

## CHEMICAL CHANGES OF CELLULOSE PULPS IN THE PROCESSING TO VISCOSE DOPE

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A selection of cellulose pulps was investigated for their chemical changes during the required process steps to viscose dope. The selection of the pulps was based on pulping process, original wood type and intrinsic viscosity. In total, five sulfite pulps and four sulfate pulps were chosen, of which all but one sulfate pulp were of dissolving grades. The physical and chemical properties of the pulps were analyzed as well as important qualitative parameters of the cellulose intermediates during mercerization, pre-aging and in the final viscose dope. Pre-aging curves were reported as a measure of each pulp's reactivity with respect to oxidative degradation, where high hemicellulose content and small pore area and pore diameter were found to hamper cellulose degradation. The correlations in pre-aged pulps of intrinsic viscosity to Mz, Mv and Mw were found to be ambiguous and show the need for a description of total molecular weight distribution of the alkali celluloses to better understand the degradation behavior of each pulp, instead of only intrinsic viscosity. It was also shown that R18 and R10 are insufficient analyses to determine pulp, and to predict viscose quality. Further, many pulps, independently of initial hemicellulose content, reached the same level of hemicellulose content after mercerization. The presence of crystalline hemicelluloses could be a possible cause for this level-off behavior, combined with hemicelluloses resistant to caustic lye treatment. The change of both low-molecular-weight celluloses and PD in the process to viscose dope was investigated due to the importance of these variables on dope spinnability and viscose fiber strength. Caustic resistance of cellulose and hemicelluloses and a more rigid fiber structure in some pulps are suggested to contribute to the different degradation behavior.

**Keywords:** aging, cellulose pulp, hemicelluloses, long fiber, short fiber, sulfate, sulfite, mercerization, molecular weight, reactivity, viscose

### INTRODUCTION

Regenerated cellulosic fibers are increasingly in focus due to their sustainability and unique performances in textiles and industrial applications.<sup>1</sup> A major group within the area of regenerated cellulosic material has its origin in the viscose fiber, discovered by the dissolution of cellulose with caustic and carbon disulfide by Cross, Bevan and Beadle in 1891. Today, the volumes of viscose fiber production have increased to almost 4 million tons per year, with only the staple fiber segment increase of 11.4% to a total of 2.7 million tons in 2010. These numbers have resulted from a shortage in cotton and an increasing requirement for comfort, which cotton cannot meet.<sup>2</sup>

The manufacturing of viscose consists in the

following steps: steeping of the cellulose pulps with caustic, pressing and shredding of the achieved activated cellulose, pre-aging of the cellulose to a set intrinsic viscosity by oxidative hydrolysis and later xanthation with carbon disulfide. After the yellow to brown cellulose xanthate crumbs have been formed, water and caustic is added for dissolution of the cellulose and the formation of the viscose dope. After filtration, the viscose dope is then pressed through spinnerets into an acid spin bath, carbon disulfide is released, while the regenerated cellulose fiber is stretched and treated for further processing.<sup>1,3,4</sup>

The steeping and aging steps are important in the production of viscose fibers, as both determine the overall processability of the

cellulose and the final fiber quality. For an effective xanthate formation and thus an effective dissolution of the cellulose later in the dissolving step, it is important that the cellulose is well mercerized during steeping in both its amorphous and crystalline regions. It is also important that undesirable short-chain materials, such as hemicelluloses, as well as  $\beta$ - and  $\gamma$ -celluloses, are removed. The removal of these celluloses is vital as they will consume carbon disulfide during xanthation and potentially deteriorate fiber quality.<sup>1</sup> The change of molecular weight and molecular weight distribution during pre-aging, and thus the final weight distribution in the fiber, is of extreme importance for the tensile properties of the cellulosic fibers.<sup>5</sup> In particular, fibers with high demand on tenacity and fatigue resistance require a pre-aged cellulose with as uniform and high molecular weight distribution as possible.<sup>4</sup>

The impact of different physical and chemical properties of cellulose pulps on viscose dope quality has been communicated earlier.<sup>6</sup> However, no information on the effect of pulp alteration during the separate intermediate steps on the viscose dope and the final viscose dope quality has been reported. The present paper addresses chemical changes of these different pulps during the intermediate steps of mercerization and pre-aging, and the way these changes can affect the spinnability of viscose dope and viscose fiber quality. Alternative analytical methods were compared to the more traditionally methods, such as intrinsic viscosity and R18/S18.

## EXPERIMENTAL

### Materials

Cellulose pulps were chosen by process type (sulfate and sulfite), as well as wood type (softwood or hardwood). For each sample, the highest and lowest

commercially available viscosity was chosen, ranging from 420 to 850 ml g<sup>-1</sup> by SCAN viscosity. Hence, the conditioning factors were established with two qualitative factors (process type and wood type) and a quantitative factor (viscosity). These samples were provided by 6 different producers. A sample with intermediate viscosity from producer B was also included. Even though producers B and C presented similar samples regarding the applied design factors, samples from both manufacturers were included to evaluate differences between them. This resulted in a set of ten pulp samples (Table 1).

### Methods

Analyses of mercury porosimetry were performed in our laboratories at Umeå University. All other analyses were done at MoRe Research in Örnsköldsvik, Sweden.

### Chemical analysis

On each of the selected cellulose pulps, chemical analyses, such as viscosity and alkali resistance with 18% sodium hydroxide (R18), as well as with 10% sodium hydroxide (R10), were performed (see Table 3). Intrinsic viscosity was measured using a capillary tube viscometer according to ISO 5351/1, whereas alkali resistance was determined according to ISO 699. Furthermore, alpha-, beta- and gamma-cellulose content was analyzed according to TAPPI T203 rev-88.

### Analysis of residual cellulose – “Fock reactivity”

An analysis of residual cellulose<sup>7</sup> was performed through three major steps. It consisted in the preparation of viscose dope from cellulose pulp, the separation of regenerated cellulose, the measurement of the residual cellulose, as well as the calculation step according to previous reports,<sup>8</sup> where residual cellulose (%) = 100% - regenerated cellulose (%). In this paper, regenerated cellulose (%) is reported as Fock reactivity. Three analyses per sample were performed.

