

PRODUCTION AND POTENTIAL OF PCC-FUNCTIONALIZED NANOCELLULOSE COMPOSITES

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ABSTRACT

Mineral fillers are indispensable in many industrial branches and are used in a variety of different materials. In plastic technology they act as a classic extender to lower the costs of the production process but also as “active fillers” to improve the mechanical and optical property profile. In the paper industry, fillers are also used to reduce raw material costs and to adjust the optical as well as surface properties. However, fillers entail the problem that their application quantity is sharply limited. Inorganic fillers show no binding properties. They reduce the product strength with higher use and lead to complications in the further processing of the products (e.g. increased dust propensity during the packaging and printing processes). In order to expand the use of fillers and their positive effects on varying products and to prevent the negative effects of the material in parallel, mineralized cellulosic structures should be created for versatile applications in different branches of industry.

1 INTRODUCTION

1.1 State of the Art

Since the middle of the 20th century, intensive research has been carried out to find alternative possibilities for the efficient use of mineral particles in paper production in order to improve filler retention as well as mechanical, optical and surface properties of the paper and to increase the filler content in the paper, among other things to reduce raw material costs. The different concepts that were pursued in this context were the addition or incorporation of mineral fillers (mainly calcium carbonate and kaolin) into the fibre lumen or onto the fibre surface either mechanically or chemically, including:

- the in-situ precipitation of filler into the fibre lumen (*lumen loading*) [1] or into the mesopore spaces of the fibre cell wall (*cell wall loading*) [2] or onto the fibre/fine surface
- the in-situ precipitation of filler into the fibre lumen (lumen loading) [1] or into the mesopore spaces of the fibre cell wall (cell wall loading) [2] or onto the fibre/fine surface (SuperFill, fibre loading, ultrafine bubble method) [3-10],
- in-situ precipitation of filler onto micro- and nanofibrillated cellulose [11-14],
- pre-flocculation of fibre/fine and filler (*In-line PCC™ Filler*) [15-19],
- co-grinding of filler and fibre (*FiberLean®*) [20-23], and
- polyelectrolyte multilayering (modifying the filler surface with polyelectrolyte layers to improve the interactions between fillers and pulp fibres and thus the filler retention as well as the strength properties of paper) [24-26].

In the previous methods for fibre loading (predominantly using $\text{Ca}(\text{OH})_2$ and CO_2 for PCC precipitation), different difficulties were encountered. On the one hand, there was insufficient diffusion of the Ca^{2+} -ions into the fibre wall during the precipitation reaction. Furthermore, there were limits to the loading of fibre lumen or cell wall due to the usable concentration gradient as a driving force and there was a deterioration of the optical properties during paper production. [3, 10] Another difficulty was that the precipitation of the filler took place predominantly into the aqueous phase rather than onto/into the fibre. [3, 15-17] Composite formation with micro/nanofibrillated cellulose, on the other hand, resulted in more difficult material handling, as the nanocellulose caused reduced drainability during paper production. [11-14]

Trials on composite formation with $\text{Ca}(\text{OH})_2$ in an extruder (twin-screw extruder) started in 2014 showed that PCC precipitation has potential, but complete $\text{Ca}(\text{OH})_2$ conversion could not be achieved. Likewise, the PCC precipitation also took place to a large extent in the aqueous phase. [27, 28]

1.2 Motivation

The compounding of carbonates with micro- or nanofibrillated cellulose, which is produced by chemical-mechanical degradation of the fibre wall into its basic constituents, has gained particular attention, since the material properties of these compounds permit various applications beyond paper production such as plastic and filter production (foam forming processes), construction and building materials, automotive or medical products. [3, 11] Disadvantage of previously used processes for composite production (precipitation reactions by means of $\text{Ca}(\text{OH})_2$ and CO_2 or co-grinding of carbonates with cellulose) is that there is no irreversible deposition of the filler. A mechanical accumulation of the inorganic species into fibrillar cellulosic structures is formed which compensate for the loss of strength in the paper during conventional PCC application, but no longer contribute fully to light scattering and thus to an increase in opacity. [15, 23]

To counteract this problem and based on the numerous studies on CaCO_3 precipitation on surfaces, a novel process was developed to produce hybrid fillers from chemically as well as mechanically modified fibrous cellulose materials and CaCO_3 precipitated on them insitu via a double-exchange reaction with CaCl_2 and Na_2CO_3 in a twin-screw extruder, as shown schematically in Figure 1.

The special fibre-reinforced fillers produced by this new process are characterised by the fact that the PCC-filler is irreversibly attached to the cellulosic fibres through targeted fibre selection/modification. The difficulties of strength loss

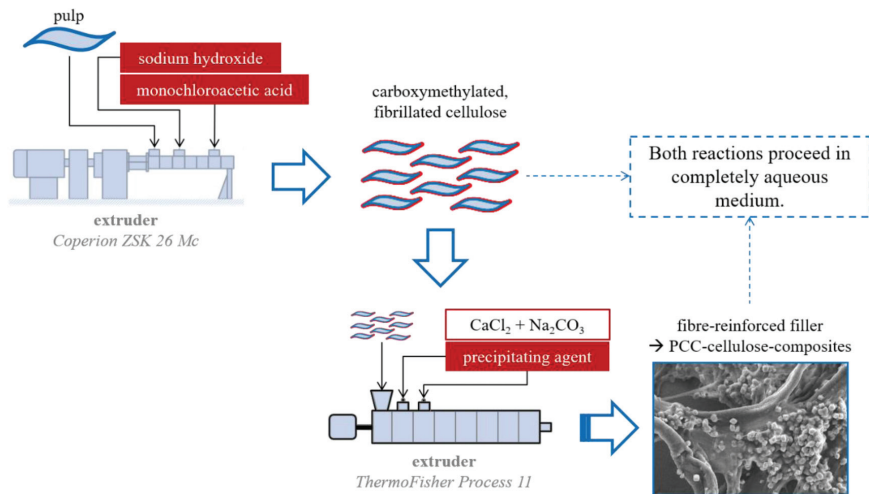


Figure 1. Schematic representation of reactive extrusion for chemical-mechanical cellulose treatment and in-situ PCC precipitation to get PCC-functionalized nanocellulose composites [30].

and/or loss of surface or optical properties observed so far are to be reduced and in addition the filler retention during sheet formation is to be increased in order to prevent material losses. Despite being based on chemically and mechanically pre-treated fibres, the new hybrid material is said to be characterised by simple material handling. Consequently, it should not lead to any dewatering difficulties during application. A novelty of fibre-reinforced fillers should be that they can be used not only in paper production to improve the property profile, but also beyond that (e.g. in plastics, construction fibre boards, filters/filter aids . . .).

