Combined Effect of the Morphology and Rate of Addition of Fine Cellulosic Materials Produced from Chemical Pulp on Paper Properties

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ABSTRACT

Recently fine cellulosic materials such as microfibrillated celluloses (MFCs) have become an interesting additive in papermaking, improving paper mechanical properties thanks to their intrinsic high mechanical strength along with high potential to interact with cellulosic fibres.

In this study, we produced and compared: (i) a mixture of primary and secondary fines isolated from the pulp by means of a purpose-built laboratory pressure screen and (ii) MFC-like materials obtained by refining and subsequent steps of high-pressure homogenization. Morphological properties were determined using flow cell based and microscopic techniques, showing a wide size distribution of the fibrillated materials produced. The thus obtained materials were applied in handsheet forming in blends of different proportions to evaluate their influence on paper properties. Already at low concentration all tested products lead to a substantial decrease in air permeability and to improved mechanical properties, independent of the type and morphological character of the added fine cellulosic material. At higher addition rates, only highly fibrillated materials allowed a further considerable increase in tensile strength, which could be explained by the creation of a secondary network structure of highly fibrillated materials improving the load-bearing capacity of the whole paper structure.

INTRODUCTION

Paper manufacturers are continually striving to reduce production costs while at the same time attempting to improve the quality and environmental performance of their end products. A possible way to achieve these goals is to apply efficient strength additives to meet the requested mechanical properties of the final product at a reduced raw material input.

In this context, fine cellulosic materials, such as cellulose nanofibres (CNF) as well as the coarser microfibrillated celluloses (MFC) have emerged over the last twenty years as promising and sustainable reinforcement materials, showing a high potential in material sciences as e.g. their application in composite materials based on polymeric matrices [1-3]. Also their use in papermaking in recent studies showed interesting results regarding the improvement of paper properties using MFCs as additives [4-6]. Thanks to their intrinsic high mechanical strength along with good flexibility and high potential to interact with cellulosic fibres, authors report a significant improvement of paper properties by the application of highly fibrillated additives.

While such arguments motivate the interest of using MFC in papermaking, production of these materials is still limited. Another obstacle is the high price of MFCs, originating from the high energy consumption involved during their production [7,8]. To take advantage of the reinforcement potential of such materials in papermaking, development of new solutions to produce highly fibrillated fibrous materials directly on site is needed to maintain the balance between costs and benefits. As an alternative to commercial MFC, fine fibrillar materials generated in the course of pulp and paper production processes and then separated from the pulp could be a promising approach to achieve similar results as with MFC addition [9,10].

The basis for such innovations is a better understanding of the mechanisms behind the reinforcing effect of fine cellulosic materials such as MFC on the paper network. A precise characterization of the morphological properties and the corresponding processing conditions and their effect on technological paper properties is needed. Pulp origin and treatment, as well as both type and amount of added MFC, has been reported to affect the various paper properties, but leading in some cases to contrasting results [5,6,11]. However, this variability in the results also

demonstrates that fine cellulosic materials might be suitable to tailor various paper properties, when the requirements regarding their quality and their mode of action are better understood. Retulainen et al. [9] have already proposed this approach in his work with the fines fractions from pulp by suggesting that fines quality and rate of addition could be used as a potential control variable in papermaking. A similar behavior can be expected with MFCs, with their effects on paper properties being potentially even stronger than observed for fines [9,10].

By fractionation and by mechanical processing steps, different fine cellulosic materials are produced, covering a wide range of particle sizes and degrees of fibrillation:
(i) Two types of fine fibres fragments produced during pulping and papermaking can be separated from the pulp through fractionation [12]. Primary fines are released in the pulping process and mainly consist of ray cells, parenchyma cells, fragments of the middle lamella and only a small portion of fibrils. Secondary fines are produced during refining and fibrils are the main component. Because of their different nature, they have different effects on paper properties. Primary fines are assumed to act more or less as fillers and contribute to optical properties [13], whereas fibrillar secondary fines were reported to have a strong impact on strength properties of paper [13-15].
(ii) Another well-established approach to produce fine cellulosic materials is to mechanically process virgin pulp fibres to increase their fibrillar character through grinding and/or high-pressure homogenization. Since the introduction of MFC by Turbak [16], these techniques are the main methods used to effectively produce MFC [17]. In high-pressure homogenization the disintegration of fibres into fibrils is promoted by the high mechanical shearing forces, the rapid drop in pressure, the turbulent flow and the frictional forces of the particles against each other [18]. The degree of fibrillation is controlled by adapting the applied pressure and number of passes through the homogenizer.

This work aims at investigating the effect on paper properties of different types of fine MFC-like cellulosic materials described above. All materials originated from the same batch of pulp and thus issues arising from variations due to differences in morphological and chemical properties of the pulp are avoided.

MATERIAL AND METHODS

Preparation of Fine Fibrous Materials

The same batch of softwood bleached kraft (SBK) pulp (Zellstoff Pöls AG, Austria) was used to produce all the materials used in this study. To produce a sufficient amount of pulp fines, a sample of this pulp was refined in an industrial double-disc refiner to 38SR and then fractionated using a lab-scale pressure screen. The screen was equipped with a perforated plate (hole diameter 100 µm) to separate the primary fines already contained in the unrefined pulp and the secondary fines produced during refining from the fibres [19]. As the major part of the obtained fines at a degree of beating of 38 SR belongs to the class of secondary fines this term is further used for this material. The pulp was recirculated in the screening system until the remaining volumetric fines content in the pulp was below 0.5%. The fines were allowed to settle for three days, before the supernatant was removed and a concentration of approximately 1% w/w was reached.

The unrefined pulp from the same production batch was used to produce materials of increasing fibrillar character. For this purpose, the unrefined pulp was refined in a standard Valley Laboratory Beater (VB) for 2 hours. Subsequently the VB refined pulp was further fibrillated in a high-pressure homogenizer (APV 1000, 1000Bars – 30Hz, APV Poland) using a different number of passes and different pressures. For the refined and homogenized materials no fractionation was applied. The different materials produced in this study and used to be added to the reference pulp are summarized in *Table I*.