Table 1  
Overview of investigated pulp samples, including sample number, producer, wood and process type

Sample	Producer	Wood type	Process <sup>a</sup>
1	A	HW (Beech)	Sulfite, Mg
2,3,5	B	SW (Spruce, Pine)	Sulfite, Na
4,6	C	SW (Spruce)	Sulfite, Ca
7,9	D	HW (Eucalyptus)	Sulfate, PHK
8	E	SW (Pine)	Sulfate, MK
10	F	SW (Pine, Loblolly)	Sulfate, K

<sup>a</sup> For the sulfite process, the cation used is indicated. The type of sulfate process is indicated by PHK (prehydrolysis Kraft), MK (Modified Kraft) or K (Kraft)

Table 2  
Rate of degradation during pre-aging for all cellulose pulps investigated

Rate of degradation v'	
ml g <sup>-1</sup> min <sup>-1</sup>	
A:1	2.78
B:2	2.22
B:3	2.13
C:4	2.37
B:5	2.07
C:6	2.04
D:7	2.13
E:8	1.55
D:9	2.05
F:10	1.58

Table 3  
Cellulose pulp properties of each investigated sample

Pulps		A:1	B:2	B:3	C:4	B:5	C:6	D:7	E:8	D:9	F:10
Viscosity	ml g <sup>-1</sup>	587	465	573	423	845	785	516	419	609	794
$\alpha$ -cellulose	%	91.9	92.9	92.8	92.4	93.5	94.8	97.9	91.0	98.1	89.6
$\beta$ -cellulose	%	7.6	4.9	5.5	8.0	4.8	3.7	3.6	8.2	2.9	8.9
$\gamma$ -cellulose	%	2.3	1.8	2.2	2.0	3.4	2.0	1.0	2.3	0.8	3.2
Absorption	g cm <sup>-2</sup>	0.7	0.5	0.6	0.4	0.6	0.5	0.5	0.5	0.7	0.5
Absorp rate	cm min <sup>-1</sup>	1.8	2.1	2.2	1.8	2.8	2.4	2.5	3.6	3.3	3.4
Hemicell. <sup>a</sup>	g kg <sup>-1</sup>	51	32	37	32	56	44	18	131	20	163
Xylose	g kg <sup>-1</sup>	42	16	17	22	34	27	15	70	18	86
Pore area <sup>c</sup>	m <sup>2</sup> g <sup>-1</sup>	4.0	5.7	5.1	4.0	4.3	4.0	3.4	2.4	3.5	2.0
Pore diam. <sup>c</sup>	mm	4.5	3.9	4.9	5.0	4.7	5.0	4.2	8.3	5.3	8.2
Permeab.	mdarcy	35	20	38	50	29	45	40	163	66	155
Polydisp.		12.2	7.9	8.0	6.9	9.0	8.0	4.6	5.8	4.8	8.0
Mw	g mol <sup>-1</sup>	485 500	397 154	383 647	354 086	520 837	655 788	358 058	292 104	514 295	483 635
Mn	g mol <sup>-1</sup>	39 647	50 075	47 922	51 650	57 961	59 674	78 542	50 368	106 288	60 448
Mz	g mol <sup>-1</sup>	1 448 770	1 128 330	944 096	916 896	1 218 016	1 796 578	776 672	740 331	1 149 563	1 187 755
R18	%	93.1	95.4	94.7	95.1	94.2	95.1	98.2	90.5	98.2	87.7
R10	%	88.3	89	89.4	87.3	91.4	91.8	95.2	87.1	95.6	86.8
Extractives	mg kg <sup>-1</sup>	160.8	22.1	36.5	19.3	20.6	17.4	40.8	17.8	23.7	14.9
Fock react.	%	69	86	79	91	47	49	36	31	38	34
Mercerized											
Polydisp.		6.0	4.6	5.7	4.3	5.2	5.2	3.7	3.9	3.8	5.5
Mw	g mol <sup>-1</sup>	438 634	348 338	431 583	342 491	498 206	534 019	387 787	314 229	455 868	590 215
Mn	g mol <sup>-1</sup>	68 731	69 715	78 023	77 403	99 757	118 334	105 461	76 059	106 579	112 660
Mz	g mol <sup>-1</sup>	1 065 817	754 895	1 124 564	820 688	1 167 522	1 541 953	833 623	681 844	850 897	1 520 444
Hemicell. <sup>a</sup>	g kg <sup>-1</sup>	11	7	8	7	9	10	5	40	6	59
Xylose	g kg <sup>-1</sup>	9	4	4	4	4	6	5	15	5	16
R18	%	99.8	99.1	99.0	99.1	98.9	98.8	99.5	97.2	99.6	97.1
R10	%	93.6	95.1	95.5	95.1	95.4	95.0	97.7	95.5	97.8	95.7
Aged											
Polydisp.		3.4	3.2	3.1	3.1	2.9	2.8	2.8	3.2	2.9	3.0
Mw	g mol <sup>-1</sup>	160 129	157 477	158 264	165 472	148 873	143 814	168 016	161 104	168 424	141 730
Mn	g mol <sup>-1</sup>	46 433	49 589	49 617	55 733	54 818	50 085	57 280	49 253	58 133	50 276
Mz	g mol <sup>-1</sup>	362 846	347 717	336 759	390 002	325 623	288 800	331 565	342 669	358 193	303 429
Hemicell. <sup>a</sup>	g kg <sup>-1</sup>	6	7	7	6	8	8	5	28	5	27
Xylose	g kg <sup>-1</sup>	6	4	4	4	4	5	4	11	4	9
R18	%	98.6	98.7	98.8	98.8	98.9	99.0	99.3	97.6	99.4	97.1
R10	%	94.2	93.4	93.6	93.3	95.7	95.0	96.5	95.7	96.6	95.8
Viscosity		230	228	228	231	240	234	235	256	240	235
Fock react.	%	64	53	41	54	35	33	51	21	50	18
Viscose											
Polydisp.		3.0	2.9	2.9	2.7	2.6	2.7	2.7	3.0	2.7	n/a
Mw	g mol <sup>-1</sup>	146 882	160 921	138 183	149 451	157 640	142 674	147 049	179 830	151 343	n/a
Mn	g mol <sup>-1</sup>	47 733	55 225	46 977	55 195	64 695	53 029	55 279	59 391	57 325	n/a