2 MATERIALS AND METHODS

2.1 Materials

An unrefined spruce/pine pulp, elementary chlorine-free bleached (NBSK) supplied by Zellstoff Stendal GmbH, Germany, was used for the production of the fibre-reinforced fillers. The length-weighted fibre length, measured with the kajaaniFiberLab™ of Metso, was 1.91 mm, the water retention value (WRV) – determined according to ISO 23714 standard – 1.33 g/g and the degree of polymerization (DP) 834. It was evaluated from the limiting viscosity in cupriethylenediamine (CED) solution according to the ISO 5351 standard. The surface charge determined using the PTS-METHODE RH-102/2009 was $-30.80 \mu\text{eq/g}$ and the carboxyl group content 35.53 mmol/kg (determination based on European patent specification 1 106 732 B1). The analytical grade chemicals used for the fibre pre-treatment and purification (sodium hydroxide (NaOH), monochloroacetic acid (MCA) and ethanol ($\text{C}_2\text{H}_5\text{OH}$)) were purchased from Th.Geyer (CHEMSOLUTE®), Germany and hydrochloric acid (HCl) was from Merck KGaA, Germany. All analytical grade chemicals used for precipitation of calcium carbonate (calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium carbonate (Na_2CO_3)) were purchased from Bernd Kraft GmbH, Germany. All of the chemicals were used without any further purification. Deionized water, which was produced with an ion exchanger of Mieth GmbH, Germany, was used throughout the experiments for purification of the fibre-reinforced fillers as well as for dissolution of the reagents.

2.2 Fibre Pre-treatment – Carboxymethylation and Fibrillation in an Extruder

The NBSK was defibred, thickened and then separated by a brushing machine for better processability in the extruder. A co-rotating twin-screw extruder (Copenhagen, ZSK 26 Mc) was used for mechanical and chemical fibre pre-treatment. The screw used consisted of various thread elements, kneading block elements as well

as return kneading block elements. The cellulose pulp is added to the extruder via a Coperion K-Tron differential gravimetric feeder. In a single-stage reactive extrusion at 60°C in an aqueous medium, the cellulose is activated with 20–50% NaOH and etherified with approx. 40% MCA. [29] In this way, side reactions can be reduced. After the extrusion process, the carboxymethylated cellulose needs to be neutralized by HCl to pH 4. Afterwards the neutralized cellulose needs to be purified to an electrical conductivity of less than 0,7 mS/cm. This can be achieved either with a gentle purification with 85% vol. ethanol, or with a technical cleaning by means of tap water in a CEPA centrifuge TZ4 (rotation speed 1,600 min⁻¹, filling capacity 30 kg). In the first case it is possible to obtain the water-soluble fraction of carboxymethylated-fibrillated cellulose (CMFC), while in the second process the water-soluble fraction is washed out. [30]

2.3 Characterization of Carboxymethylated-fibrillated Cellulose

The degree of substitution was determined according to Eyer method [31] using a Metrohm Titrando 888 with automatic sample processor 814 USB and the degree of polymerization (DP) according to the ISO 5351 standard. In addition, Dynamic Vapour Sorption (with DVS Advantage of Surface Measurements System) was measured at room temperature using a 1 Cycle 0–90–0 dm/dt with a sequence of 0–15–30–45–60–75–90 target% P/Po. The fibre morphology (length-weighted fibre length, fines, fibre width, fibre length fractions and fibrillation) was analysed with a Valmet Fractionator. Furthermore, scanning electron microscopy (SEM) images were taken (with the device JEOL JSM-6510) to visualize the chemical and mechanical modified fibres, their fibrillation and water-soluble fractions. For the exact determination of the water-soluble fraction, it was determined as follows. First, the dry content was measured with an IR-scale (Sartorius MA30 Moisture Analyzer) to prepare 200 g of a homogeneous 2 wt.-% fibre slurry. The fibre slurry is left to soak overnight on a shaker. The next day the slurry is centrifuged with a Hettich Centrifuge (Universal 320R) for 30 min with 5000 rpm. The resulting aqueous supernatant is poured off. The remaining moist pulp is dried in balanced weighing jars in a Memmet model 100–800 drying cabinet at 105°C. Finally, the glasses are balanced and the water-soluble fraction is calculated according to Equation 1.

Equation 1. Calculation of the water-soluble fraction w_s [%] of modified and unmodified cellulosic fibres

$$w_s [\%] = \frac{(\text{initial weight fibres}_{\text{oven dry}} [\text{g}] - \text{weight out fibres}_{\text{oven dry}} [\text{g}]) \times 100\%}{\text{initial weight fibres}_{\text{oven dry}} [\text{g}]} \text{ with}$$

$$\text{weight out fibres}_{\text{oven dry}} [\text{g}] = \text{total weight}_{\text{oven dry}} [\text{g}] - \text{weighing jar}_{\text{oven dry}} [\text{g}]$$

The charge properties of the fibres also were investigated. On the one hand, the surface charge (see PTS method, heading 2.1) was determined. On the other hand, the total charge or the carboxyl group content was analysed based on the method also mentioned above, under point 2.1. *Materials*. According to ISO 23714 standard the water retention value (WRV) was determined, too.

