

STRUCTURE AND PROPERTIES OF SOME NATURAL CELLULOSIC FIBRILS

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This study examines the properties of cellulosic fibrillar fines manufactured from different pulp raw materials, bleached softwood kraft (BSWK), thermomechanical pulp (TMP), and non-wood sisal. Chemical characterisation showed that the carbohydrate and lignin contents of sisal were between those of BSWK and TMP. Sisal was found to contain about three times more calcium than BSWK and TMP. Measurements from the immobilization kinetics showed that the solids content after immobilization was highest for the sisal suspension, followed by TMP and BSWK. This indicates that the dewatering ability of the fines suspension increased in the order BSWK, TMP and sisal. The loss modulus (G'') was maximum with BSWK, indicating that the greatest viscous dissipation before immobilisation took place in the BSWK suspension. The strength properties of fines sheets decreased in the order BSWK, TMP and sisal. This is due to the highly fibrillated nature of BSWK fines, as illustrated by fibre saturation point (FSP), differential scanning calorimetric (DSC), and hydrodynamic specific volume (HSV) measurements.

Keywords: Microfibrils; Fines; Rheology; Immobilization; Dewatering; Strength; Chemical characterization

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INTRODUCTION

There is currently renewed interest in engineering new cellulosic products from the structural elements of cellulosic fibres. Biodegradable, renewable, and ubiquitous, plant and wood fibres have a hierarchical structure consisting of smaller and mechanically stronger entities. An example of this structural hierarchy was illustrated by Frey-Wyssling (1957), who discussed the various scales of structure in cotton (Table 1).

Table 1. Structural Hierarchy in Cotton Fibres (after Frey-Wyssling 1957)

Scale	Area of cross section	Number of cellulosic chains on cross section
Cotton hair	314 000 000 nm ²	1*10 ⁹
Macro fibril	160 000 nm ²	5*10 ⁵
Micro fibril	625 nm ²	2*10 ³
Elementary fibril	30 nm ²	1*10 ²
Cellulose molecule	0.32 nm ²	1

Fibrillar fines obtained from cellulosic fibres are known for their unique structure, many useful characteristics, and large number of potential industrial, techno-logical, and commercial applications. It has been concluded earlier that the crystallinity of the fibrils and their accessibility to swelling or hydrolysis vary with the biological origin of the material and its pre-treatment (Berglund 2005).

Recently, several routes towards synthesizing fibrillar fines have been described in the literature. One industrial approach to produce cellulosic fibrils is based on the dissolution of cellulose in solvents, regeneration, and even potentially electrospinning (Liu and Hsieh 2002), where the dissolution process causes formation of structural elements of cellulose. Microcrystalline cellulose can be prepared by acid hydrolysis, eliminating the amorphous regions of cellulose (Dong et al. 1998). The cellulose microcrystals formed by this process, which randomly aggregate through hydrogen bonding, have diameters of 10-30nm. Formation of cellulosic microfibrils by a bacterial process has been studied by Tokoh et al. (1998). Production of microfibrils from non-wood resources, through separation of microfibrils from sugar beet and potato tuber cells, has been reported by Dufresne et al. (2000).

High-shear mechanical treatment to generate fibrillar fines have been described by Matsuda (2001). Formation and application of microfibrils from wood fibres has been studied by Taniguchi et al. (1998). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenisation has been used for preparing cellulosic fibrils in gel form, as shown by Pääkkö et al. (2007).

Although various means of generating microfibrils have been tried in recent times, we have insufficient knowledge about the effect of the source, pulps of different origin, on the nature and characteristics of cellulosic microfibrils.

In this work, our preliminary aim was to examine pulps produced by two major pulping processes, chemical and mechanical pulps, as raw materials for cellulosic fibril production. On the other hand, initial tests with sisal pulp grinding showed that the sisal fines exhibited characteristics that were far different from those of chemical and mechanical pulp fines. Thus, we hypothesised that by using distinguished market pulps, composed of varying amounts of lignin - bleached softwood kraft (BSWK), thermomechanical (TMP), and non-wood sisal - it is possible to gain a better understanding of the effect of the raw material on the type of fibrillar fines produced with high-shear grinding. The pulps were degraded into fines by treating them in a high-shear Supermasscolloider[®]. The fines were analysed for chemical, rheological, water interactions, and strength properties. An optical microscope was used to study the structure of the fines. The information obtained from this study can be used for engineering new composite materials, and for process and product optimisations.

