Rheological investigation of complex micro and nanofibrillated cellulose (MNFC) suspensions: Discussion of flow curves and gel stability

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ABSTRACT: Micro and nanofibrillated cellulose in aqueous suspension presents many challenges when considering its use, for example, in forming nanocomposites. The inclusion of filler particles either as extender or as functional additive allows the range of strength and deformation properties to be extended. These properties, however, are linked in many cases to the rheological properties of the raw material mix. Interactions under dynamic shear or under controlled stress at low amplitude reveal the potential to generate functional interactions, not only between the cellulose components themselves but also between the cellulose and polymer additives, as well as surface modified pigment fillers. Examples are given demonstrating the action of adding cellulosic polymer in the form of carboxymethyl cellulose (CMC) to micro and nanofibrillated cellulose (MNFC). Rheological studies show how these combinations with CMC, added either in free form or preadsorbed onto calcium carbonate filler particles, lead to a variety of responses. Dispersability of the MNFC is increased by the use of free CMC polymer addition, and the usually expected flocculating action on added filler is seen not to occur. Alternatively, the preadsorbed CMC on the calcium carbonate pigment filler leads to an interaction between the fibrillar cellulose and the surface modified calcium carbonate pigment filler, to which incorporation of cationic polymer leads to a reduction of interaction, provided the addition level does not exceed the isoelectric point of the mix. The observations are viewed in the context of a combination of proposed physical contact dynamics in the form of disordered and ordered alignment.

Application: The present work confirms findings of others in respect to the influence of additives like polyelectrolytes and pigment particles on MNFC suspension rheology. However, previously unreported effects are described for polyelectrolyte treated pigment particles, indicating an increased interaction with MNFC to the advantage of future products, such as fibrillar-based nanocomposites.

Micro and nanofibrillated cellulose (MNFC) materials are very interesting for many different applications in various fields [1] due to their excellent mechanical and barrier properties [2]. Even though these materials were already reported quite some time ago by Turbak, Snyder, and Sandberg [3], who pointed out the materials' great potential in various applications, there are not yet well established, large, full scale applications of them.

On the one hand, the originally very high energy consumption of the manufacturing process was a hindering factor to produce a cost efficient product. Intensive work has been carried out to overcome this hurdle by using different approaches such as applying enzymatic [4] or chemical pretreatments [5]; using alternative pulp sources [6-8]; or introducing grinding aids in the mechanical breakdown process [9-10]. These efforts led to the setup of numerous pilot and pre-commercial manufacturing plants for different kinds of MNFC products.

On the other hand, the application of MNFC products in various applications remains challenging, especially on the large (industrial) scale where economic factors also come into play. One of the key factors that makes an application of MNFC in production challenging is the high water content and the strong associated interaction with water. In addition to the challenge of water removal, MNFC suspensions also show a complex, non-Newtonian rheological behavior over a large span of shear rate- and time scales [11]. The investigation of MNFC suspension rheology and the influence of different material parameters on it has two main benefits, among others. First, one is prepared for problems that may arise in large scale applications where different kinds of shear forces and shear rates may be introduced in MNFC, as well as MNFC containing, suspensions. Second, rheology allows the observer to hypothesize models describing the structure and interactions within MNFC suspensions and to subsequently test these hypotheses accordingly. This in turn can be used, for instance, to predict potential shear force assisted dewatering [12,13]. This work investigates the influence of basic MNFC material parameters on the respective suspension rheological behavior, thus setting

out to explain the effects seen using previously proposed models by other researchers [14,15] and then extending them suitably for application to as yet novel unreported effects.

A special focus is placed here on the effect of CMC and pigment particle addition on MNFC suspension rheology. A dry ground, chemical-free calcium carbonate was used as reference pigment particle filler. Furthermore, special surface modified pigment particle fillers, so-called pigment hydrocolloid hybrid pigments, were used as co-additives. CMC, and optionally additional polydiallyldimethylammonium chloride (polyDADMAC), is adsorbed on the pigment particle surface to form the pigment filler hydrocolloid hybrid. This localization of CMC (and additional polyDADMAC) leads to previously unreported rheological changes in the MNFC suspension response, which in turn correlate with increased pigment filler-MNFC nanocomposite strength as previously reported in earlier work by the same authors [9].

EXPERIMENTAL

Materials

Preparation of the fillers

Two different types of pigment particle fillers were used, standard pigment filler and functional pigment filler, respectively: a fine, dry ground dispersant free calcium carbonate of marble source (fGCC), and functional surface modified calcium carbonate in the form of so-called filler pigment hydrocolloid hybrid (PHCH) in slurry suspension. The PHCH pigments are formed from dispersant free calcium carbonate, also of marble source, that is surface modified by wet co-processing with 1.5 w/w% (based on dry pigment) carboxymethyl cellulose (CMC), either alone (PHCHa) or in the combination with 0.6 w/w% cationic polyDADMAC (PHCHb). To exclude potential filler particle size distribution (PSD)-related effects on the composite suspension rheology, the PSD of the two filler types was carefully controlled to be closely similar (fGCC: volume based d_{50} of 1.7 µm; PHCHa and b: volume based d_{50} of 1.8 µm, measured by a static laser diffraction method, using a Mastersizer 2000 [Malvern Instruments Ltd.; Malvern, UK]).

The CMC used had a degree of substitution of 0.8 and a molecular weight M_w of 60 kgmol^{-1} (Finnfix 10, CP Kelco; Atlanta, GA, USA), and the polyDADMAC used was Catiofast BP (BASF; Ludwigshafen, Germany).