2.4 Filler production – Precipitation of PCC onto Pre-treated (Carboxymethylated-fibrillated) Cellulose in an Extruder

The mineralization of the modified fibres (carboxymethylated-fibrillated cellulose) also takes place in a co-rotating twin-screw extruder (ThermoFisher, Process 11) with various screw elements (among other thread, kneading block and return kneading block elements). [28, 30] According to the procedure developed at the PTS [30] calcium carbonate (PCC) was precipitated on the increased specific surface of the pre-treated cellulose (CMFC) performing a double exchange reaction of carbonate salts and alkali metal carbonates. [29, 30, 32, 33] In this case, calcium chloride ($c_{\text{CaCl}_2} = 3.25 \text{ mol/l}$) and sodium carbonate ($c_{\text{Na}_2\text{CO}_3} = 1.9 \text{ mol/l}$) solutions were used for PCC precipitation. Depending on which PCC amount should be reached, the volume flow of the reagents needed to be adjusted. In order to continue the fibrillation of the modified cellulose in the second extrusion step and to push back the PCC precipitation into the aqueous phase, the stock consistency in the extruder was set as high as possible – depending on the fibre material between 13% and 54%. The CMFC dosing (0.2 kg/h) was carried out via a gravimetric feeder of ThermoFisher Scientific (Process 11 Gravimetric MiniTwin-Feeder). Furthermore, the temperature of the extruder blocks was set to 65°C to promote the calcite formation of the calcium carbonate. [34] After extruder precipitation, the cellulose-PCC filler needs to be purified with deionized water till an electrical conductivity of less than 0.7 mS/cm to remove the undesired by-product sodium chloride. The resulting mineralized cellulose has a dry content of roundabout 9 wt.-%. Thereafter parts of the hybrid fillers were dried by solvent exchange with acetone, so that the application of the fillers could be investigated as paste as well as powder.

2.5 Characterization of Fibre-reinforced Fillers

Thermogravimetric analysis was used to determine the dry content and the ash content (PCC content in the hybrid filler) of the cellulose-PCC fillers. The dry content was determined at 105°C according to DIN EN 20287 and the ash content at 525°C according to DIN 54370. In addition, it was analysed how much of the precipitated PCC is irreversibly attached to the fibres. To this end, washing tests were carried out in a DEGUSSA washing cell (see Figure 2).

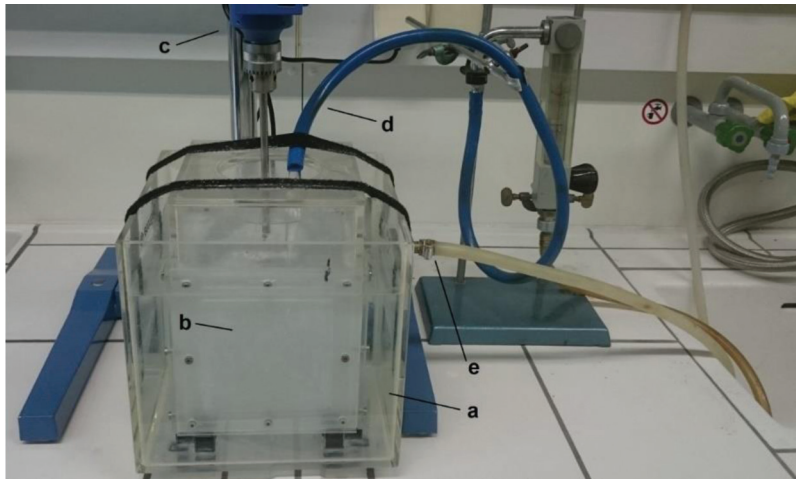


Figure 2. DEGUSSA washing cell consisting of (a) outer cell (edge length 30 cm), (b) inner cell (edge length 16.5 cm), (c) stirrer, (d) wash water and (e) outlet.

The composite was stirred for 10 min in the washing cell covered with sieves (inner cell) with a mesh size of $31\ \mu\text{m}$, at a constant addition of water of $7\ \text{l/min}$ and at a constant stirrer speed of $1,370\ \text{rpm}$. The ash content of the material remaining in the cell was measured every two minutes. The morphology of the fibre-reinforced fillers was also measured using a Valmet Field Flow Fractionator to determine the extent to which the second extrusion step influences the fibre dimensions. SEM images with a JEOL JSM-6510 (high-vacuum electron microscope) were taken to visualize the PCC crystal shape as well as the attachment and binding of the crystals to the modified cellulose. To determine the PCC morphology (Calcite, Aragonite, Vaterite) IR-Spectroscopy measurements were carried out with a Bruker FT-IR-Spectrometer Tensor 27 with ATR-Unit. In addition, XRD measurements were made using the powder diffractometer GE Inspection Technologies XRD3003 TT (Bragg-Brentano Geometry in reflection) to find out the quantitative composition of the cellulose-PCC filler (quantitative phase analysis by Rietveld refinement).

3 RESULTS AND DISCUSSION

3.1 Properties of Pre-treated (Carboxymethylated-fibrillated) Cellulose

The fibre pre-treatment in the extruder serves to provide varying fibre materials of different morphology and charge properties (through the introduction of carboxyl

groups) for composite formation. By carrying out both mechanical and chemical fibre modification in the twin-screw extruder, different methods can thus be used in parallel in just one process step to generate fibres with specific properties – for example, for increasing the strength of paper. The exact adjustment of fibre morphology and chemical properties of the fibre material (DS, charge, functional group . . .) offers great potential beyond paper production.

A summary of the characteristic properties of the fibre materials used for composite formation is shown in Table 1 below. As already described, the NBSK is the basic raw material from which the REX-0/-CMFC1/-CMFC2 fibres, chemically and mechanically pre-treated in the extruder by means of reactive extrusion (REX), were produced. While REX-0 was only mechanically (fibrillation) pre-treated in the extruder, REX-CMFC1 and -CMFC2 were also chemically modified (carboxymethylation), which is why they differ in terms of fibre length (L(l)c), water-soluble fraction (WS), degree of substitution (DS), average degree of polymerisation (DP), water retention value (WRV) and charge (SC, TC). REX-CMFC1 also has a lower water-soluble fraction than REX-CMFC2, as the former was technically washed in a centrifuge. REX-CMFX2, on the other hand, was washed gently to obtain the water-soluble fraction (as described in 2.2). In addition, REX-CMFC1 had to be dried after the technical washing process to make the material processable for the subsequent extruder precipitation (see DC in Table 1).