EXPERIMENTAL

Raw Materials

ECF-bleached softwood kraft pulp (non-dried pulp containing Scandinavian spruce and pine in equal amounts) was obtained from a Finnish pulp mill. TMP (made from Norway spruce), sampled from a reject line, was obtained from a Finnish pulp mill

at 30% consistency and stored in freezer to await experiments. Defrosted samples were disintegrated at 3% consistency and used for further grinding to produce fines. Commercial sisal pulp (obtained from Africa), cut into 5-cm pieces, was disintegrated and ground in the SuperMasscolloider[®] to produce fines.

Grinding

The grinding was carried out with an ultra-fine friction grinder (Super masscolloider^{®1}). The grinder reduces the fibres into fines by mechanical shearing (Matsuda et al. 2001). More details about operation of this grinder have been reported (Kang 2006). In this device, the grinding takes place between rotating and stationary abrasive stones made of silicon carbide (SiC). The gap between the stones with a grit class #46 (grit size 297-420 μm) was adjusted to 80 μm . The treated pulp was discharged by centrifugal force enhanced by rotor blades. The grinding degree was advanced by re-circulating the pulp suspension. Determination of energy consumption was somehow difficult, due to small operating gap. At this gap occasional contacts between stones have been reported.

Grinding was performed at room temperature with cooling of the stones by running water at the consistency of 3%. The BSWK and TMP pulps were re-circulated for 5 times and sisal pulp 4 times, respectively. The estimated maximum residence time in the gap for one path was in the order of 0.5 sec. The total time between grinding stones was in the range of 180 sec per path.

Sheet Forming and Mechanical Testing

Round sheets were formed from the fines in a dynamic drainage jar (DDJ) by filtering a stirred fines suspension onto a Whatman #604 filter paper with a diameter of 110 mm. The Whatman filter paper was removed from the DDJ, and the fines sheet was placed on a pressing plate. Old blotters were placed on the filter paper and couched by hand to remove the excess of water. Subsequently, filter paper was removed from the sheet. A new blotter was then placed over the sheet and gently pressed by hand to attach the blotter to the fines sheet. Finally, the sheets were air-dried using drying plates on a rack in a conditioning room (23°C, 50% RH).

Fines sheets strength properties were analysed according to ISO 1924-2:1994, except that the span length was 70 mm. Light scattering was measured according to ISO 9416-1998.

Fines Characterisation

The blend of fines was fractioned in a Bauer-McNett classifier, which segregates the fines suspension into different streams based on physical properties, such as fiber length and flexibility (Gooding and Oslon 2001). We slightly modified the standard, SCAN-M6:69, operating conditions by using 30g oven-dry pulp and 20 minutes of operating time. Progressively decreasing 100, 200, 300, 400 screen meshes were used in this study.

The immobilisation kinetics of the fines suspensions were measured with a Physica MCR 300 rheometer. Measurements were conducted with a plate-plate assembly

¹ Supermasscolloider[®] (Model MKZA 10-15J) is a trademark product of Masuko Sangyo Co. Ltd, Japan.

for the direct strain controlled oscillatory test (DSO) under constant conditions. Test conditions were as follows: temperature of 23°C, strain γ of 1%, angular frequency ω of 10 s⁻¹, and initial gap of 1 mm. Fines suspension at a consistency of 3% was applied onto the special polycarbonate filter with pore size of 0.22 μm . At consistency lower than 3% the test reproducibility was difficult to achieve. Vacuum of 300 mbar was applied after closing the gap and starting oscillation. The zero normal force between plate and sample was maintained by the decreasing gap during the process of dewatering. Immobilisation of the sample took place when solids content of pad reached the point where particles had established a spatial structure and could no longer move freely. The maximum of loss modulus G'' corresponded to this point (Wollny 2001).