Mz	g mol <sup>-1</sup>	309 952	384 740	289 472	321 492	338 728	285 019	300 756	384 740	303 325	n/a
Hemicell. <sup>a</sup>	g kg <sup>-1</sup>	1	1	1	0	1	0	0	3	0	n/a
Xylose	g kg <sup>-1</sup>	1	0	0	0	1	0	0	2	0	n/a
γ-number		38	37	37	42	38	31	39	37	40	25
Kr		202	398	1124	1073	1572	499	295	10 <sup>Δ5b</sup>	514	10 <sup>Δ5b</sup>

<sup>a</sup>Total amount of hemicelluloses expressed as sum of xylose, mannose, arabinose and galactose

<sup>b</sup>This sample was assigned a high value to indicate poor filter clogging value

<sup>c</sup>An average pore area and pore diameter from pore size distribution is presented

### Carbohydrate composition

The characterization of the carbohydrate composition was performed according to a company internal procedure at MoRe Research AB. All pulps were pre-hydrolyzed with 72% sulphuric acid for 1 h in a 30 °C water bath, after which the samples were hydrolyzed in an autoclave for 1 h at 120 °C. The solution was then neutralized with sodium hydroxide and the samples were transferred into a Dionex DX500 ion chromatograph consisting of a GP40 gradient pump, a CarboPac PA1 pre-column and analytical column, and a pulsated ED40 amperometrical detector. Elution was carried out on a mixture of sodium hydroxide and sodium acetate at 1 ml min<sup>-1</sup>, according to an internal procedure. The sum of the hemicelluloses was determined from the amount of xylose, mannose, galactose and arabinose, derived by this method as monosugars.

### Acetone extractives and GC-MS

The acetone-soluble matter of each sample was determined using ISO-14453, and then the obtained extractives were silanized, dried and analyzed by GC-MS according to an established method.<sup>9</sup> The instrument used is a Finnigan Trace GCultra connected to a Trace DSQ combined with XC-alibur software. The total sum of extractives is reported.

### Molecular weight distribution

All viscose dope samples were washed twice with an excess of 5 wt% acetic acid for the cellulose to regenerate. The solids were then filtered and washed with de-ionized water. All samples, including the dissolving pulp samples, were activated by adding DMAc (N,N-dimethylacetamide) and were dissolved by a mixture of LiCl (lithium chloride) in DMAc<sup>10,11</sup> with the following modifications. A 25 mg portion of each pulp was solvent exchanged three times for 30 minutes with 5 ml of methanol followed by three times for 30 minutes with DMAc. The excess of MeOH/DMAc was then removed, after which 5 ml of 8 wt% LiCl in DMAc and 0.6 ml of the derivatizing reagent ethyl isocyanate was added and left overnight at room temperature with gentle stirring. No filtration of the samples was required. The dissolved cellulose samples were then chromatographed with a Polymer Laboratories PL-GPC 210 instrument, having a 100 microliter injection loop and three size exclusion PL-Gel microM Mixed B chromatography columns with a guard column, an internal refractive index detector and a HPLC compact pump model 2250 provided by

Bischoff. The flow rate for the 0.5 wt% LiCl in DMAc eluent was set to 1 ml min<sup>-1</sup> at a temperature of 70 °C. For calibration, a standard solution of Pullulan Polysaccharide SAC-10/10, supplied by Polymer Laboratories Ltd., was used with a molecular weight of 788, 404, 212, 112, 47.3, 22.8, 11.8 and 5.9 kD. Data acquisition and calculation was performed by the software Cirus 3.0 from Polymer Laboratories. The polydispersity (PD), expressed by the ratio of the weight-averaged molecular weight (Mw) and the number-averaged molecular weight (Mn) of each sample, is shown in Table 3.

### Caustic properties

All cellulose pulps were tested for their ability to absorb a caustic solution, presented in Table 3 as the rate of absorption and the total amount of caustic absorbed. The used method followed the instructions and the apparatus described earlier,<sup>12</sup> modified to an 18% caustic solution at room temperature.

### Mercury porosimetry

A Micromeritics AutoPoreIV 9500 mercury porosimeter was used to determine median pore diameter, total pore area and permeability.<sup>13</sup> All samples were analyzed using a 3 cm<sup>3</sup> powder penetrometer with a stem volume of 1190 mm<sup>3</sup>. Each sample had an average weight of total 1 g and was cut in smaller pieces to fill the stem. The number of recorded data points was 49 during intrusion and 31 during extrusion. An evacuation pressure of 6.7 mPa(a) and a maximum mercury pressure of 413 MPa(a) was applied. Three analyses per sample were performed.

### Viscose dope preparation

The filter value of each pulp was determined according to Treiber<sup>14</sup> with some modifications. A bench pilot plant was built for the preparation of viscose dope from cellulose pulp, as well as the filter apparatus. Viscose dope was prepared by cutting sheets of cellulose pulp into smaller pieces of approximately 1 cm<sup>2</sup>. The flakes were dried in an oven with air circulation at 105 °C and mixed with an excess of 18 wt% caustic solution at 40 °C during 20 min. The press factor – the weight ratio of mercerized cellulose and initial cellulose amount – was set to be 2.8 and shredding time was 45 min. Pre-aging was done at 50 °C until viscosity was reduced to approximately 250 ml g<sup>-1</sup>. Carbon disulfide was added to a total concentration of 36 wt% based on the cellulose content in the alkali cellulose and left for reaction for 150 min.

Caustic solution was then added to achieve a viscose dope containing 5 wt% caustic and 10 wt% cellulose and an additional 10 min of reaction was allowed. The reaction jar was kept under vacuum, both during carbon disulfide and caustic addition, whereas the temperature was 30 °C. The material was transferred to the dissolving unit and stirred for 180 min at 2 °C, after which the ripening step was performed, where the viscose dope was covered by a perforated stretch film and kept in a fume hood for 16 h.