Characterization of Fine Fibrous Materials

Fibres and fibril morphology of the samples was determined using a L&W Fiber Tester Plus. Frequency distribution, average fibre length and ECD (Equivalent Circular Diameter) were calculated (weight weighted) using a MATLAB routine processing the raw data obtained by the device. The fines fraction of the different cellulosic materials produced in high-pressure homogenization was measured using a Britt Dynamic Drainage Jar according to TAPPI Test Method T-261 cm-10 (fines fraction by weight of paper stock by wet screening).

Flow imaging based devices allow only limited detection of highly fibrillated material due to resolution. Further the contrast of highly swollen fibrillar particles in the flow cell images from the L&W Fiber Tester Plus is sometimes too low, which strongly affects the detection of the highly fibrillated parts. In order to accurately identify the fibrillar content of the cellulosic fine materials, microscopic samples were produced, using a specific staining procedure to improve the identification of the fibrillar content. The different cellulosic materials were diluted to 0.01% w/w and

dyed using a combination of a tall oil - water emulsion (0.2 wt.% in water) with a methylene blue solution (1 wt.% in water) [20]. Microscope slides were prepared from the stained samples and characterized using a method described by Mayr et al. [20], using a conventional transmission light microscope (Leica 301-371.010) equipped with a standard CCD camera (Jai AM-200GE/AB-200GE) and an automated stage control (Märzhäuser Multicontrol 2000). Image analysis was performed using the open source software ImageJ for automated capturing of 700-800 single images per microscope slide (1600x1200 pixels per image; image area: 1380x1035 µm2). From these images, the Total Detectable Area and the Flake-like Area (darker) has been identified using thresholding. The Fibril Area (i.e. the microfibrillar content of the analysed fraction) was then calculated according to *Equation (1)*:

$$Fibril\ Area\ [\%] = \frac{[(\text{Total Detectable Area}) - (\text{Flake-like Area})]}{\text{Total Detectable Area}} \quad (1)$$

with Total Detectable Area and Flake-like Area measured as pixel count for the respective class.

An example for the application of this method is illustrated in *Figure 1*, where the discrimination between Fibril and Flake-like Area is presented for the sample 20H.

Material	Sample	Beating of pulp (degree of beating [SR])	Fractionation	Homogenization
Reference SBK Pulp	REF	PFI mill (16 SR)	-	-
Secondary Fines	SFines	Industrial disc refiner (38 SR)	Screen 100µm	-
Valley Beater pulp	VB	2h of Valley Beater (~90 SR)	-	-
VB+1 Step of homogenization	1H	2h of Valley Beater	-	1 pass, 300bars
VB+3 Steps of homogenization	3H	2h of Valley Beater	-	3 passes, 300, 400, 500 bars
VB+5 Steps of homogenization	5H	2h of Valley Beater	-	5 passes, 300, 400, 500, 600, 700 bars
VB+20 Steps of homogenization	20H	2h of Valley Beater	-	4 passes, 300 to 600 bars and 16 passes 700 bar

Tab. I Materials used in this work and fibre treatment steps

Handsheet Preparation and Paper Testing

The same softwood bleached kraft pulp used for production of the materials listed in *Tab. 1* was also used in the blends as the main component of the furnish. For this purpose, the SBK pulp was refined using a PFI - mill (ISO 5264-2; 2000 revolutions; SR°: 16). This refined pulp also serves as reference for the comparison to the blends with the fine fibrous materials. The produced fine fibrous materials (see *Table I*) were added to the PFI-refined pulp in different proportions of 1%, 2%, 4%, 7% and 10%. The thus produced furnish blends were then mixed using a disintegrator (DIN EN ISO 5263-1) for 25 min.

Handsheets with a basis weight of 60 g/m² were prepared on a Rapid – Köthen sheet former (ISO 5269-2:2004) using white water recirculation in order to guarantee the desired cellulosic fines content in the sheets ([21] Giner Tovar 2015). The first five sheets were discarded until a stable fines content in the sheets was achieved. Seven sheets were formed and wet pressed (150 bar, 90 sec) between two blotting papers, directly after sheet formation and before drying, to limit the influence of capillary forces and their effects on sheet consolidation and to better approach industrial production conditions.

The resulting handsheets were conditioned for 24h in a climate room (23°C; 50%RH) before testing. Bendtsen air permeability (ISO 5636-3:2013), tensile index (EN ISO 1924-2) and z-strength (Scott Bond, ISO 15754:2009) were measured on the handsheets. Data analysis was performed using the free software enivronment R (R Development Core Team, 2008). High-resolution surface images of the different papers were obtained using low-voltage scanning electron microscopy (LVSEM, Everhart-Thornley detector for detection of secondary electrons; Zeiss Sigma 300, Oberkochen, Germany) using the method described in Fischer et al. [22]. The samples were cut (1 cm x 1 cm), then attached to SEM stubs using a double-sided conductive carbon tape, and imaging (magnification 500x) was performed at an acceleration voltage of 0.65 kV.