Solute exclusion and thermoporosimetric measurements were performed to determine the fibre saturation point (FSP), the freezing bound water (FBW), and the non-freezing bound water (NFW) according to the methods described in the literature (Stone and Scallan 1968; Maloney and Paulapuro 2001). The hydrodynamic specific volume of pulp fines was determined as a fines sediment volume per solids after 24 hours of settling at a consistency of 1g/l under conditions described by Marton and Robie (1969).

Extractives, carbohydrates, free sugars, and cellulose were determined according to the test methods listed in Table 2.

Table 2. Chemical Analytical Methods Used for Analysing Organics and Inorganics in Fines

Components	Analytical Techniques
Cellulose	Tappi T249 cm-85
Extractives	Ekman, R. (1980), "Wood extractives of Norway spruce - A study of nonvolatile constituents and their effects on <i>Fomes annosus</i> ," PhD thesis, Laboratory of Forest Products Chemistry, Åbo Akademi University.
Lignin	Iiyama, K., and Wallis, A.F.A. (1988). "An improved acetyl bromide procedure for determining lignin in woods and wood pulps," <i>Wood Science and Technology</i> 22(3), 271-280.
Total carbohydrates	Bertaud, F., Sundberg, A., and Holmbom, B. (2002). "Evaluation of acid methanolysis for analysis of wood hemicelluloses and pectins," <i>Carbohydr. Polym.</i> 48(3), 319-324.
Free monomeric sugars	Pedro, F., and Holmbom, B. (1996). "Anionic groups in papermaking fibres: Origin, depth profile and surface distribution," <i>Nordic Pulp Paper Res. J.</i> 226(11), 216-219.
Metals	Mass spectrometry

Optical Microscopy Study

The structure of fines was studied qualitatively with a Leica DM LAM light microscope, equipped with a phase contrast optical system. Phase contrast microscopy is an optical technique that can be used to produce high contrast images of transparent specimens (Pluta 1989). In effect, phase contrast microscopy translates a phase shift of light waves into the differences in amplitude. This means that the samples can be examined in their natural state without staining. In particular, this is an advantageous for fines, as they are hard to detect even with stains.

RESULTS AND DISCUSSION

The fractional composition of the studied fines is shown in Fig. 1. It was found that the fines content (pass fraction, 200 mesh) was the highest for BSWK, followed by TMP and sisal fines. In addition, the BSWK fines contained the highest and sisal the lowest percentage of 400-pass fines. Optical microscopic observation of the BSWK fines passing the 200-mesh showed that a significant proportion of fines had dimensions which were larger than the size of apertures, i.e., above 76 μm . Hence, we infer that BSWK fines should be highly flexible in order to pass openings of smaller size.

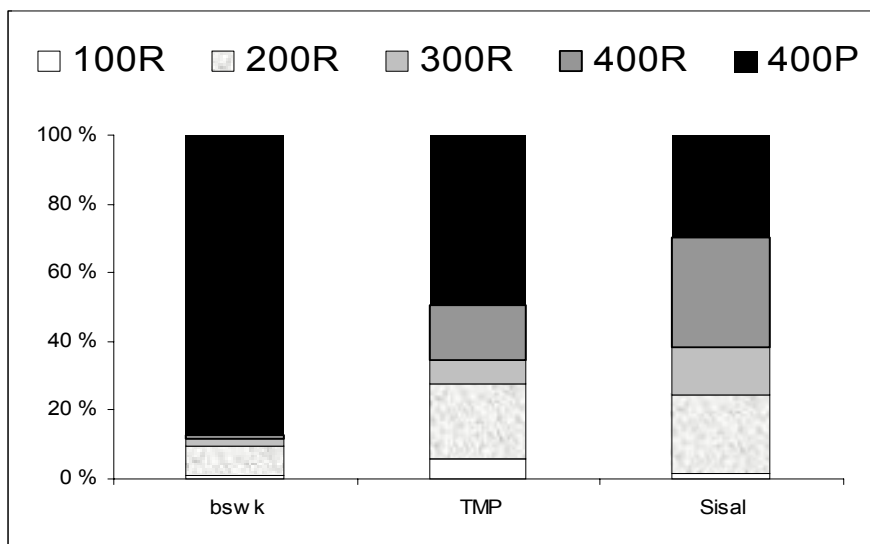


Figure 1. Bauer McNett fractions obtained for the three different fines materials. Abbreviations: R – Retained; P–Passed