#### Filter value

The filter value was determined with the filter apparatus as described by Treiber<sup>14</sup> modified with one sheet of steel filter BekaertBekiporST 15FP. First, the filter clogging value was calculated<sup>15</sup> by Eq. 1

$$K_w = \frac{2 * \left[ \frac{t_2}{M_2} - \frac{t_1}{M_1} \right] * 10^5}{t_2 - t_1} \quad [1]$$

where  $t_1$ ,  $t_2$  – filtration time in min (20 and 60 min), respectively,  $M_1$  and  $M_2$  – the amount of viscose dope in grams, filtered during 0-20 min and 0-60 min, respectively. The filter clogging value calculated by Eq. 1 was then adjusted for viscosity to report the reduced filter clogging value  $K_r$ ,<sup>16</sup> Eq. 2 (see Table 3):

$$K_r = \frac{K_w}{\eta^{0.4}} \quad [2]$$

where  $\eta$  is the ball fall time in seconds for a standard viscose dope viscosity analysis.

#### Gamma number

The gamma number is defined as the number of xanthogenate groups per 100 anhydro glucose units (AGU) and describes the level of degree of substitution (DS). Since three hydroxyl groups are available per one AGU, the highest DS achievable is 3, corresponding to a gamma number of 300. The gamma number is measured spectrophotometrically after the ripening process. A viscose sample of about 1 g was collected and its exact weight noted. The viscose was dissolved in 50 ml, 1 wt% NaOH by stirring for 30-40 min. After the viscose was dissolved, the solution was transferred into a 100 ml volumetric flask and filled with 1 wt% NaOH to the graduation mark. The flask was shaken rigorously and five ml were transferred to a bottle containing 1.8 g of ion exchange resin (Amberlite, IRA 402). The solution was left to react with the resin for 10 min, after which it was filtered by using a filter paper (Munktell 5) into a 250 ml volumetric flask, diluted with de-ionised water to the graduation mark and shaken rigorously. Measurements were done with a CARY 100Scan UV/visible spectrophotometer, at a wavelength of 303 nm within 20 min after filtration. A 1 cm quartz cuvette with de-ionised water was used as reference, and the gamma number was calculated according to Eq. 3:

$$\gamma = \text{number} = \frac{A_{303}}{C} \quad [3]$$

where A is the absorbance measured at 303 nm, B the viscose amount (g) and C the cellulose content of the viscose dope (wt%).

## RESULTS AND DISCUSSION

An overview of the investigated process steps from dissolving pulp to viscose dope and of the analyses performed for each step is shown in Fig. 1. The analytical results are presented in Table 3, section “Pulps” for the dissolving pulp samples, section “Mercerized” for the mercerized cellulose, section “Aged” for the aged cellulose and section “Viscose” for the final viscose dope produced. However, viscose dope for sample F:10 could not be analyzed due to a high gelling behavior in the ripening step.

#### Pulp pre-aging curves

Each pulp was pre-aged three times and intrinsic viscosity was measured in intervals to determine the total required pre-aging time to a set viscosity of 250 ml g<sup>-1</sup>. The average times for all three analyses were determined and the exponential trend lines representing all pre-aging curves are presented in Fig. 2. To determine the rate of degradation [ml g<sup>-1</sup> min<sup>-1</sup>], a linear slope for  $f(x)=0$  and  $f(y)=250$  was calculated, denoted by  $v'$  for each pulp.

The shortest pre-aging times have been found for samples A:1, B:2 and C:4, see Table 2. A long time for degradation is noted for pulps F:10 and E:8, which is no surprise. Since both pulps present the highest amount of hemicelluloses and hemicelluloses are relatively easily oxidized by oxygen, less oxygen is available for the degradation of cellulose, thus delaying the pre-aging step.<sup>3</sup> However, the amount of hemicelluloses is not the only explanation, since sample D:7 and D:9 both have the lowest concentration of hemicelluloses after the mercerization step, yet the rate of degradation is fairly low. The explanation can be found in a lower pore area of those two samples, which prevents the access and reaction of caustic to the cellulose and thus lower the rate of formation of mercerized cellulose, a requirement for the subsequent oxidative cleavage of cellulose chains. The importance of pore structure and inner surface in the reactivity of cellulose was well described earlier,<sup>17</sup> where different pore properties were reported in pulps from different wood species and pulping processes. Interesting to note is also the increase of degradation speed with lower intrinsic viscosity with pulps from the same

producer. Hence, when choosing a pulp with lower viscosity, pre-aging time will be reduced not only by the lower initial viscosity, but also by a slightly higher rate of degradation.

The pulp viscosity level after pre-aging is a highly important process variable in the viscose manufacturing, since it will determine the

filterability and de-aeration properties, as well as spinnability of the viscose dope and final tenacity properties in the fiber.<sup>3,18</sup> A controlled level of intrinsic viscosity after pre-aging is thus a requirement for a good processability of the dope and quality of the final fiber.

	Dissolving pulps	Mercerized cellulose	Aged cellulose	Viscose dope
$\alpha$ -, $\beta$ -, $\gamma$ - cellulose	X	-	-	-
Caustic properties	X	-	-	-
Porosity	X	-	-	-
Extractives	X	-	-	-
R18 and R10	X	X	X	-
Fock Reactivity	X	-	X	-
Carbohydrates	X	X	X	X
MWD: PD, Mn, Mz	X	X	X	X
Intrinsic viscosity	X	-	X	-
$\eta$ - number	-	-	-	X
Kr	-	-	-	X

Figure 1: Overview of investigated process steps to viscose dope and analyses performed (X) or excluded (-)