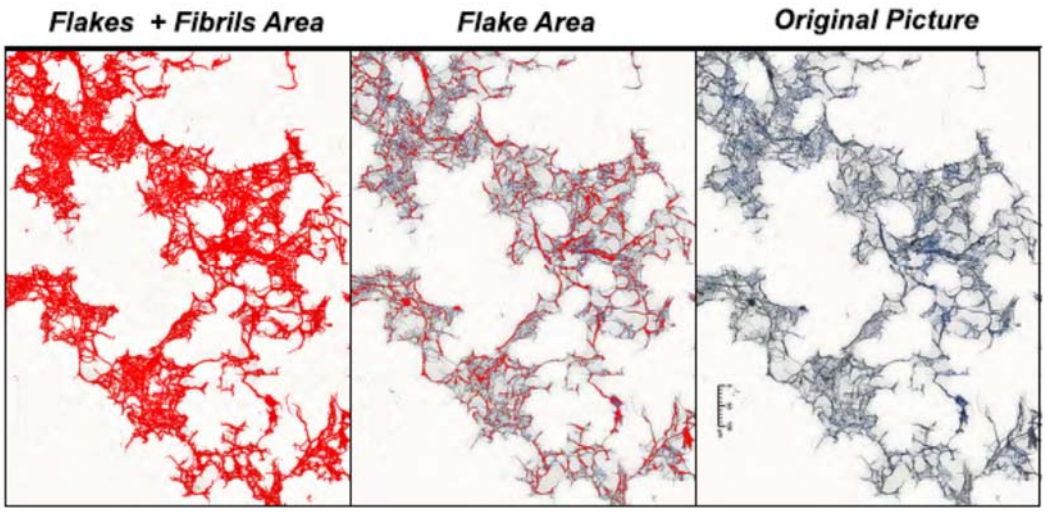

Fig. 1. Example for the result of image analysis using ImageJ Software to identify Flakes and Total detected Area in one of the 800 images realized per samples, sample 20H

RESULTS & DISCUSSION

Morphological Properties - Flow Cell-Based Device

The average values for equivalent circular diameter (ECD) and length (weight weighted) obtained for the reference pulp and the produced fine fibrous materials is shown in *Table II.* The values were calculated from three independent measurements realized per material using the raw data from the L&W Fiber Tester Plus device.

Material	ECD [µm]	Length [µm]
Reference (refined pulp)	244,1	2478,3
SFines	50,6	185,3
VBeater	141,5	1226,9
1H	122,5	1073,9
3H	100,8	873,7
5H	75,3	607,9
20H	53,6	379,5

Tab. II: Average values for equivalent circular diameter (ECD) and length (weight weighted) obtained for reference refined pulp and the fine fibrous materials.

Fibre length distribution (weight weighted) of all the materials in comparison to the refined reference pulp (raw pulp) is shown in *Figure 2*. After two hours of beating in the valley beater (VB), the length distribution, as expected, changes considerably compared to the refined pulp, with the largest amount of fibres now being much shorter (*Figure 2*). Indeed, the average length of VB fibres is already only half (1226,9 µm in average) compared to the unrefined pulp. While the average length of the fibres is reduced, there are still long fibres remaining in the material with 14% of the detected fibres being longer than 2000µm. For the fine fibrous materials produced by high-pressure homogenization treatment, an increasing number of homogenization passes lead to the expected substantial increase in the amount of short fibres/fines (from 1H to 20H, the proportion of fibres under 100µm increases from 15.1 to 44.1%) (see *Figure 2*). The average fibre lengths calculated from the distributions for the different materials are presented in *Table II*.

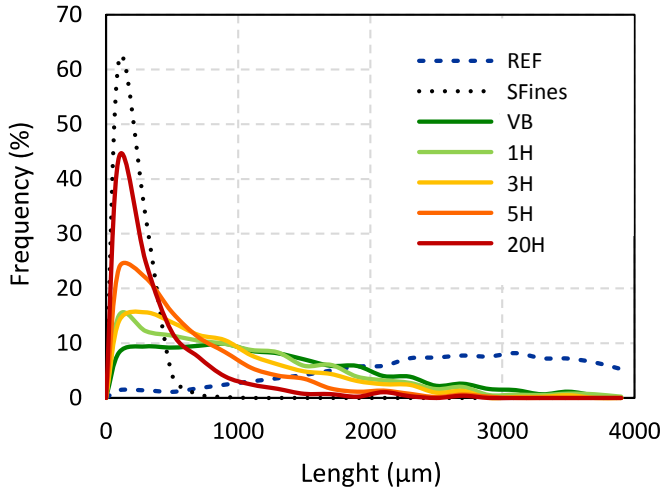

Fig. 2. Average distribution of fibre length (weight weighted) of used fibrous materials

The secondary fines (SFines) are the shortest fibres (185,3µm in average) with the narrowest distribution. Since this material results from a fractionation through a pressure screen, it is only natural to observe the narrowest distribution, since long fibres have been separated. SFines also show the lowest values for average ECD (50.6µm in average), being even lower than the one observed for 20H (53.6µm in average). The average ECD for SFines we obtained here is a slightly higher than the one reported by Retulainen et al. [9] (40µm), but in accordance with more recent work from Mayr et al. [20] for a similar pulp (47µm). Fischer et al. [10] reported similar values for an industrial MFC grades (52.11µm), which tends to confirm that the fine fibrous materials produced in this study are comparable to MFC.

Fines Fraction and Morphological Properties - Microscope Method

For the fine fibrillated materials produced, the fines fraction was determined using the Britt Jar method. In this method, the separation of the fine particles is performed by wet screening and the fines fraction is defined as particles that pass a round hole of 76µm in diameter (i.e. a nominally 200 mesh screen). The untreated pulp shows a fines content of 4,5% (see *Figure 3*).

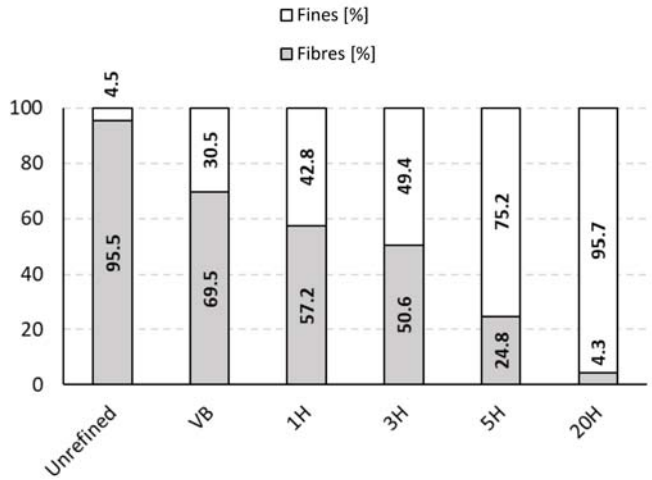

Fig. 3. Fibres (white area) and fines (grey area) fraction measured for VB and the high-pressure homogenized samples according to Tappi T-261 cm-10

After refining the pulp in the Valley Beater, the fines content is more than 6 times higher than in the control sample, with 30,5%. 1 to 3 passed through the homogenizer led to an additional increase in the fines content value, with 49.4% and 42.8% of fines content for 1H and 3H samples respectively. In the case of the samples 5H and 20H,

resulting from the most intensive mechanical treatment, fines are the main components, representing 75.2% and 95.7% of the material.