The organic chemical constituents of the studied fines materials are shown in Fig. 2. It can be noted that sisal had a higher cellulosic content than TMP pulp fines. Also, the lignin content was the highest in TMP fines, followed by sisal and BSWK fines. TMP fines had a high content of free sugars, while sisal and BSWK fines contained minimal amounts of free sugars and extractives.

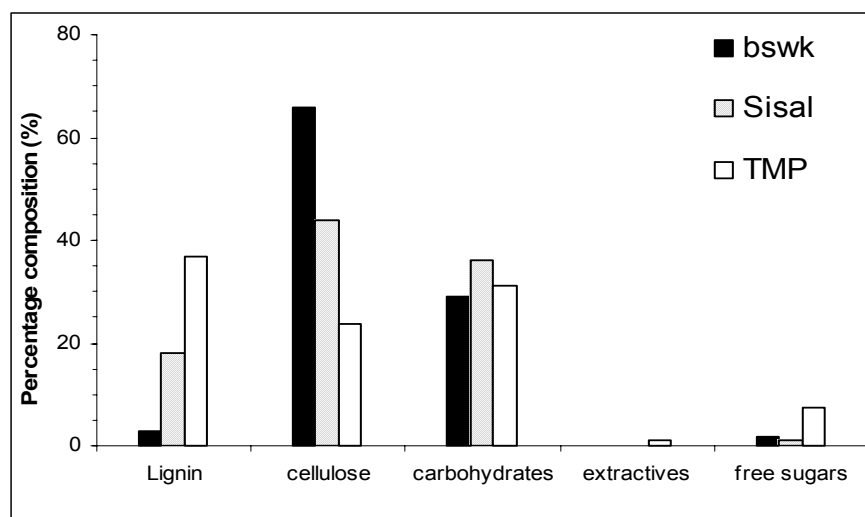


Figure 2. Organic composition of the three different pulp materials

Among the inorganic components found in the pulp fines (Fig. 3), sisal had the highest calcium content. Calcium is found as calcium oxalate in sisal pulp fines. Bleached softwood kraft pulp fines had the highest content of sodium in the structure. TMP pulp fines contained more manganese than the fines materials from the other two sources. The difference in the metal composition is attributed both to the raw material and the process. However, since the studied pulps are from the most common processes the information about metal composition is valuable.

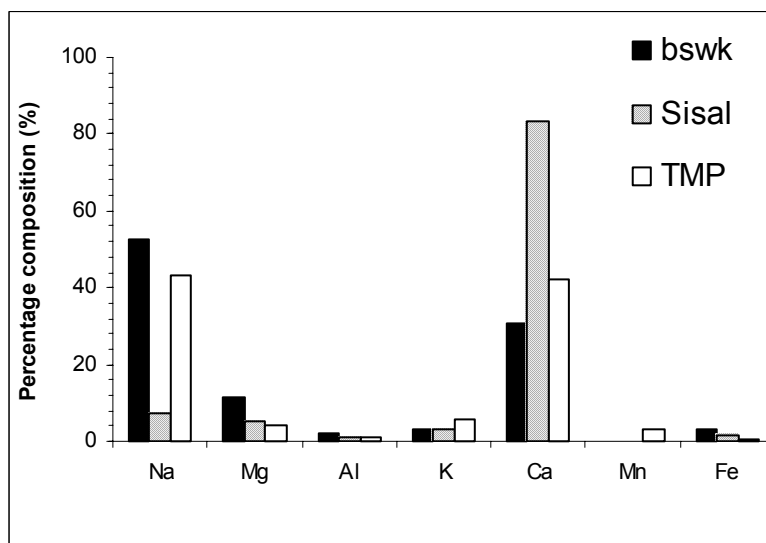


Figure 3. Metal composition of the three different pulp materials

Rheology is a powerful tool for characterising fines suspensions, as shown in Table 3. The rheological behaviour and dewatering process of the fines suspensions were examined using an immobilisation cell. The simultaneous measurement of dewatering

kinetics and the corresponding rheological properties reveals possible flow and dewatering behaviour of fines in forming or coating operations.

