardwood dissolving pulps. The color tone becomes darker with the drying temperature.

Figure 10. Initial dissolution rate as function of DP. The forms represent different types of pulps: circles – softwood kraft pulps, squares – hardwood kraft pulps, and triangle – hardwood dissolving pulps. The color tone becomes darker with the drying temperature.
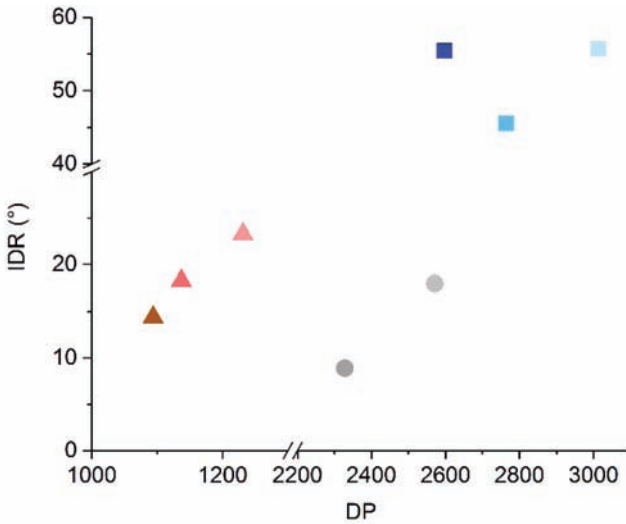
lower DPs corresponded to higher ODTs and lower IDRs. Also this behavior was attributed to the thermal degradation, and in particular to the increase of carbonyl groups associated to the decrease of carboxyl groups [21].

As already mentioned for pulp accessibility, the degree of polymerization is not the only parameter affecting pulp reactivity. Its influence interacts with other pulp features, among which surface-to-volume ratio and pore size distribution have an important role.

3.2 Effects of enzymatic hydrolysis on pulp features

The hydrolytic action of enzymes and specifically of endoglucanases is known to improves pulp reactivity considerably [26]. This leads to higher degrees of solubility in alkaline conditions [27].

The improvement of pulp reactivity produced by endoglucanases is the result of various factors, such as the decrease in DP, breakage of hydrogen bonds, the removal of the external cell walls and the destructuring of fibers at the macrostructural level [27], [28].

The reactivity of hardwood kraft pulps hydrolyzed at different extents was measured with the DTR test. The hydrolyzed samples were characterized with water retention values and degree of polymerization.

3.2.1 Pulp reactivity

The reactivity of the hydrolyzed samples was measured with the DTR test. The rheograms of the enzymatically hydrolyzed pulps (Figure 11) were analyzed in terms of plateau, initial dissolution rate, and optimal dissolution time. The results are reported in Figure 12.

The enzymatic hydrolysis results in an increase of the IDR and the decrease of both torque plateau and ODT. In other words, as the pulp was hydrolyzed, its initial dissolution rate was higher, its dissolution time shortened, and the torque plateau decreased because of the lowering DP. The trend in the data was more consistent than the DTR values for the hornified series in section 3.1.

The water retention values of the ENZ-NDBHW K-series increased with longer hydrolysis times. As the outer cell wall degraded and internal bonds were cleaved, the cell wall expanded. The endoglucanases promoted the swelling of the cell wall by attacking and hydrolyzing less crystalline regions [29]. As shown in Figure 13, the IDR and the ODT correlated well with the WRV. The increased accessibility of the cell wall and the lower DP on the cellulose explain the increase in the reactivity as measured with the DTR test.
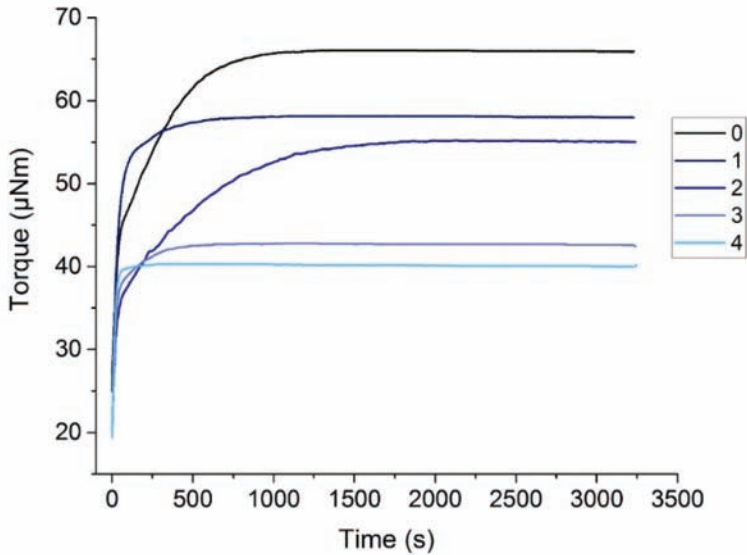
Figure 11. Torque rheograms of the enzymatically hydrolyzed samples (ENZ-NDBHW K series). The hydrolysis time is reported by colors. Longer hydrolyses corresponded to lighter tones.
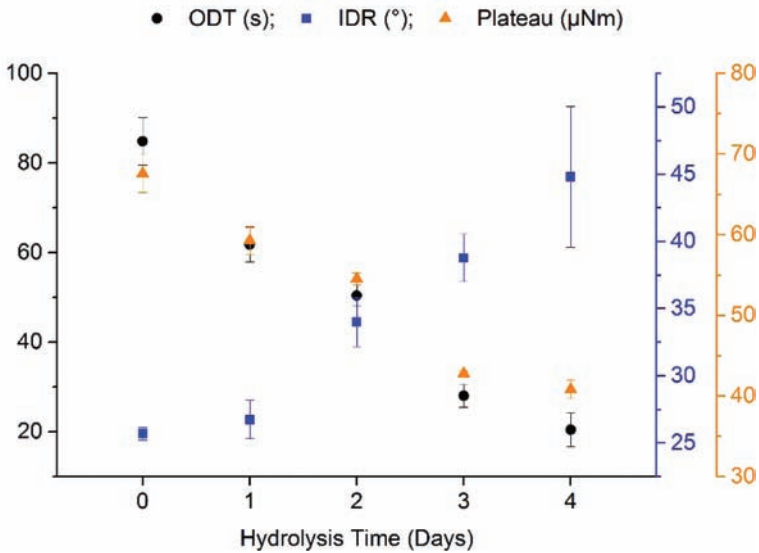