Figure 4 allows a qualitative comparison of the microscopic images obtained for all the fine fibrous materials used in this study. Because of fractionation, only small particles are visible for secondary fines, which rarely exceed 100µm in length. This observation matches the results obtained with L&W Fiber Tester+ where the fractions under 100µm of length represent 61.8% of the detected particles. Longer particles are observable in the images corresponding to the fine fibrous materials obtained after mechanical treatment. These images illustrate both the expected gradual reduction of fibre length and the increase of fine elements when increasing the intensity of the mechanical treatment. In the image for VB, a fraction of an untreated fibre section is mixed with fine material. In the image of 20H only fines elements are observable, the proportion of small particles being dominant in this sample (95.7% of fines accordingly to Britt Jar measurements).

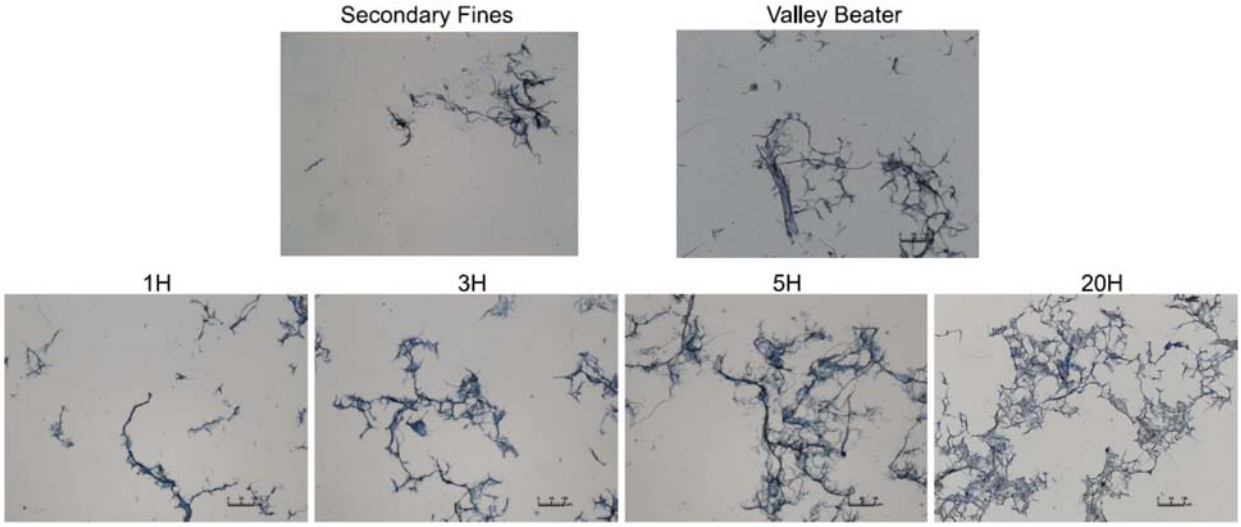

Fig. 4. Microscope images of the different stained fine fibrous materials (scale bar in images is 100 µm)

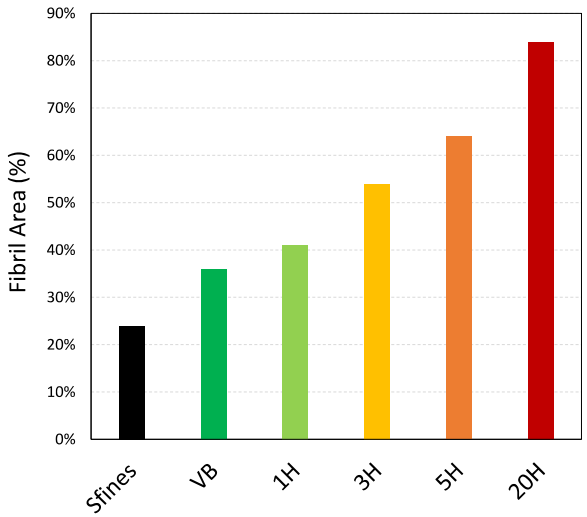

Fig. 5. Result of average fibril area for each fine fibrous material resulting from image analysis of stained microscope samples.

The result of the analysis of the microscope samples using an automated image analytical routine shows a linear increase of fibril area from secondary fines to 20H (see *Figure 5*), confirming some of the previous qualitative observations in the microscope images. Compared to the fines fraction measured using Britt Jar, this method enables

to discriminate more precisely between fibrillar and flake like material, which allows to quantify the highly fibrillated part of the material expected to bring more bonding between the fibres when mixed to the refined pulp.

Effect on Paper Thickness and Air Permeability

When adding fine fibrous materials to the furnish the increase in specific surface area is assumed to promote the formation of fibre–fibre bonds consolidating the paper structure and increasing density. Indeed, at constant basis weight, one can observe a reduction in paper's thickness (data not shown). This phenomenon results in a significant decrease in air permeability of paper, a result which has frequently been reported by other authors [23,23]. In our experiments, the reference paper produced from the refined reference pulp without the addition of any fine material shows an air permeability of 2283ml/min (see Figure 6A). Upon addition of the added materials, all mixtures showed a substantial decrease compared to this initial value. At 1% of addition to the pulp, all the different materials already showed a decrease in air permeability of at least 19.2% from the initial value. At an addition of 4% air permeability was reduced by 78.2% on average. At higher addition rate air permeability decreases further but the effect is not as pronounced anymore. Finally, for 10% of addition, the value reaches ~90ml/min, i.e. a total decrease of 96% on average.