The ability of the material to store energy (and therefore, the structural strength, gel strength, and stiffness) is defined in terms of the storage modulus (G'). It was the highest for BSWK and practically the same for TMP and sisal suspensions. The loss modulus, G'' , is associated with the ability of the material to dissipate mechanical energy to heat in viscous flow. The mechanical loss factor, $\tan(\delta)$, which is a ratio of G''/G' , was smaller than 1 at immobilization point for all samples. Thus, the studied fines suspensions can be considered as gels (Almdal et al. 1993).

Table 3. Rheology of Different Pulp Fines Suspensions

Item	G'' @IMMO point (kPa)	Final bulk (cm ³ /g)	Final solids (%)	IMMO time (s)	Solids (mg)	$\tan(\delta)$ @ IMMO point	Consist. (g/l)
BSWK	29	5.49	8.5	15.3	63	0.33	20
TMP	13	2.73	11.2	29.8	115	0.41	38
Sisal	16	5.15	17.3	14.4	95	0.45	32

The loss modulus G'' at the immobilization point was highest for BSWK, which shows that the biggest energy dissipation to heat took place in the BSWK suspension, i.e., it had the highest viscosity just before immobilization. The energy dissipation in sisal and TMP fines was roughly similar and significantly lower than in BSWK. This observation is in agreement with the notion about high specific surface of the BSWK. The final bulk was lowest for TMP fines, showing that the structure of TMP fines was more compact than that of the other two fines materials.

The solids content obtained at the immobilisation point indicates the maximum possible dewatering from the mobile viscous fines suspension. The dewatering degree was highest for sisal fines, followed by TMP and BSWK fines. On the other hand, the immobilisation time varied for the fines suspensions, because of the different solids contents of the initial samples. With the BSWK samples, higher solids could not be reached, due to the developed internal surface, which able to hold more water.

The strength properties of the fines sheets are listed in Table 4. The basis weights of the fines sheets were not similar due to difficulties encountered in the forming process. It was difficult to dewater higher grammage BSWK sheets, while lower grammage TMP and sisal handsheets were too brittle to handle. According to our findings, the highly fibrillated BSWK fines formed structures with high density, tensile index, and stiffness. This is attributed to the increased specific surface area of the BSWK fines, resulting in an enhanced relative bonded area and tougher structure (Retulainen et al. 2002). In contrast, the stiff and the least conformable sisal fines particles gave the lowest tensile strength.

Table 4. Strength Properties of Sheets Composed of Fines

Sample	Basis weight (gsm)	Apparent density (kg/m ³)	Thickness (µm)	Tensile index (N*m/g)	TEA index (J/kg)	T. Stiff. index (MN*m/kg)	Light scattering (m ² /kg)
BSWK	86	1020	84	79	2839	6.7	3
TMP	138	586	226	28	198	3.0	49
Sisal	163	454	359	11	36	1.9	70

As expected, the light scattering was highest for the sisal fines and the lowest for the BSWK fine sheets. This is attributed to the bulkier structure of sisal handsheets and higher extension of solids-air interface. Furthermore, compared to TMP fines, sisal fines had higher brightness.

The higher fibrillation degree of BSWK has been confirmed by studies of fibril-water interaction, based on fibre saturation point (FSP) and differential scanning calorimetry (DSC) measurements. The measured FSP of the BSWK, TMP, and sisal samples was 4.43 g/g, 1.32 g/g, and 1.32 g/g, respectively. The total water held inside the fibrous material is classified in terms of bulk water (BW), freezing-bound water (FBW) and non-freezing bound water (NFW) (Fig. 4).