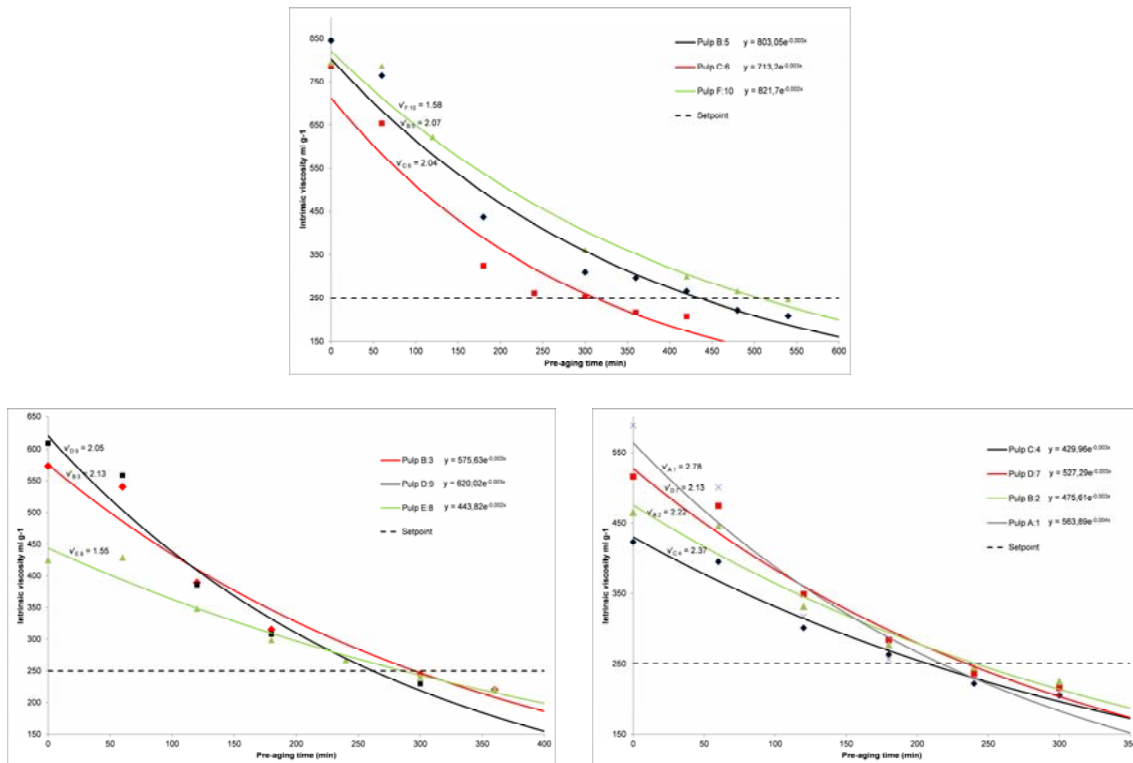


Figure 2: Pre-aging curves for all samples investigated, separated as to their initial viscosity level

The differences between the commonly used intrinsic viscosity and average molecular weights by molecular weight distribution are presented in

Table 4. The average molecular weight by viscosity was derived from intrinsic viscosity by the Mark-Houwink equation, using relevant

coefficients for cellulose in Cuen.<sup>19</sup> Even though Mw for the pre-aged cellulose is considered an important parameter for fiber strength and Mz (representing the cellulose chains with the highest DP) for spinnability, the most common industrial analysis for pre-aged cellulose is still intrinsic viscosity. However, as the results presented in Table 4 show, the differences between the calculated Mv derived from intrinsic viscosity and the actual Mv from molecular weight distribution are sometimes more than double. This deviation is reflected in the values of  $\Delta Mv_{\text{calc, MWD}}$  and the high ratios for  $Mw_{\text{MWD}}/Mv_{\text{calc}}$ . The deviations between intrinsic viscosity and Mv, and in particular the high weight molecular celluloses

represented by Mz in this group of pulps, are clearly demonstrated by the differences in  $\Delta Mv_{\text{calc, MWD}}$  (41.4-52.0%) and the ratio  $Mz_{\text{MWD}}/Mv_{\text{calc}}$  (3.9-5.1). These deviations and variations from the intrinsic viscosity measurements show clearly the need for a total molecular weight analysis of pre-aged samples prior to xanthation. This is of particular interest when introducing new pulps or new compositions of pulp mixtures to the process, to determine required adjustments of process parameters for achieving the optimal molecular weight distribution for the best viscose dope and fiber quality.

Table 4

Differences of intrinsic viscosity  $\eta$ , an analysis mostly used in the determination of the pre-aging characteristics, to calculated  $Mv_{\text{calc}}$  and analyzed Mv, Mw and Mz by molecular weight distribution

	$\eta$ ml g <sup>-1</sup>	$Mv_{\text{calc}}^a$ g mol <sup>-1</sup>	$Mv_{\text{MWD}}$ g mol <sup>-1</sup>	$Mw_{\text{MWD}}$ g mol <sup>-1</sup>	$Mz_{\text{MWD}}$	$\Delta Mv_{\text{calc, MWD}}$ %	$Mw_{\text{MWD}}/Mv_{\text{calc}}$	$Mz_{\text{MWD}}/Mv_{\text{calc}}$
A:1	230	71 798	137 886	160 129	362 846	47.9	2.2	5.1
B:2	228	71 105	136 968	157 477	347 717	48.1	2.2	4.9
B:3	228	71 104	141 089	158 264	336 759	49.6	2.2	4.8
C:4	231	72 145	149 887	165 472	390 002	51.9	2.3	5.4
B:5	240	75 275	140 786	148 873	325 623	46.5	2.0	4.3
C:6	234	73 187	124 996	143 814	288 800	41.4	2.0	3.9
D:7	235	73 534	153 125	168 016	331 565	52.0	2.3	4.5
E:8	256	80 871	138 145	161 104	342 669	41.5	2.0	4.2
D:9	240	75 275	148 404	168 424	358 193	49.3	2.2	4.8
F:10	235	73 534	134 253	141 730	303 429	45.2	1.9	4.1

<sup>a</sup> calculated by Mark-Houwink equation, where intrinsic viscosity  $[\eta]=K \cdot Mv^a$ , with  $K=9.8 \cdot 10^{-3}$  and  $a=0.9$  for cellulose solved in copper (II) ethylenediamine at 25 °C