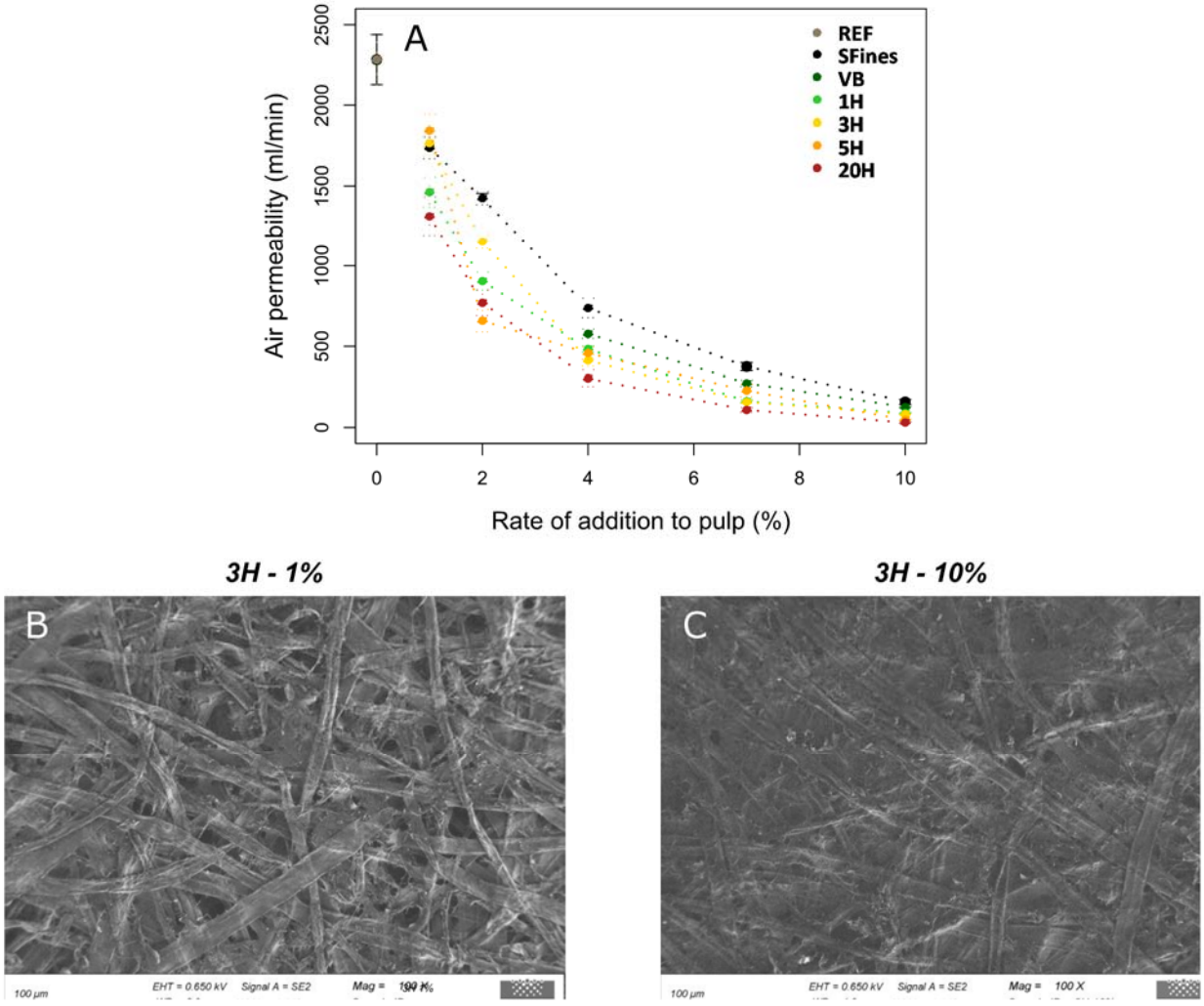

Fig. 6. A) Influence of the type and addition rate of the different fine materials on air permeability of handsheets B) and C) SEM images of surfaces of handsheets produced with (B) 1% and (C) 10% addition of 3H (magnification 100x)

These effects of densification of the paper structure are also visible in the SEM images where a clear difference in the paper structure is observed when increasing the quantity of additives (see Figure 7B and 7C). Here, for the

material 3H, the increase of the addition rate from 1% to 10% leads to a filling of the voids between the fibres and to a denser structure and smoother surface, resulting in a significantly lower air permeability.

Regarding the influence of the type of material, the most fibrillated material 20H has the strongest effect on air permeability. Comparing all material shows that the higher the fibril area, the lower is the air permeability. This observation highlights the fact that increasing the fibrillation rate of such additives leads to a better closing of the paper structure. This might be related to the relatively large and highly fibrillated structures shown in the microscope images for highly fibrillated material (Figure 4). The size distribution as it is measured using the L&W Fibre Tester does not correlate as well with air permeability. One would suspect the material SFines – showing the smallest particles – would be most efficient in closing the sheet. But on the contrary VB, which is characterized by a larger amount of longer and thicker fibres compared to SFines, leads to a lower air permeability compared to SFines apparently because of its higher fibril area. Increasing fibrillation is suspected here to decrease air permeability by increasing pore tortuosity and decreasing pore area and connectivity.

Effect on Paper Mechanical Properties

The structural modifications caused by addition of the different fine fibrous materials also has an impact on paper mechanical properties. *Figure 7* illustrates the results obtained for tensile index (TI) for the handheets made from the different blends. The results presented here illustrate the effect of each additive on the improvement of the paper properties, compared to the reference paper made from the refined pulp.