An increased degree of refining through fibre degradation leads to formation of fibrillar fines materials. In the case of BSWK, these fines particles form an intertwined, highly branched network structure. The highest amount of water, bulk water, was trapped in the inter-fibrillar space, corresponding to the macropores level. In addition, the amount of the intermediate pores, corresponding to FBW, was also higher for BSWK. On the other hand, bulk water was significantly lower in TMP and sisal fines due to their stiffer structure and higher hydrophobicity. Since the amount of non-freezing water, strongly associated with cell wall constituents, was similar for all the fines samples, their submolecular structure can be considered to be similar.

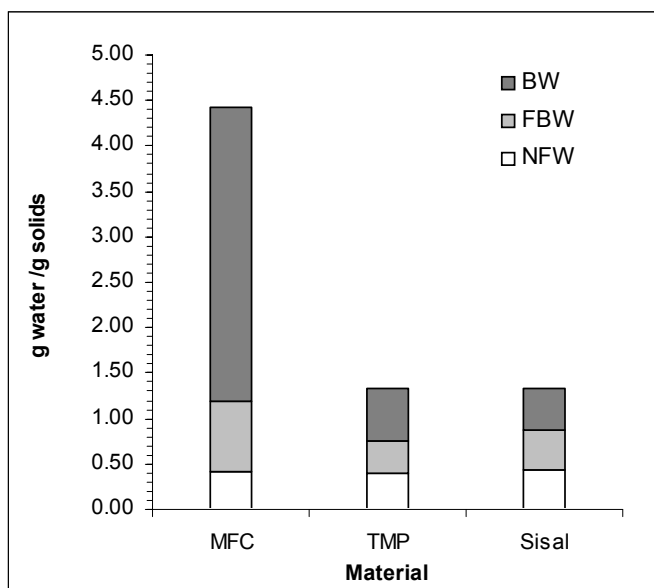


Figure 4. Water adsorption in the inter- and intra-fibrillar matrix, obtained with the differential scanning calorimetric technique and solute exclusion

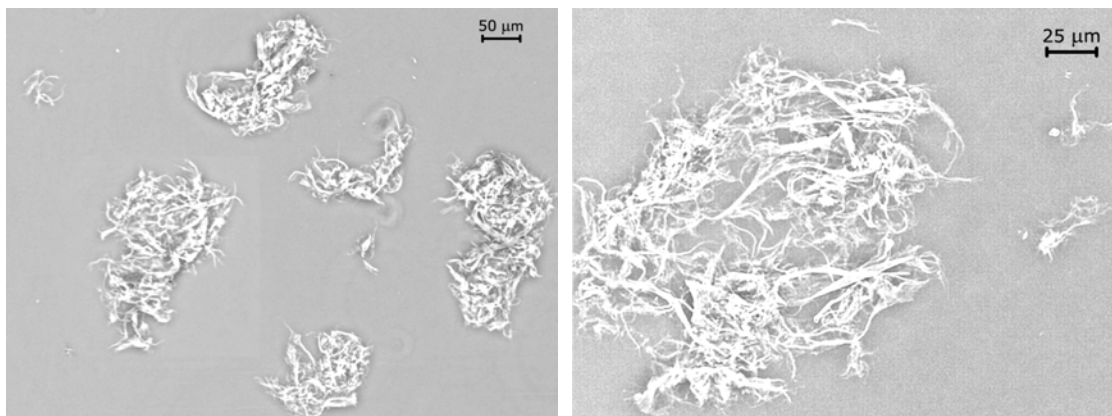
The hydrodynamic specific volume (HSV) of the different fines, obtained from the sediment by settling of suspended materials, is shown in Table 5. According to the table, the BSWK had the highest HSV, showing that the fibrillar fines produced from bleached kraft pulp had the highest specific surface and occupied volume. On the other hand, sisal fines formed much denser sediment, showing that the fines were packed tighter and had the smallest specific surface area. However, higher density of sediment can be partly due to the higher acidity of sisal fines.