Figure 3 shows an example of the visualisation of the water-soluble and water-insoluble areas of the chemically-mechanically modified cellulose using SEM on

Table 1. (Pre-treated) fibres for composite formation in the extruder and their characteristic properties (after purification)

<i>Property</i>	<i>DC</i> %	<i>L(l)c</i> mm	<i>W_s</i> %	<i>DS</i> –	<i>DP</i> ¹ –	<i>WRV</i> g/g	<i>SC</i> µeq/g	<i>TC</i> mmol/kg
NBSK	34.28	1.91	0.00	0.01	834	1.33	30.8	35.53
REX-0	29.30	0.79	2.19	0.01	510	0.71	–12.6	19.12
REX-CMFC1	94.10	0.83	1.18	0.30	703	3.47	–470.9	1272.59
REX-CMFC2	24.48	1.39	21.75	0.29	688	8.71	–552.1	1390.80

DC . . . Dry content

L(l)c . . . Length related fibre length

W_s . . . Water soluble fraction

DS . . . Degree of substitution

DP . . . Degree of polymerization

WRV . . . Water retention value

SC . . . Surface charge

TC . . . Total charge (corresponds to the carboxyl group content)

¹ DP values of carboxymethylated cellulose were determined according to ISO 5351 standard, being assumed that the carboxymethylation has a little influence on the DP values (because of low DS values).

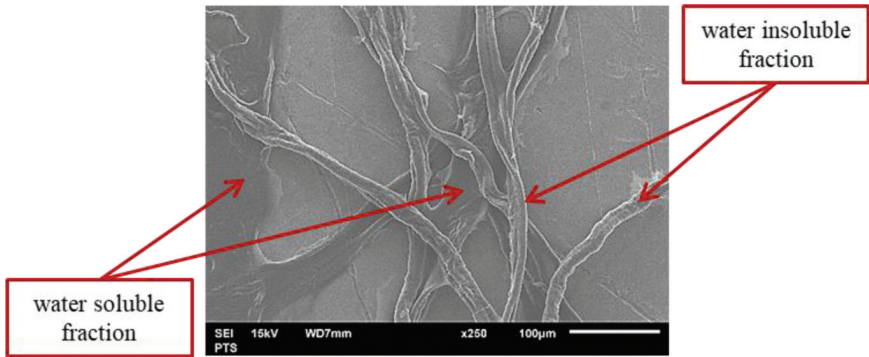


Figure 3. Visualisation of the water-soluble and non-water-soluble fractions of carboxymethylated-fibrillated cellulose (REX-CMFC1) using SEM.

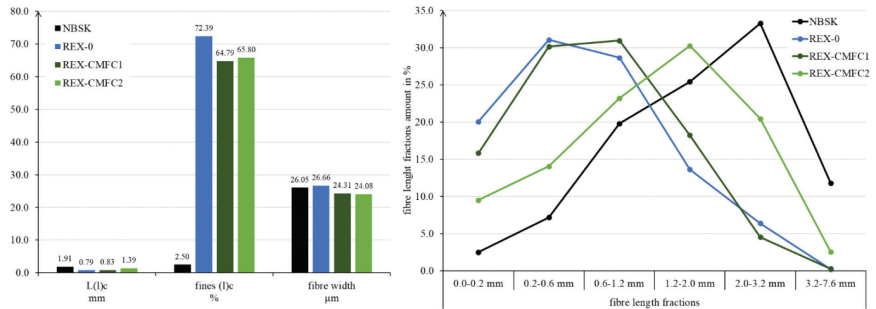


Figure 4. Fibre morphology (fibre length $L(l)_c$, fines, fibre width; left side) and fibre length fractions (right side) of the (pre-treated) fibres measured with Valmet Field-Flow Fractionator.

the material REXCMFC1. It can be seen that the water-soluble areas form cellulose films after drying.

The way in which the extrusion process affects the fibre morphology is illustrated in the following figure. Figure 4 (left side) shows how the original fibre length of the NBSK is reduced by the extrusion process for mechanical and chemical modification (REX-0/-CMFC1/-CMFC2) and how the proportion of fines is increased in parallel. The right-hand side also visualises the shift in the proportions of the different fibre length fractions due to the intensive mechanical treatment (delamination and fibrillation by shear force application) of the fibres during the extrusion process. It is clear that the proportion of the long fibre length fractions is reduced by the extrusion and that of the short fibre length fractions is increased.

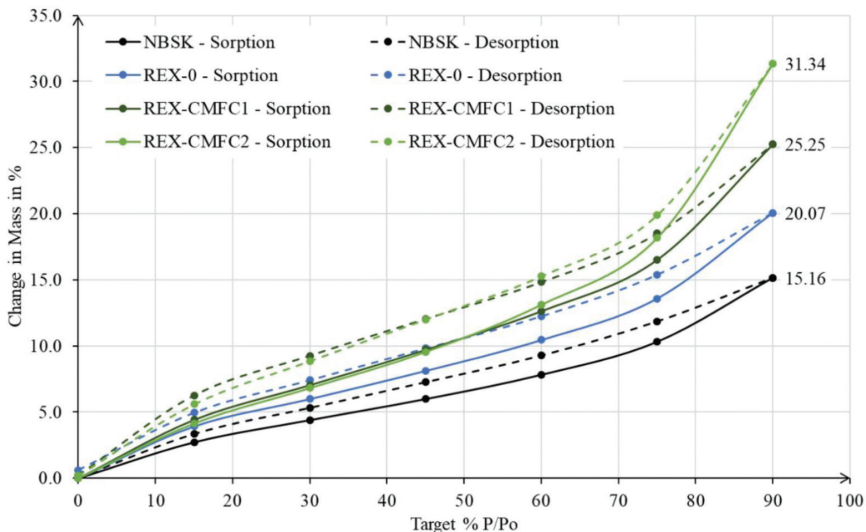


Figure 5. DVS isotherms of the (pre-treated) fibres recorded with DVS Advantage of Surface Measurements System at room temperature using a 1 Cycle 0–90–0 dm/dt with a sequence of 0–15–30–45–60–75–90 target% P/Po.

As expected, both mechanical (delamination and fibrillation see Figure 4) and chemical fibre treatment (carboxymethylation) in the extruder lead to an increase in the moisture sorption capacity of the fibre materials, as shown in Figure 5. While the untreated NBSK absorbs 15.16% water, the mechanical fibre treatment in the extruder increases the absorption to 20.07% of REX-0 and to 25.25% (CMFC1) and 31.34% (CMFC2) of the CMFC fibre materials.