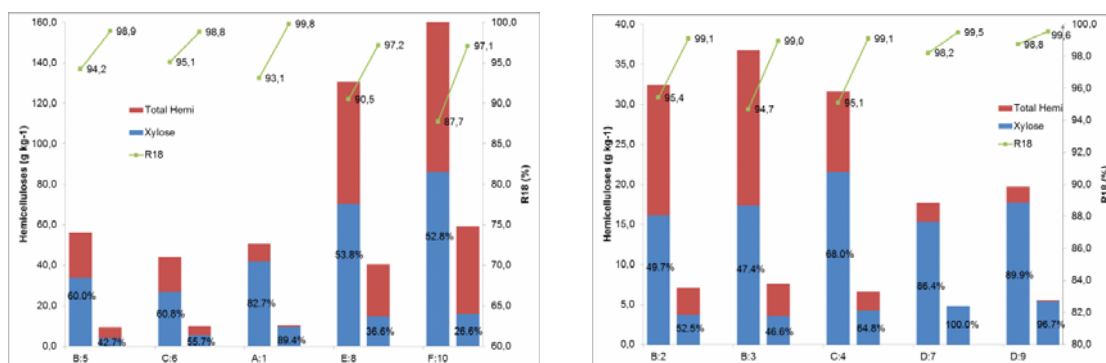


Figure 3: Change of hemicelluloses content in raw pulp and pre-aged cellulose and parallel increase of R18 (the numbers in percentage denote the part of xylose in the total amount of hemicelluloses)

### Carbohydrates after pre-aging

Special attention has been given to the xylose content, since xylose is known to be a major component of chemical-resistant hemicelluloses undergoing chemical association to cellulose, increasing the amount of the regenerative non-

cellulosic material ( $\beta$ -cellulose) and thus affecting, for example, the production of viscose filaments. This negative influence of  $\beta$ -cellulose on tenacity, fatigue and spinnability on the viscose fiber has been well studied.<sup>3</sup> Figure 3 shows the reduction of hemicelluloses and

increase of R18 in the mercerization step, that is, after the removal from hemicelluloses and the excess of caustic in the pressing step. Additional information obtained from Fig. 3 is the correlation between R18 and the hemicellulose content in the dissolving pulp and aged cellulose. Even though extensively applied in the pulping and viscose industry as a cellulose purity measurement, it is clear that R18 does not reflect the amount of hemicelluloses in the sample, but only the dissolvable amount within the sample with 18% caustic at room temperature. The relative reduction of xylose (difference in xylose content in the pulps and after pre-aging divided by the xylose content in the pulps) is in general between 70 and 80% after pressing, with a tendency of being lowest for the PHK hardwood pulp D:7 (67.9%, see Table 5). For the PHK hardwood pulps, a clear alkali resistance of the xylose is indicated, since in total more other hemicelluloses are reduced, compared to the reduction of xylose (D:7 and D:9). Similar results were reported earlier on alkali-resistant cellulose and hemicelluloses in alkaline processed pulps.<sup>20</sup> Interesting to note is that irrespective of the initial viscosity level of the pulp with higher hemicellulose content for higher viscosities, the overall hemicellulose content after pressing is leveling off at a concentration of 8-10 g kg<sup>-1</sup>. Exceptions are the modified paper pulp samples E:8 and F:10 with extreme higher values of hemicellulose content in both the original pulp and mercerized cellulose. One reason for the leveling off of hemicellulose content in the mercerized cellulose could be a certain saturation point in the caustic lye at the given temperatures and caustic concentrations allowing an extraction of hemicelluloses to this level only. Another contribution to this result could be the existence of hemicelluloses in crystalline or semi-crystalline form, that is, hemicelluloses with altered morphology in particular during the pulping process. These hemicelluloses may lie between the cellulosic microfibrils as granular material or even as formation of their own microfibrils and may thus be strong enough to withstand dissolution by 18% caustic solution.<sup>21</sup> The results seem to indicate that in order to achieve the lowest hemicellulose content in the viscose dope, the choice for dissolving pulp does not have to be limited to more costly pulps with low viscosity and hence low hemicellulose content. In fact, cheaper pulps with higher viscosity and hemicellulose content can still be reduced to the

same amount in the viscose dope under same process conditions.

As seen in Table 3, the hemicellulose content remains fairly stable between the pressing step and after the aging step, to sharply drop to very small amounts in the viscose dope. The low hemicellulose content in the viscose dope is explained by the reaction of carbon disulfide with hemicelluloses, making them impossible to detect by ion chromatography. Only pulps with extremely high hemicellulose content in the original pulp (E:8 and F:10) remain with high hemicellulose content in the aged cellulose and hence in the viscose dope, indicating a deficit of carbon disulfide for the reaction with hemicelluloses and, more fatally, with the cellulose resulting in unreacted parts of cellulose. Hence, the explanation for the gelling behavior of sample F:10 can be found in the high hemicellulose content and in the low  $\gamma$ -number (see Table 3), since high hemicellulose content in the pulps was earlier found to be a contributing factor in gel formation of a cellulose derivative and low filterability of viscose dope.<sup>6</sup>

As seen in Fig. 3, a higher ratio of the xylose amounts in the PHK pulp resistible to caustic treatment will remain in the pulp after mercerization and pressing. This resistance to caustic extraction is fatal as it is affecting R18 values and the pulps' purity numbers derived therefrom. These hemicelluloses can mistakenly be included in R18 results, indicating higher cellulose purity than there actually is. Since R18 is an important analysis for determining the use of certain pulp in the viscose process, a separate study to pre-aged cellulose has been undertaken on sample B:3 and one softwood PHK not included in Table 1 to demonstrate the importance of alternative methods for suitability of pulps (Table 6).

Even though the content of hemicelluloses in the softwood PHK original pulp is remarkably lower compared with sample B:3, the total amount of hemicelluloses in general and the xylose content in particular in the pre-aged cellulose has not been extracted to the same extent as for sample B:3. Hence, the results obtained suggest the following statements: i) some hemicelluloses, and in particular xylose in PHK pulps, are resistant to caustic extraction and can follow the viscose stream all the way to fiber spinning, ii) the original composition in the pulps does not reflect the composition in the pulps after pre-aging and iii) R18/S18 is not a sufficient



quality parameter in pulps to determine pulp behavior in the viscose process, but is rather a process yield indicator.