The development of TI at increasing addition rate of the fine fibrous materials is divided into three parts:
First, up to 2% of addition, bringing fine fibrillated material to the pulp is highly efficient: it results in a significant increase of TI, regardless of the nature of the additive (*Figure 7A*). In *Figure 7C*, which shows the contribution of each successive rate of addition of fine materials to the increase of TI, we can observe that a rather high proportion of the final TI increase is already achieved at 2% addition. Indeed, at 2% of addition, we can observe an increase of +10.43Nm/g on average over all the materials, which is almost half of the total average TI increase for all materials. From similar observations, Zimmerman [25] defined the concept of a "filling threshold", a concentration of fine cellulosic additives corresponding to the formation of a network structure. At this specific point, most of the mechanical improvement is achieved. Studying the effect of the addition of MFC produced by homogenization of never dried softwood pulp, Sehaqui et al. [26] also showed that most of the mechanical improvement of the paper occur between 0 and 2% of addition of MFC. Later, Alcalá et al. [27] established this filling threshold to be 2.25% for nanofibrillated cellulose produced from bleached eucalyptus pulp through a tempo-oxidation process. On the contrary, the addition of SFines showed a more or less linear increase of TI for 0% to 7% addition, a result already reported by several authors [9,12,28,29]. So this filling threshold is less pronounced and this could have the reason, that the addition of SFines does not promote the creation of a network but only consolidates existing fibre-fibre bonds.

Second, between 2% and 7% addition rate, there is little effect on paper tensile properties. The increase of TI is less marked for almost all materials (see Figure 8C). This observation follows a trend already observed for the air permeability measurements, where the effect of the rate of addition was more pronounced at low addition rates and then decreases more slowly until reaching a certain level (Figure 6A). Here we can assume that passing the filling threshold of paper mentioned earlier, most of the structuring effect of the fibrillated materials to favour fibre-fibre bonding already occurred, meaning that only a small quantity of fibrillated material seems sufficient to reach a significant improvement of paper in density and to a noticeably consolidation of its structure.

The third and final phase of the development of TI shows an interesting effect, which is in contrast to the results of air permeability measurements. Between 7% and 10% addition rate a further significant increase of tensile properties is observed, which strongly depends on the nature of the additives. For SFines and VB, characterized by the lowest fibril area, there is almost no change in TI from 7% to 10% of addition. For 1H and 3H, TI increases almost linearly between 4% and 10% addition rate. Materials 5H and 20H with the highest degree of fibrillation, however, show a further significant increase of TI, which is similar to the increase obtained at low addition rates (average increase of TI between 7% and 10% of +13.2 and +12.42Nm/g for 5H and 20H respectively). Thus, only at these high rates of addition, a clear dependency on the character of the fibrillated fine materials becomes evident: The higher the fibril area, the stronger is the increase of TI. Comparing fines and MFC like additives, Manninen et al. [28] also reported an increase of TI at higher content only for MFC like additives but not for fines. Once again, this result tends to discriminate two different mechanism between MFC and fines reinforcement ability.