3.2 Properties of Fibre-reinforced Fillers

The trials for composite formation served to find out to what extent the extrusion process affects CaCO₃ precipitation and the properties of the resulting hybrid fillers made of CaCO₃ and varying fibre materials. Accordingly, the precipitation was carried out via doubleexchange reaction with CaCl₂ and Na₂CO₃ on three different matrix materials (see REX-0/-CMFC1/-CMFC2 under point 3.1), while changing the CaCO₃ content in the composite.

The extruder parameters, fibre quantity and fibre mass flow as well as the concentrations of the precipitation reagents were kept constant, only the quantity and volume flow of the reagents were changed to control the composite composition. The aim was to verify precipitation and extrusion conditions under which the

Table 2. Composition of fibre-reinforced fillers produced in a twin-screw extruder by means of a double-exchange reaction of CaCl_2 and Na_2CO_3

<i>Fibre material</i>	<i>PCC content target wt.-%</i>	<i>Fibre content actual wt.-%</i>	<i>PCC content actual wt.-%</i>	<i>Dry content paste wt.-%</i>	<i>Dry content powder wt.-%</i>
REX-0	9.18	91.78	8.22	25.45	–
REX-CMFC1		87.17	12.83	54.02	–
REX-0	20.00	82.13	17.87	21.86	92.50
REX-CMFC1		77.22	22.78	36.46	92.85
REX-CMFC2		75.68	24.32	21.05	96.77
REX-0	70.00	32.27	67.73	13.25	–
REX-CMFC1		32.17	67.83	14.57	–

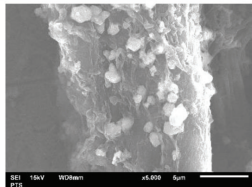
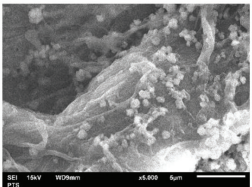
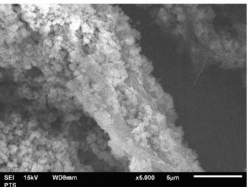
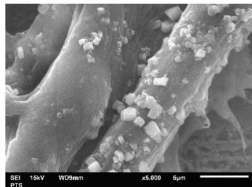
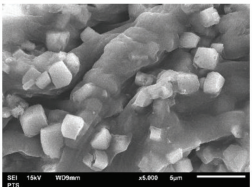
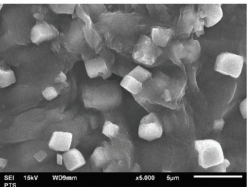
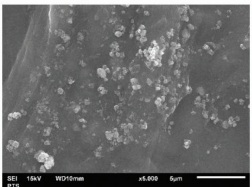
largest possible quantities of precipitated CaCO_3 are irreversibly attached to the fibres and thus also retain in the composite during further processing steps.

Table 2 shows that with the aimed adjustment of the volume flow of the reagents during precipitation fibre-reinforced fillers with varying PCC content between 8 wt.-% and nearly 68 wt.-% could be achieved. The dry content of the paste was between 13 wt.-% and 54 wt.-% and of the powder between 92 wt.-% and almost 97 wt.-%.

As can be seen on the SEM images in Table 3, mainly rhombohedral Calcite crystals (cubic structure) with a size between 0.1 μm and 3 μm are formed whereby the crystals are primarily present individually and not as agglomerates. They adhere mainly to the fibre matrix or are embedded in the hydrogel-like surface of the modified fibres. Due to the very high PCC content of almost 70 wt.-%, the sample with REX-0 (DS = 0.01) shows a covering of the fibre surface by a lot of smaller crystals. In the sample made with REX-CMFC1 with a similarly high CaCO_3 content, on the other hand no ‘incrustation’ occurs. A few large crystals of round about 3 μm are visible on or in the hydrogel-like surface of the REX-0 CMFC1 (DS = 0.30).

The IR-Spectroscopy measurements (see IR spectra of three samples in Figure 6) and XRD measurements (see Table 3) make clear that not only Calcite but also Vaterite is present in two of the fibre-reinforced filler materials. Whereas with the unmodified REX-0 only Calcite was formed at a precipitation temperature of 65°C and high solution concentrations of the precipitation reagents, the carboxymethylated, fibrillated cellulose REX-CMFC1 led to an inhibited precipitation of or conversion to Calcite [35, 36, 37], which is why large amounts of Vaterite were present in the samples with REX-CMFC1.

Table 3. SEM images with 5.000 times magnification and proportion of PCC modifications based on XRD measurement of fibre-reinforced fillers with a targeted PCC content of 9.18 wt.%, 20 wt.-% and 70 wt.-%

Fibres	SEM images and proportion of PCC modifications in the composite (XRD)		
	targeted PCC content		
	9.18 wt.-%	20 wt.-%	70 wt.-%
REX-0	 <p>100 wt.-% Calcite</p>	 <p>100 wt.-% Calcite</p>	 <p>100 wt.-% Calcite</p>
REX-CMFC1	 <p>22 wt.-% Calcite 78 wt.-% Vaterite</p>	 <p>17 wt.-% Calcite 83 wt.-% Vaterite</p>	 <p>100 wt.-% Calcite</p>
REX-CMFC2	-	 <p>100 wt.-% Calcite</p>	-

Washing tests were carried out in a DEGUSSA washing cell to determine the irreversible attached PCC content in the composites. Figure 7 shows the decrease of the normalised PCC content, whereas Table 4 shows the actual PCC contents over the washing period of 10 minutes.