Table 5. Hydrodynamic Specific Volume of the Three Different Types of Fines Materials

Samples	Hydrodynamic specific volume (cm ³ /g)	pH
BSWK	778	6.7
TMP	180	6.0
Sisal	56	5.6

Optical Microscopic Study of Fines

Each particle of the BSWK fibrillar fines comprises a complex network, as shown in Fig. 5. The fibrils are flexible and capable of holding water in the inter-fibrillar space of their network structure. Thus, the high fibre saturation point (FSP) and free bound water (FBW), as shown in Fig. 4, can be attributed to the fibrillar networks. According to the micrographs, the fibrils have high aspect ratios. On the other hand, the network nature makes it difficult to apply conventional particle size measurements for determining the particle size distribution for these fines suspensions.

**Figure 5.** Negative phase contrast images of fibrillar fines obtained from bleached softwood kraft pulp; lower (left) and higher (right) magnification

TMP fines consisted of fibrillar and flake-like fines (Fig. 6). The TMP fibrillar fines were stiffer than BSWK fines. Sisal fines had the least flocculating tendency among the three types of fines (Fig. 6). Also, some of the fibrillar fines seemed to be longer and thicker.

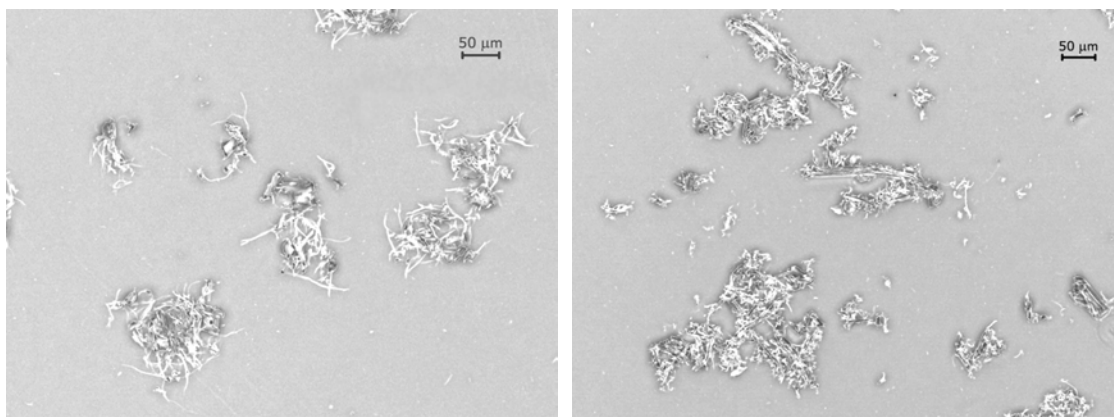


Figure 6. Negative phase contrast images of TMP fines (left) and sisal fines (right) obtained by pulp degradation in a Supermasscolloider®

CONCLUSIONS

In this study, fines material produced from two distinguished types of market pulps as well as from exotic sisal pulp were examined to determine their potential for use in various applications.

Chemical characterisation showed that the fines from typical sisal pulp contained significantly higher calcium ions, which may be a significant factor for some possible applications. Rheology studies showed that all the fines behaved viscoelastically, and that the dewatering degree was highest for sisal and lowest for BSWK pulps. The loss modulus was highest for BSWK, showing that the viscosity was greatest for these fines.

The highest and lowest density and tensile strength values were obtained for samples produced from BSWK and sisal fines, respectively. Highest strength and density of BSWK sheets were attributed to the augmented specific surface area, as indicated by fibril-water interaction and settling studies, of these fibrils.

Microscopic investigations confirmed that the BSWK fibrils form an intertwined extended network structure. On the other hand, TMP and sisal fibrils were stiffer and contained more flakes and coarser materials.

Fines material obtained from typical TMP and BSWK pulps, as well as from exotic sisal pulp, showed the range of properties that can be used to achieve different strength-dewatering combinations in paper or other composite products.

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