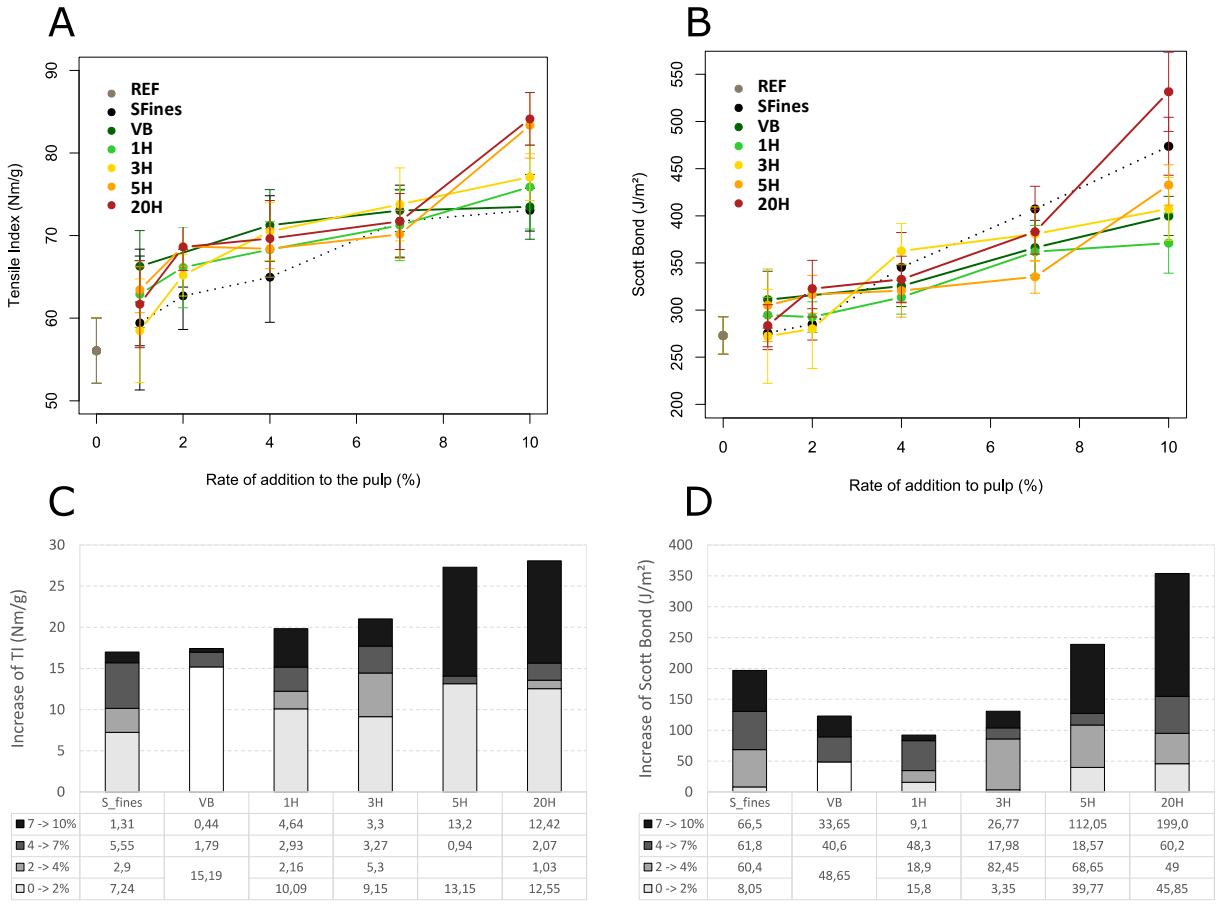

Fig. 7. A) Influence of material type and rate of addition on tensile index (TI); B) Influence of material type and rate of addition on z-strength (Scott Bond); C) Contribution of each successive rate of addition to the increase of TI; D) Contribution of the partial increases of SB for each successive rate of addition

Figure 8 illustrates the combined effect of both type and quantity of the additive on paper tensile properties with the type being characterized by fibril area. Again, one can observe that the degree of fibrillation of the various materials (represented here by the fibril area calculated from the microscope images) has a more significant influence at high rates of addition. From 1% to 7%, TI shows a limited growth function with the rate of addition, which does not depend on the fibril area. From 7% to 10%, a clear effect of quality (degree of fibrillation) of the additive is evident, with an almost linear increase of TI with fibril area.

To explain this observation, we propose that two different phenomena come into play here: First, the introduction of a low amount of fibrillated materials results in a noticeable improvement of the interactions between fibres. Paper strength is largely dependent on the number and bonding strength of fibre-fibre bonds formed during the consolidation and drying phases of the fibre network. The tensile properties are therefore improved already by small amounts of added fine cellulosic materials. This hypothesis is supported by the work of several authors, who reported similar observations and explained the phenomenon with the following mechanism: the higher hydrogen bonding between the now larger bonded areas in molecular contact result in an increase of the cohesion between fibres in contact and therefore improve tensile strength. Sehaqui et al. [26] for example, showed that the initial increase of TI up to 2% of MFC addition to the pulp also corresponded to the largest decrease of paper porosity, supporting then the hypothesis of a “consolidation” of the structure which is achieved already at 2% of addition of MFC.

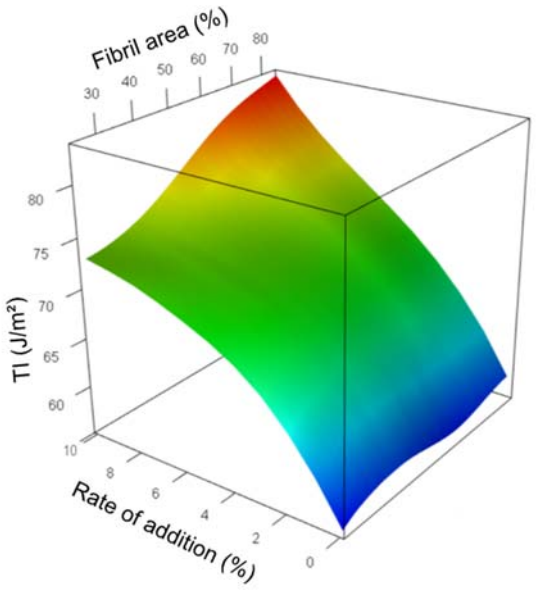

Fig. 8. Combined influence of the morphological characteristics (fibril area) of the added materials and rate of addition on tensile index (TI).

The SEM images of the paper handsheets also illustrate this mechanism (see *Figure 9A*). In this image of the handsheet made with an addition of 1% of 20H, it is possible to identify several zones where small fibrils, being likely the added fibrillar material, act as connections between two fibres (indicated in *Figure 9A* by the white arrows). From the stabilization stage observed at addition above 2%, we can thus infer that fibres are already well bonded to the adjacent ones at low addition rates. After that point, adding more fibrillated fine material to the fibres does not seem to be able to increase the bonded area to the same extent any more.

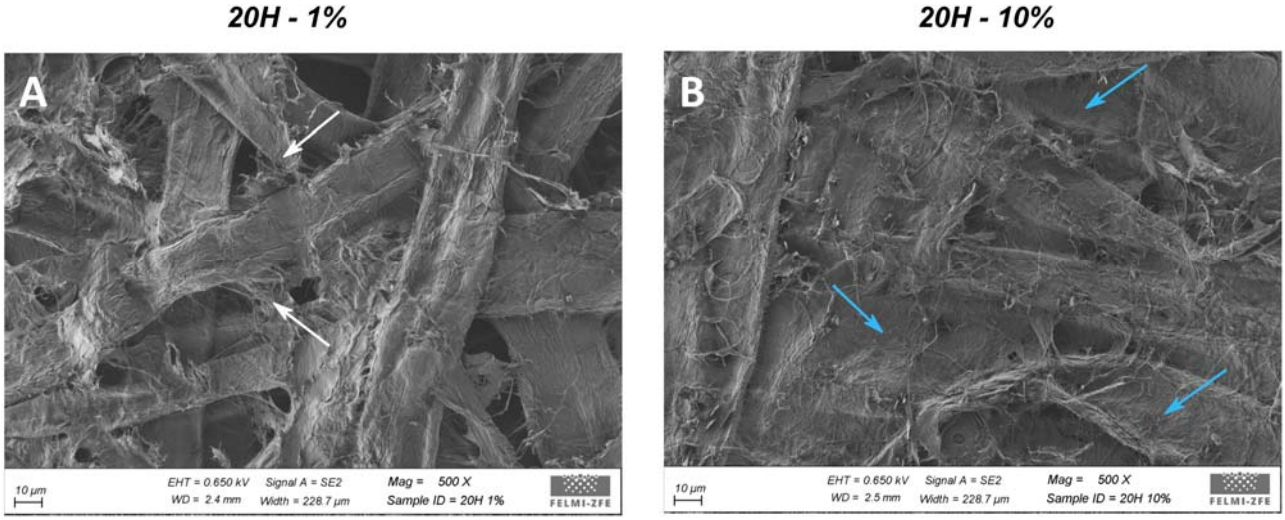

Fig.9. SEM images of handsheets with A) 1% and B) 10% of material 20H (magnification 500x). A) The white arrows indicate zones where fibrils from the added fibrous material act as additional connections between two fibres. B) The blue arrows indicate the areas forming a secondary network of fibrillar elements composed of the added fine fibrous material