The green curves (composite with REX-0) clearly show that with increasing CaCO_3 content in the composite ($\blacktriangle < \blacksquare < \bullet$) a larger proportion of the precipitated CaCO_3 is washed out and is thus not irreversibly bound. The composites with REX-CMFC1 ($\blacktriangle < \blacksquare < \bullet$) show a similar tendency, but generally larger CaCO_3 yields (between 97.11 wt.-% and 23.55 wt.-%) are present in the composite

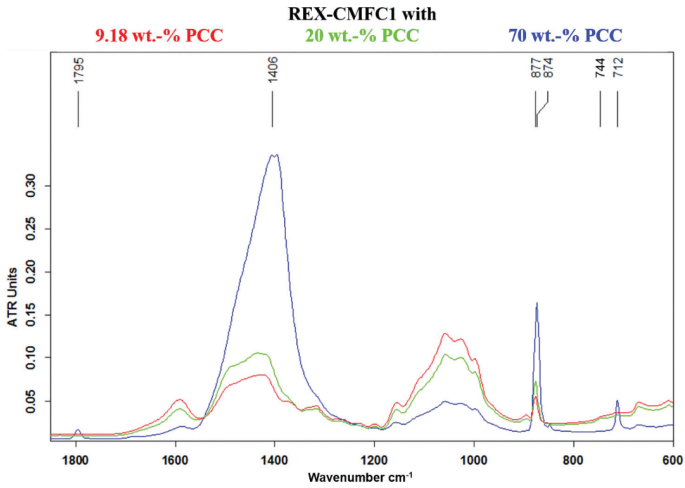


Figure 6. IR spectra of fibre-reinforced fillers made of REX-CMFC1 with a targeted PCC content of 9.18 wt.%, 20 wt.% and 70 wt.% with Calcite bands (wavenumber cm^{-1}) 1795, 1406, 874, 712) and Vaterite bands (wavenumber cm^{-1}) 877, 744).

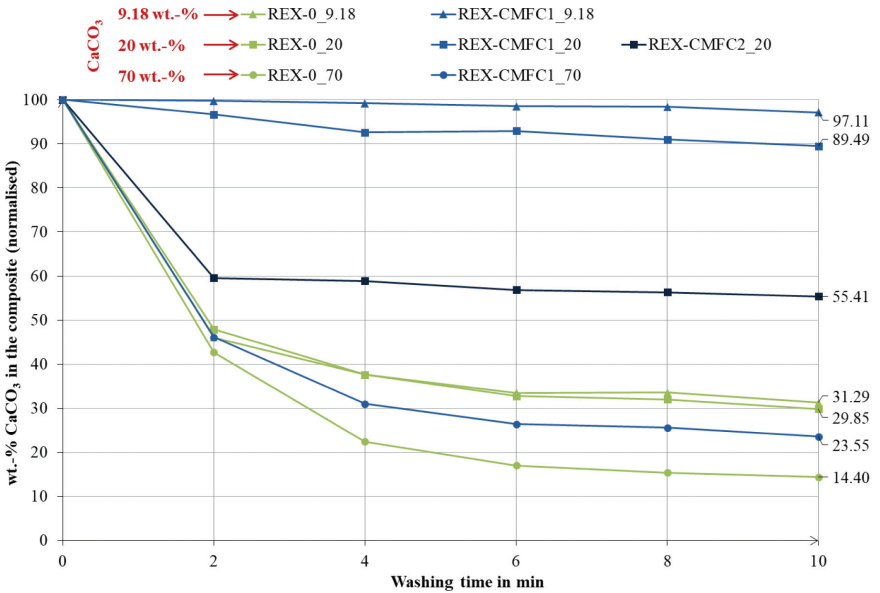


Figure 7. Change in CaCO_3 content (residue on ignition in wt.-%) of the composite over a ten-minute washing process in a Degussa washing cell (normalised).

Table 4. Change in CaCO₃ content (residue on ignition in wt.-%) of the composite over a ten-minute washing process in a Degussa washing cell (actual)

Fibre material	PCC content target	Washing time in min					
	wt.-%	0	2	4	6	8	10
REX-0	9.18	8.22	3.79	3.09	2.75	2.76	2.57
REX-CMFC1		12.83	12.79	12.73	12.64	12.63	12.46
REX-0	20.00	17.87	8.55	6.72	5.86	5.72	5.33
REX-CMFC1		22.78	22.02	21.09	21.17	20.72	20.39
REX-CMFC2		24.32	14.49	14.32	13.83	13.70	13.48
REX-0	70.00	67.73	28.93	15.20	11.51	10.44	9.75
REX-CMFC1		67.83	31.30	21.04	17.91	17.36	15.97

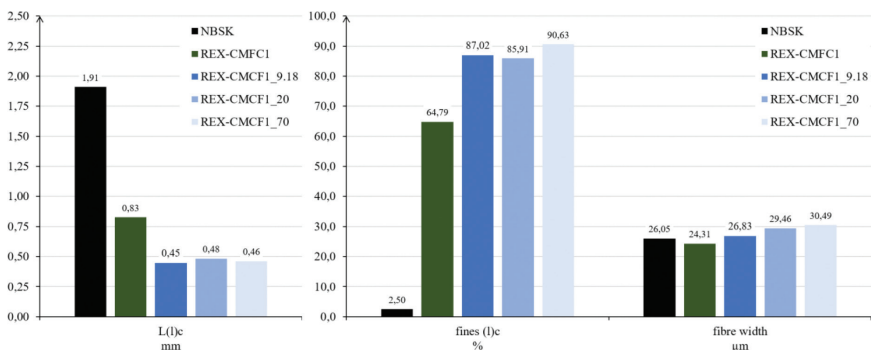


Figure 8. Fibre morphology (fibre length L(l)c, fines, fibre width) of the basic raw material (NBSK), the pre-treated carboxymethylated-fibrillated Cellulose (REX-CMFC1) and fibrereinforced fillers made of REX-CMFC1 with varying PCC content of targeted 9.18 wt.-%, 20 wt.-% and 70 wt.-% measured with Valmet Field-Flow Fractionator.

even after washing. It is interesting to note that for the composite with REX-CMFC2 (■), only slightly more than 55 wt.-% of the precipitated CaCO₃ remains in the composite after the washing process. It can be assumed that in this case not only CaCO₃ but also large parts of the water-soluble fraction of REX-CMFC2 (Ws = 21.75%) were washed out. The washing tests show that up to 97 wt.-% of the precipitated CaCO₃ is irreversibly bound to the cellulose fibres, depending on the PCC amount that was precipitated originally. In case of that, the hybrid fillers should be able to withstand further processing steps as a whole.

The fibre morphology changes associated with fibre extrusion during PCC precipitation can be seen in Figure 8. The re-extrusion of the modified fibre material REX-CMFC1 leads to a further reduction in fibre length (L(l)c) and thus to

an increase in fines content (fines (I)c). Furthermore, there is a slight increase in the fibre width – presumably due to PCC accumulation on the fibre surfaces.