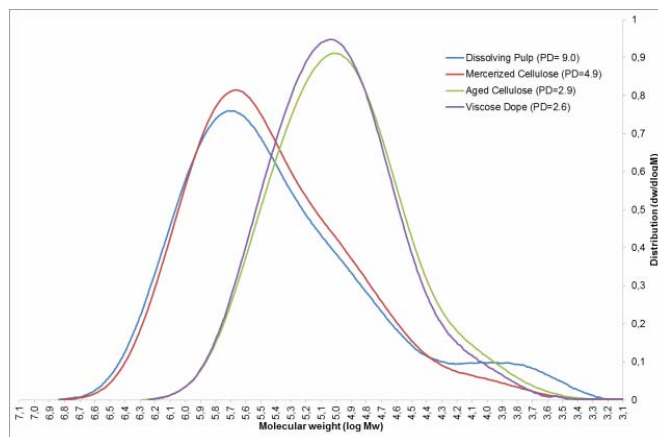


Figure 4: Typical change of molecular weight distribution during viscose dope preparation, here demonstrated by sample B:5

Table 5

Xylose and hemicellulose reduction in the mercerization and pressing stage for the investigated pulp samples

	Xylose reduction, %	Hemicellulose reduction, <sup>a</sup> %
A:1	77.6	87.5
B:2	77.0	78.3
B:3	79.9	79.3
C:4	80.5	77.2
B:5	88.2	76.4
C:6	79.1	74.6
D:7	67.9	100.0
E:8	78.9	57.6
D:9	69.5	90.0
F:10	81.6	43.4

<sup>a</sup> Hemicelluloses excluding xylose

Table 6

Comparison between sulfite SW and PHK SW pulps as to hemicellulose concentration in both original and pre-aged state

		Sample B:3	PHK SW
Original			
Viscosity	ml g <sup>-1</sup>	543	603
Mannose	g kg <sup>-1</sup>	11.0	4.6
Xylose	g kg <sup>-1</sup>	12.4	8.2
Pre-aged			
Viscosity	ml g <sup>-1</sup>	210	195
Mannose	g kg <sup>-1</sup>	5.1	3.8
Xylose	g kg <sup>-1</sup>	3.9	6.4

#### Molecular weight distribution in viscose dope

An important demand on the raw material pulp for achieving a viscose fiber with high tenacity

and strength is a low content of  $\beta$ - and  $\gamma$ -cellulose with Mw below 20000 g mol<sup>-1</sup>, and a narrow molecular weight distribution indicated by a PD

of the viscose dope as low as possible.<sup>4</sup> The effect of molecular mass on tensile properties was already reported by Staudinger,<sup>22</sup> where a linear relationship between the reciprocal of the DP or the molecular mass of the cellulose and the tensile properties of cellulosic fibers was reported. For a viscose producer, this ultimately implies that any pulp used for the purpose of producing fibers with high tenacity properties should be purified to a

high content of  $\alpha$ -cellulose during mercerization and pressing, while a uniform distribution curve with a high ratio of high Mw should be retained during pre-aging. A typical variation of DP is shown in Fig. 4, visualizing the change of molecular weight and molecular weight distribution during the process steps to viscose dope.

Table 7

PD values and percentage of Mw below 20000 g mol<sup>-1</sup> from the total molecular weight distribution, for both pulp and viscose dope, and for the change of these by processing to viscose dope

	PD <sub>pulp</sub>	PD <sub>dope</sub>	M <sub>w,pulp</sub> , %	M <sub>w,dope</sub> , %	$\Delta$ PD	$\Delta$ M <sub>w</sub>
A:1	12.2	3.0	11.8	9.2	-9.2	-2.6
B:2	7.9	2.9	8.5	7.1	-5.0	-1.4
B:3	8.0	2.9	9.0	8.9	-5.1	-0.1
C:4	6.9	2.7	8.1	6.9	-4.2	-1.2
B:5	9.0	2.6	7.7	5.3	-6.4	-2.4
C:6	8.0	2.7	7.0	7.7	-5.3	+0.7
D:7	4.6	2.7	3.2	7.0	-1.9	+3.8
E:8	5.8	3.0	10.1	6.7	-2.8	-3.4
D:9	4.8	2.7	4.7	6.4	-2.1	+1.7
F:10	8.0	3.0 <sup>a</sup>	9.1	8.4 <sup>a</sup>	-5.0	-0.7

<sup>a</sup>data from aged cellulose

Important to note is the removal of the top in the low molecular area with Mw below 20000 g mol<sup>-1</sup> in the original pulp and the move of the main peak towards lower molecular weights. Hence, an optimal pulp candidate for a strong viscose fiber is a pulp that results in a viscose dope showing a uniform, monodisperse distribution curve, with a small fraction of molecular weights below 20000 g mol<sup>-1</sup> representing the  $\beta$ - and  $\gamma$ -celluloses. The decrease of PD and of low-molecular-weight celluloses (Mw below 20000 g mol<sup>-1</sup>), from the raw material to the viscose dope, are shown in Table 7.

Clearly, some pulps show a greater reduction of PD and of the low-molecular-weight fraction, compared with others, under the given viscose production conditions. To some extent, the reduction of PD and Mw goes hand in hand with the reduction of cellulose and hemicelluloses after treatment with caustic lye, as described in the section for carbohydrates after pre-aging (Table 5). However, as Table 7 demonstrates, this parallel is not applicable to all pulps. The sulfite hardwood sample A:1 showed the highest reduction in both Mw and PD in absolute terms, but did not reach as low numbers for both values as the high-viscosity sulfite softwood sample B:5 did. Interesting to note is the unexpected increase

of the low-molecular-weight ratio for the PHK hardwood samples D:7 and D:9 combined with a fairly high reduction of PD, indicating a broader base, yet steeper top, at the high-molecular-weight portion for Mw and Mn. Surprisingly, a similar conclusion as that for the hemicellulose content in the previous section can be drawn for the high-viscosity sulfite softwood sample B:5. Despite the high content of hemicelluloses in the original pulp expressed by a high fraction of Mw below 20000 g mol<sup>-1</sup> and a high PD, this pulp still shows low values of all variables in the viscose dope. This phenomenon could be explained by the shorter cooking in the sulfite pulping sequence for high viscosity pulps, where the morphological structure of the fibers is kept more rigid, preventing the formation of celluloses of lower weight during mercerization and aging.