Secondly, at higher addition rates (above 7% in our study) a further improvement of paper tensile strength depends on the degree of fibrillation of the added fine fibrous materials. Here, the fibre surfaces might largely be covered by fibrillar material and addition of a higher quantity of fibrillated material should not result in a further increase of the bonding area between the fibres at that point. Thus we propose that above 7% of addition, a secondary network of highly fibrillated material could be generated, resulting in a further increase of bonding in the sheet. This hypothesis

is supported by Sehaqui et al. [26] who observed that strength and strain- to-failure is dramatically increased for the composition with 10% added MFC. This secondary network from highly fibrillary materials might introduce an additional capacity to transfer stresses and absorb energy during failure events at smaller length scales leading to improved mechanical properties. Additionally to the filling threshold reported to occur at 2% of addition, higher level of addition (7% in our study) seems to be another threshold corresponding to the forming of a secondary network by highly fibrillated fine materials.

This hypothesis is supported by the SEM image of the surface of the paper containing 10% of 20H (see *Figure 9B*). Indeed, in this picture one can observe that the fibres are covered by a smooth layer of fibrillar elements, with areas in the interstices between the fibres being entirely composed of additives (indicated in *Figure 9B* by the blue arrows). Other authors also observed a similar change in paper structure in SEM or AFM pictures when adding microfibrillar additives [4, 24]. Taipale et al. [24] proved that highly fibrillated additives show a more homogeneous structure and better interact with the fibres. Hii et al. [4] proposed that higher amount of highly fibrillated, swollen and flexible MFC added to a furnish fills the interstices between fibres and thus influences porosity. Boufi et al. [11] also already proposed that MFC may generate a separate network embedded among larger fibres that contributes to boost the load-bearing capacity of the paper. Based on SEM images with 10% of MFC, Sehaqui et al. [26] proposed that MFCs act as porous membranes or foams in the pores of the larger scale wood fiber network and conclude that "it becomes clear that dense regions of MFC contribute to substantial load-carrying ability to the material". The fines fractions observed in SFines and VB, which show the lowest degree of fibrillation based on our evaluation of fibril area, do not seem not be able to interact and do not generate a strong cohesive secondary network.

Comparing nano- and micro-scale fine fibrous materials obtained from softwood pulp by grinding or refining processes, Afra et al. [30] observed that refining creates a partial skin fibrillation while grinding resulted in actual micro- and nanoscale fibrils leading to more pronounced changes in paper properties when mixed to the pulp. The authors suppose that this result can be attributed to the reduction of potential defect points of cellulose fibers by grinding, which increases their homogeneity leads to a higher ability of individuals fibrils to attach and entangle cellulosic fibers, leading to a homogeneous and well-connected network.

All these elements might explain the difference observed depending on the quantity and quality of each fine fibrous material studied in this work. The discussion of these results might allow a better understanding of the intrinsic effect of each type of added fine fibrous material on paper strength. The concept of a paper network consisting of two fibrous networks at different scale levels might be of interest for the development of new types of papers with improved mechanical performance.

CONCLUSIONS

We compared the effect on paper properties of the addition of different fine fibrous materials produced from the same bleached softwood kraft pulp, i.e. secondary cellulosic fines isolated from the industrially refined pulp by means of fractionation in a laboratory pressure screen and MFC-like materials of increasing fibrillar character obtained by refining and subsequent high-pressure homogenization.

The microscopic techniques used in this work allowed the characterization of the morphological properties of the produced materials and lead to a better understanding of their structuring effect when added to a paper furnish. The results showed that the fibril area as well as the size of the fractions (ECD) are key elements to be considered, but that their influence on paper properties varies depending on the quantity of additive added to the furnish. At low addition rates all of the applied MFC-like fine fibrous materials have a significantly positive effect on permeability and mechanical properties, which is more or less independent from the morphology of the materials. At low addition rates, it seems not necessary to use highly fibrillated additives, which are costlier to produce. At higher addition rates, however, the additional effort to produce highly fibrillated material is worthwhile, since a significant further improvement of paper properties can be achieved.

These results also allow a better understanding of the involved mechanisms. Up to an addition rate of around 7% in our study, fine fibrous materials improve bonding between fibres more or less independent of their morphology and increase the cohesion between the fibres and therefore improve strength properties. Up to this addition rate the key parameter is the rate of addition, which correlates to the improvement of all paper properties determined in this study. At higher addition rates the morphological character of the added fine fibrous material strongly influences the results. A significant positive effect of fibril area on tensile strength, becomes evident. These observations could be

explained by the creation of a second network structure of highly fibrillated materials at higher addition rates, which improves the load-bearing capacity of the whole paper structure leading to higher tensile strength.

In order to verify our hypothesis, further studies are needed to identify the exact location of the fine cellulosic materials in the paper network depending on their morphology. It would also be of interest to study further how the required level of addition to form the proposed secondary network is influenced by the morphology of highly fibrillated materials, where also the state of dispersion of these materials might play an important role. Additionally, the intrinsic mechanical properties of the proposed secondary network built up by fine, highly fibrillated materials could be evaluated by determining the mechanical properties of handsheets of different basis weights containing these materials and comparing them to sheets formed exclusively from these materials. Finally, it could also be interesting to study the effect of these materials on wet strength, which also might be improved due to this effect of secondary network generation.

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