Figure 12. Summary of the variations of plateau, initial dissolution rate and optimal dissolution time induced as a function of the hydrolysis time.
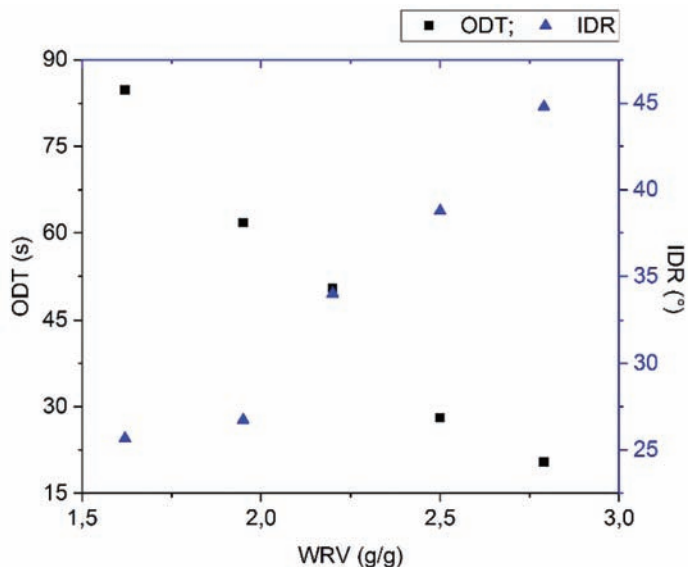
Figure 13. Evolution of optimal dissolution time (black squares) and initial dissolution rate (blue triangles) as function of water retention value.

3.3 Inspection of fiber dissolution by imaging

To prove that pulp dissolution stages were represented by torque profiles, dispersions/solutions at different stages were filtrated to estimate the amount of undissolved material.

The different degrees of dissolution could be estimated by naked eye. With the progress of the reaction, the amount of dissolved material increased. However, a numerical estimation of the undissolved material was not possible. Notwithstanding the filtration, part of the solvent remained inside and in between the fibers affecting the weight of the filtrate and preventing the permanent interruption of the reaction.

At the end of the measurement, the plateau did not correspond to a total dissolution, leaving behind about a dozen of ballooned fibers and collars per sample (Figure 14). This minimum fraction of undissolved pulp was believed irrelevant to the reliability of the CED-based pulp reactivity test, but it was studied by optical microscope and scanning electron microscope.

The images showed fibers interchanging solid to dissolved fragments (Figure 14). Moreover, the spaces between the undissolved fractions presented circular shadows. These details agreed with the well-established concept of dissolution
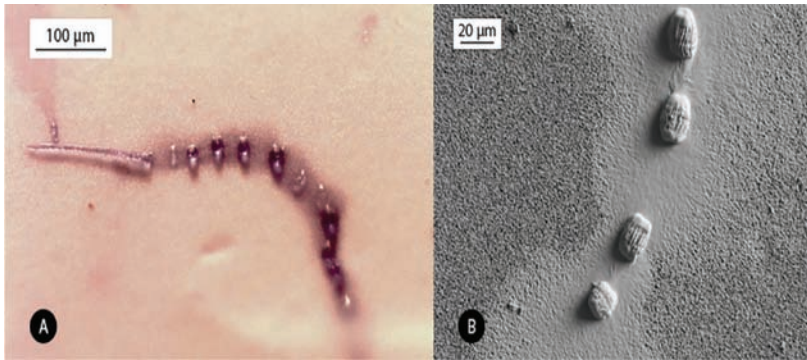
Figure 14. Fragments of undissolved MDHW-D fibers (collars) detected at the end of the plateau observed at the optical microscope (A) and scanning electron microscope (B).

via "ballooning", which states that fibers swell heterogeneously interchanging swollen structures (*balloons*) with unswollen fragments (*collars*) [28].