3.3 Potential of PCC-functionalized Nanocellulose Composites

In the investigation of the use of the novel hybrid fillers made of CaCO_3 and varying fibre materials, the focus was placed on the use in paper production to improve the mechanical and optical properties and in plastic products to improve the property profile. A successful application was recorded both in paper (laboratory sheets) and in plastic (PP test specimens).

Here is a brief overview of the results obtained when using the composites in laboratory sheet formation with a sheet composition of 75 wt.-% fibres and 25 wt.-% PCC with a 50 wt.-% PCC-CMFC composite (REX-CMFC1) content in relation to the total fiber amount. The tensile strength was increased by 110%, the breaking elongation by 44% and the retention by 53%. The optical properties (such as whiteness and opacity) could be kept almost constant whereas there was a reduction in the light scattering coefficient due to the film-forming properties of the CMFC. In addition, the composite was very easy and uncomplicated to handle. It became clear that a compromise between the desired mechanical properties and the required optical properties must be made when using the novel composite materials in papermaking.

Trials which included the application of the novel PCC-functionalized nanocellulose composites as a paste (5 wt.-%, 10 wt.-% and 20 wt.-%) or as a powder (10 wt.-%) in polypropylene, showed that the modulus of elasticity remains constant or could be slightly increased, the yield stress could be increased by about 9% (depending on the composite content in the PP) and that the material could be processed well. But, the elongation at break, on the other hand, was reduced by the use of composites. However, it became clear that an optimization of the composite composition and addition is necessary in order to achieve a better elongation at break as well as a uniform distribution in plastic materials.

3.4 Discussion

The experiments on composite formation in the extruder show that the functional properties of the fibres – including the microenvironment of the fibres, their surface structure and surface charge (functional groups) – have a significant influence on CaCO_3 precipitation and the irreversible attachment of CaCO_3 to the fibres. [38, 39] As already described in the literature [40], the fibres act as nucleation centres of the heterogeneous nucleation and decisively influence the reaction rate or the course of the reaction and thus the resulting CaCO_3 modification, shape and size. [35, 36, 40–43]

Although the experiments of the double exchange reaction were carried out at 65°C Vaterite was also present in addition to Calcite (see XRD results in Table 3 and IR spectra in Figure 6). This suggests that the presence of the fibres inhibits the crystallisation and rearrangement processes and thus more time is needed than in the fibre-free system to achieve a complete transformation to Calcite. The hydrogel-like surface of the modified fibres reduces the nucleation rate in the double-exchange reaction and promotes crystal growth [44], resulting in predominantly large CaCO_3 crystals on the fibre surfaces (see SEM images with REX-CMFC1 in Table 3).

In addition, it could be shown that a larger amount of CaCO_3 can be irreversibly attached to highly substituted fibres (see Figure 7 as well as Table 4). In general, the washing experiments show that the CaCO_3 crystals are better enclosed in the network structure of the fibres due to the strong mechanical treatment and the resulting increase in the surface area of the fibres during the parallel CaCO_3 precipitation in the extruder. As a result, the absolute, irreversibly attached amount of CaCO_3 can be increased from 12 wt.-% [9] up to 20.4 wt.-%. Furthermore, the intensive mechanical stress on the fibres during extrusion and the parallel CaCO_3 precipitation result in fibre shortening, delamination and fibrillation (see Figure 8), whereby the lower the stock consistency in the system, the greater the shear force input during the extrusion process.

The experiments also showed that a high water-soluble fraction of the modified fibre material (cf. properties of REX-CMFC2 in Table 1) in the composite has a counterproductive effect on its processability (e.g. drainability). In addition, depending on the process control, this can hardly or not be retained (see washing tests, composite with REX-CMFC2 in Figure 7), which leads to undesired material losses.

It can be seen that the double-exchange reaction, in addition to the conventional lime milk precipitation [27, 30] for the mineralization of cellulosic structures in the extruder, is suitable for producing composites with very high amounts of irreversibly attached CaCO_3 . Both processes have their advantages and disadvantages. While lime milk precipitation requires very long reaction times to achieve complete conversion of the $\text{Ca}(\text{OH})_2$ in the extruder [27, 30, 33] and thus avoid post-precipitation, the double-exchange reaction leads to the undesired by-product NaCl, which – depending on the subsequent use of the composite – has to be washed out which means another necessary process step.

Furthermore, it makes sense to optimize composite materials for use in both paper and polypropylene in order to exploit the full potential of composite materials. In the first step, it is indispensable to define the necessary composite properties in order to be able to adjust them specifically in the second step, depending on the application and requirements. Under this condition, from today's perspective, the successful use of hybrid fillers in different paper and plastics applications is possible.

Especially in the field of plastics processing, there is a high potential for mineralized cellulose structures, which should undoubtedly be pursued further. Especially with regard to bio-based materials, biodegradable plastics or recyclable, sustainable product solutions, fibre-reinforced fillers offer new possibilities for property control and enhancement.

4 CONCLUSION AND OUTLOOK

The results of the extruder experiments on composite formation show that CaCO_3 -cellulose composites can be produced by means of a double-exchange reaction (in CaCl_2 solution with the addition of carbonate salts). The test results underline that an irreversible attachment of CaCO_3 to the cellulose is possible due to its altered charge properties after modification. However, not only the chemical modification but also the mechanical fibre treatment during the in-situ precipitation of CaCO_3 in the extruder leads to an improved mineral immobilisation. Thus, up to 97.1 wt.-% could be immobilised on the carboxymethylated, fibrillated cellulose REX-CMFC1 (DS = 0.30) at a target PCC content of 9.18 wt.-% and up to 89.5 wt.-% at a target PCC content of 20 wt.-% – in contrast, only 31.3 wt.-% and 29.9 wt.-%, respectively, could be immobilised on the unmodified fibre REX-0 (DS = 0.01). It can be seen that the conditions in the high-consistency range in the twin-screw extruder are well suited for the efficient production of fibre-reinforced fillers, although the control of CaCO_3 morphology, size and crystal shape through the specific adjustment of the process parameters needs to be further investigated. It is already clear that the chemical as well as the mechanical fibre modification is decisive for the hybrid filler properties that are formed and thus for later application possibilities of the composites. [38, 39]

Reactive extrusion is a promising and, above all, forward-looking process for the efficient and targeted production of hybrid composite materials from filler and fibre and offers a wide range of possibilities for product property control due to the large number of parameters for reaction control – including speed, throughput, residence time, screw configuration/ -geometry, temperature, fibre and chemical dosage as well as chemical concentration. . . . However, as this is a novel process for composite production, process development is still pending. Since the precipitation of CaCO_3 – especially via the double-exchange reaction – on modified fibrous materials or in hydrogels and hydrogel-like media has not yet been sufficiently investigated and explained, further research is necessary in order to be able to specifically adjust the CaCO_3 morphology, crystal shape and crystal size and thus also the subsequent composite properties and tailor them for different applications.