## CONCLUSION

For a dissolving pulp producer or viscose producer, this study shows that more advanced methods are required for a sufficient selection of pulps prior to the introduction of a new pulp or pulp blend to a viscose process. More advanced methods, such as analyses of molecular weight distribution and carbohydrate compositions, rather than the commonly used R18/R10 and intrinsic

viscosity, are more suitable, as the latter can contribute to misleading results in terms of pulp purity and overall degree of polymerization before and during the viscose process. As demonstrated, it is of further interest not only to investigate the raw material, but also to follow the carbohydrate composition and molecular weight distribution all the way to viscose dope to ensure the lowest contents of  $\beta$ - and  $\gamma$ -celluloses, as well as a uniform molecular weight distribution during all process steps. This is extremely important as the results show that each pulp, depending on its origin, reacts differently to the treatments in viscose manufacturing, and therefore will have a different outcome in spinning properties and viscose fiber quality. In other words, even though a pulp is characterized with initially high hemicellulose content and high viscosity, it could, despite the higher loss of yield, still be a strong candidate for fulfilling the requirements for a strong viscose fiber, namely a low hemicellulose content, a low PD and a low amount of  $\beta$ - and  $\gamma$ -cellulose in the viscose dope.

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**ABBREVIATIONS:**

$\alpha$ -cellulose: Cellulose with high DP, residue in 18% NaOH solution

$\beta$ -cellulose: Carbohydrates with DP <200 dissolved in 18% NaOH but regenerated in acetic acid

$\gamma$ -cellulose: With alcohols regenerated carbohydrates (DP<10) from the  $\beta$ -cellulose filtrate

Cuen: Ethylenediamine-copper (II) complex

DP: Degree of polymerization

Mn: Number average molecular mass

Mv: Viscosity average molecular mass

Mw: Weight average molecular mass

Mz: Z average molecular mass

PD: Polydispersity (molecular weight distribution)

R10, R18: Weight proportion of cellulosic residue in 10% and 18% NaOH solution

**REFERENCES**

<sup>1</sup> C. Woodings, "Regenerated Cellulose Fibres", Woodhead Publishing Ltd, Cambridge, England, ISBN

1 85573 459 1, 2001, pp. 22-36.

<sup>2</sup> Oerlikon, The Fiber Year 2009/10, A World Survey on Textile and Nonwovens Industry, Issue 10, 2010.

<sup>3</sup> K. Götze, "Chemiefasern, Nach dem Viskoseverfahren", Erster Band, Springer Verlag, Berlin, 1967, pp. 118-120, 209-214.

<sup>4</sup> H. Rath, "Lehrbuch der Textilchemie", Dritte Auflage, Springer Verlag, Berlin, 1972, pp. 198-209.

<sup>5</sup> H. A. Krässig, "Cellulose. Structure, Accessibility and Reactivity", Polymer Monographs Vol. 11, Gordon and Breach Science Publishers, Amsterdam, 1993.

<sup>6</sup> P. Strunk, B. Eliasson, C. Hägglund, R. Agnemo, *Nordic Pulp Pap. Res. J.*, **26(1)**, 81 (2011).

<sup>7</sup> W. Fock, *Das Papier*, **13**, 92 (1959).

<sup>8</sup> K. E. Christoffersson, M. Sjöström, U. Edlund, Å. Lindgren, M. Dolk, *Cellulose*, **9**, 159 (2002).

<sup>9</sup> NSP, Nordic Standardization Program, Methods for determination contents of free fatty acids and resin acids and sterols and for group characterization in lipophilic wood extractives, Report no 3, **4**, 6 (2007).

<sup>10</sup> F. Berthold, K. Gustafsson, R. Berggren, E. Sjöholm, M. Lindström, *J. Appl. Polym. Sci.*, **94**, 424 (2004).

<sup>11</sup> E. Sjöholm, *Doctoral Thesis*, Royal Institute of Technology, Stockholm, Sweden, ISSN 1104-7003, 1999.

<sup>12</sup> Zellcheming, Verein der Zellstoff- und Papierchemiker und -ingenieure, Merkblatt II/2/66, 1966, Ermittlung der Laugensteiggeschwindigkeit beim Tauchen von Zellstoffblättern in Natronlauge.

<sup>13</sup> E. Byström, C. Viklund, K. Irgum, *J. Sep. Sci.*, **33**, 1 (2010).

<sup>14</sup> E. Treiber, J. Rehnström, C. Ameen, F. Kolos, *Das Papier*, **16**, 85 (1962).

<sup>15</sup> Zellcheming, Verein der Zellstoff- und Papierchemiker und -ingenieure, Merkblatt III/6B/68, 1968, Prüfung von Viskose: Filterverstopfungszahl von Viskose.

<sup>16</sup> E. Treiber, *Monatsheft Chemie*, Bd. 93 (1961).

<sup>17</sup> D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht, "Comprehensive Cellulose Chemistry", Wiley-VCH Weinheim, Chap. 2.1.3-2.1.4, 1998.

<sup>18</sup> H. Klare, *Faserforschung und Textiltechnik*, **7**, 199; **8**, 262 (1957).

<sup>19</sup> T. Lojewski, K. Zieba, J. Lojewska, *J. Chromatogr. A*, **42**, 6462 (2010).

<sup>20</sup> R. Patt, D. L.-K. Wang, *Das Papier*, **41(1)**, 7 (1987).

<sup>21</sup> H. Meier, *Pure Appl. Chem.*, **5**, 37 (1962).

<sup>22</sup> H. Staudinger, M. Sorkin, E. Franz, *Melliand Textilberichte*, **118**, 53 (1937).