4 CONCLUSIONS

This study demonstrated the possibility to measure pulp reactivity by means of the rheological monitoring of pulp dissolution in CED. The resulting torque rheogram produced two indices related to the dissolution kinetics: the initial dissolution rate (IDR) and the optimal dissolution time (ODT). The first increased with pulp reactivity, while the second decreased.

The method was used to analyze several pulps, which were expected to have different reactivities. It was found, that the IDT decreased with the amount of hornification for both kraft and dissolving pulps. On the other hand, the ODT increased with hornification for the dissolving pulps, but was nearly independent of hornification in case of kraft hardwood pulps. The changes in IDR and ODT were ascribed to collapse of surface area and porosity in hornification.

When a hardwood pulp was treated with a commercial endoglucanase, the IDR decreased as a function of the hydrolysis time, while the ODT increased. The changes in reactivity were likely due to the cellulose chain cleavage and lowering of DP in hydrolysis.

The IDR had a standard deviation around ±5. On the other hand, the standard deviation of the ODT was *ca.* ±5 for hardwood species and *ca.* ±10 for softwoods.

The results proved the reliability, sensitivity, user-friendliness, and the rapidity of the DTR test: a good empirical technique for measuring pulp reactivity.

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Transcription of Discussion

NOVEL CED-BASED RHEOLOGICAL TEST TO EVALUATE PULP REACTIVITY

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Juha Salmela   Spinnova

Very nice work again, but one question about the geometry that you are using and the homogeneity of the additive you put in the solvent. How do you know that it is homogenously dispersed within the suspension?

Sara Ceccherini   Aalto University

Well, it is still a suspension. It is not a dispersion. Previously I homogenized the pulp with a normal mixer and then I let it stir for 5 minutes at a fixed shear rate. I have tried to achieve specific conditions, including homogeneity. I tested many different cases, such as different consistencies and different ratios between pulp and solvent. Whenever there is a very bad homogenization, you see very high fluctuations, especially at the beginning. This case has been reported also by the literature. There are some publications from the USA, such as Frey from 2006, which describe this phenomenon. They report these higher fluctuations at the beginning, because the pulp is not completely homogenized. So, I think there are some hints that the profile itself shows to us. It is quite visible if the pulp is not well homogenized and if we have some particular flocs which disentangle at one point or another. If I did not homogenize my pulp well at the beginning, I would have many torque drops along the curve.

Discussion

Juha Salmela

Okay, thank you. Another question about this, have you tried different geometries? Have you tried cup and bob, or plate-plate?

Sara Ceccherini

Yes, I have tried different geometries, because I have also tried other solvents, or even enzymes. I have to say that you could use the plate-plate geometry. You could change and measure even higher consistencies, but the length of the experiment is such that you might have no more good adherence after a while. So, I do not recommend it yet. These results of mine were not so satisfying. They were not reproducible enough to characterize pulp reactivity.

Juha Salmela

Okay, very good. Thanks.

Thierry Mayade   Ahlstrom-Munksjo

I like this approach which is very practical, however I have a question. When you measure the degree of polymerization according to standards by viscosimetry, it is recommended to have inert gas above the surface, because in CED you may get cellulose depolymerization and then the viscosity can decrease along the time. How did you take into account this problem?

Sara Ceccherini

Well, I did consider this factor and I could not really close my system. I still have to face this issue, so I cannot really tell you the details. I am still considering how to improve the test, I am still at the beginning. I will consider this issue during my next studies.

Jose Iribarne   WestRock

Very interesting work, CEDs have been used for a hundred years or more for measuring pulp viscosity, so we know quite a bit about that, so I will comment also on the temperature control which needs to be very important, if you did not see a decline on the final torque, it probably indicates that the degradation that Thierry was mentioning is not that intense, but may I suggest that there might be some stapling of the fibres on the spindle?

Sara Ceccherini

No, there is none. I checked it very carefully with polarized light for whatever remained there, even the material that remained, adhered to the spindle, and it was not the case.

Jose Iribarne

I was thinking may be that is responsible when a staple detaches for the dropping torque.

Sara Ceccherini

Yes, of course. I cannot say anything about that exact moment, this is true. I could verify the situation only at the end of the analysis.

Jose Iribarne

I am not sure if the intensity of mechanical action will be sufficient, but you might want to look into a Couette flow with two concentric cylindrical and you can possibly tell more on what is happening but I am not sure if it will work.

Sara Ceccherini

Okay.