Various auxiliaries and additives are already used today to improve the product property profile in both paper and plastics production. For example, fillers are used as a favourable extender material to reduce production and raw material

costs, but also to improve mechanical and/or optical product properties, while (cellulosic) fibres are mainly used to improve strength properties. [45, 46, 47] Mineralized cellulosic structures combine both of the above-mentioned materials – fillers and fibres – in order to be able to optimize several end product properties in one.

In view of the fact that hybrid fillers (fibre reinforced fillers) could be produced on-site in paper mills, adapted to the respective current paper product, both the process and the products generated by it hold a great opportunity for optimizing existing, but also for manufacturing innovative, new paper products. In order to achieve this, however, corresponding research work is still necessary in order to be able to specifically adjust and control the composite properties. [27, 30, 33]

It is also possible to open up new, non-paper markets with the new composites. Especially in the field of plastics processing/manufacturing or in the development of sustainable, biobased materials, mineralized cellulosic structures offer great potential that is worth pursuing further. [45, 46, 48]

In summary, reactive extrusion is a new, innovative and sustainable process for hybrid filler production, and the new fibre reinforced filler materials produced in this way promise successful use in a variety of products beyond paper production – for example, in plastics, filters or filter aids, foam forming products and construction fibreboard.

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PRODUCTION AND POTENTIAL OF PCC-FUNCTIONALIZED NANOCELLULOSE COMPOSITES

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Presented by *Sandra Heckel*

Jon Phipps FiberLean Technologies Ltd

You managed to get some very nice-looking uniform crystals on your fibres. Many people have co-precipitated calcium carbonate onto fines and fibrils before, and very often they do not have any control over the size and morphology of the crystals, which tend to be a bit random. However, when PCC is made on its own in commercial production there is very good control; many different and precise shapes and sizes can be reliably produced. So do you think that, with your technique, you will be able to control and vary the size and morphology of the crystals that are precipitated onto the cellulose?

Sandra Heckel

In this project, the aim was mainly to see if it works at all which it does and now we actually have a follow up project where we are screening all the different reaction conditions quite thoroughly and I think it works. The aim now is that we can tune the PCC shape also reproducibly. A bit of the downside of reactive extrusion

Discussion

is that there are a lot of factors that you can change and it takes a bit to find the ideal ones, but it is possible to influence the type of calcium carbonate.

Warren Batchelor Monash University

What do you think the nature of the bond is between the calcium carbonate and carboxymethylated fibre?

Sandra Heckel

According to our model, the calcium ions are first complexed by the carboxylate group when we only add calcium chloride and then we add the carbonate, which precipitates the calcium carbonate. I personally think it grows directly onto the fibre, even kind of around it, so I think it is a type of mechanical adhesion. It is not really a chemical bond because, how?

William Sampson University of Manchester

You used an unrefined pulp to build these composites with. Was it a dried pulp when you started with it or was it a never dried pulp?

Sandra Heckel

I actually do not know. I cannot tell you because it was not really my project, so I would have to ask and get back to you.

William Sampson

The strength of the sheets is very very low; I suspect it was a dried pulp. Did you know if there were any experiments done with a lightly refined pulp?

Sandra Heckel

I think there were, but again I cannot really tell you, I would have to check it.

Bob Pelton McMaster University

Many years ago, we had a burst of wonderful funding to look at the influence of PCC on paper strength. We were, and still are, in the polymer business, so we were designing polymers to try and compensate for the strength loss when you put PCC into paper. There are some things you might think about. Small PCC parti-

cles have a much more negative influence on paper strength than big ones when compared at equal loading. Therefore, one has to be careful about comparing paper strengths for different crystals shapes and sizes. In this work, we made wet handsheets with no filler and then transferred a sparse layer of PCC particles onto the top surface. Next, we put a second wet handsheet on top and pressed and dried the laminate. After drying we used a peel test to measure the delamination force. In these experiments, we could put polymer on the PCC particles, or polymer on the fibres or both. What we learned from this was that it is very difficult to promote PCC/fibre adhesion. Instead, it is better to strengthen fibre/fibre contacts around the PCC particles with polymers or fines.

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Warren Batchelor

So, you did softwood and hardwood. Did you measure the size of your particles that you precipitated and was there any relationship between the size of the fibre and then the size of the particles that you grew? Maybe you would have expected at some point that with smaller and smaller fibres you would run into limits? You would expect, for example, if you try to do this on nano-cellulose where the size of the fibres might constrain the growth of the particles?

Sandra Heckel

As far as I know in the project we made sheets of hardwood and softwood pulp. But for the filler to precipitate the calcium carbonate onto, only softwood was used. But I agree with you it will have an influence, surely.

Torbjorn Wahlstrom Stora Enso

How does the customer see the sustainability of increasing the filler amount?

Sandra Heckel

I would say it is a trade-off. Firstly, we are not selling this, so we do not have any customers. With the companies we talked to, it is always a trade-off. If you increase the filler content, then it may get cheaper but it is possible that the sustainability suffers.

Discussion

Jon Phipps

Companies like Imerys are spending a lot of time trying to figure out the life cycle of minerals versus pulp and if you look at in terms of the amount of energy required, then if you take a ground calcium carbonate and I think it looks rather better than precipitated calcium carbonate, but it is certainly not the case that just because they do not grow on trees that they are necessarily bad because they do not require a lot of energy to produce them.