Surface charge of the pigments, manifest in the form of the zeta potential, was measured with a Zetasizer Nano ZS (Malvern Instruments Ltd.) at 25°C and a 0.1 w/w% solids content, using deionized water in a 10 mM NaCl salt solution for dilution. Three measurement runs were performed per sample with an automated determination of single point measurements per run using the Smoluchowski approximation to convert the electrophoretic mobility into zeta potential. The zeta potential for fGCC was -8.2 ±0.9 mV, for PHCHa it was -33.7 ±1.6 mV, and for PHCHb it was -25.2 ±0.8 mV.

Preparation of MNFC

Bleached eucalyptus pulp from a Swiss paper mill site (ex Sappi Biberist fine paper) in the form of once-dried mats was used as the cellulose basis material for all MNFC products. Pulp lumps were mixed with tap water (45° fH) using a stirrer with a dissolver disc type of rotor for about 1 h to have a pulp suspension of 3 w/w% consistency. This suspension was then run through an ultrafine friction Supermasscolloider MKCA 6-2 grinder equipped with type E 46# grinding stones (Masuko Sangyo Co.; Kawaguchi, Japan) at a contact/gap setting of "-50 µm" in single passes. The following rotational speed sequence was used for the standard MNFC: 5 passes at 2500 rpm, followed by 2 passes for each of the following speeds: 2000, 1500, 1000, 750, and 500 rpm. Two additional passes at 500 rpm were conducted for a further "17 pass" MNFC and a contact/gap setting of "-80 µm" with the standard rotational speed sequence form an "intensive treatment" MNFC.

It should be pointed out that the wear condition of the grinding stones of the ultrafine friction grinder can have a significant influence on the grinding efficiency. As a consequence, samples produced by the same procedure at different total operation times of the grinding stones may not be of the same degree of fibrillation. It is therefore important only to compare samples within a single manufacturing series, or samples from a close manufacturing series, to ensure comparability. In this manner, relative comparison studies are still possible.

MNFC morphology

In order to assess the network structure of the fibrils in suspension, scanning electron microscopic (SEM) images of freeze dried MNFC suspensions were taken. The MNFC suspension was diluted to 0.5 w/w% using tap water and followed by rotor stator mixing (Polytron PT 3000, Kinematica AG; Luzern, Switzerland) for 5 min. The suspension was frozen by immersion in liquid nitrogen and then freeze dried (Alpha 1-2 LD Freeze Dryer, Martin Christ Gefriertrocknungsanlagen; Harz, Germany). A small piece was torn out of the dried structure and mounted on a support so as to image the internal MNFC structure. The sample was sputtered with 50 nm gold before imaging using a LEO 435 VPi SEM (LEO Electron Microscopy; Cambridge, UK). Another sample was prepared where 5 w/w% (based on the cellulose dry content) CMC was added as 4 w/w% suspension (in tap water) to the MNFC suspension before dilution. The sample preparation otherwise was the same as described before.

Composite suspension preparation

The chosen amounts of additive components were added to the MNFC suspension, i.e., as-produced pigments and CMC (4 w/w% solution) were freely added and the suspension was subsequently diluted further using tap water to the target solids content, defined in relation to the cellulose fraction only. The pigment ratios are thus based on the total dry amount of cellulose and pigment, and the CMC ratios are based on the addition in relation to cellulose dry amount only. For example, a sample at 2 w/w% dilution with 50 w/w% fGCC and 2 w/w%

CMC is described as having the components added to 100 g of MNFC suspension, itself consisting of 2 g cellulose in 98 g water, in weight proportions of 2 g fGCC and 0.04 g CMC. This gives a total weight of 102.04 g, with a total solids content of 3.96 w/w%, but a cellulose based solids content of 2 w/w% (2 g cellulose and 98 g water). This definition is chosen in order to keep the cellulose-to-water ratio constant throughout all samples, as the rheological behavior of MNFC suspensions is strongly dependent on this ratio and the impact of adding the other components is then studied at constant MNFC levels. The additives alone do not exhibit a characteristic rheological behavior at such low relative ratios to water content. The samples were then stirred thoroughly using a stirrer with a dissolver disk type rotor at 750 min^{-1} for about 30 min.

Rheology measurements

All the rheological measurements were performed on an MCR 300 rheometer (Anton Paar; Graz, Austria) with a CC27 cylinder and cup geometry at 20°C. This measurement setup was recommended by Saarinen et al. [16]. They also point out that wall slip (sometimes also referred to as lubrication flow), although likely to occur, will not dominate the rheological measurements. This statement requires qualification in practice as the colloidal stability of the mix certainly plays a dominating role and can lead to phase separation with significant buildup of water at the boundary interface. However, as long as the system is continually sheared beyond the yield stress, the claim of Saarinen et al. [16] can be supported. Although serrated surfaces in plate-plate geometry are frequently used to overcome wall-slip, they have been avoided here as they create non-laminar flow close to the boundary [17]. The sample material was shaken before it was loaded to the measurement cell to avoid interim sedimentation of the suspension. In order to have the same shear history for all the samples, a preconditioning was also performed before all measurements consisting of 2 min at 50 s^{-1} shear rate (rotation), followed by 5 min rest.

Flow curves of viscosity dependence on shear rate were obtained by performing a shear rate increase ramp (0 to 1000 s^{-1} with 30 viscosity point measurements with 10 s per point measurement), followed by a shear rate decrease ramp (1000 to 0 s^{-1} with 30 viscosity point measurements at 10 s per point measurement). After 2 min rest, the same profile was applied again. In total, three of these programs were applied, and the data of the two last shear rate increase ramps and all three decrease ramps were averaged to give the data for the ramp up and ramp down, respectively.

The flow curves provide information on the dynamic interaction of the suspension system, as the structure is constantly in relative movement. Typically, strongly interacting systems including entanglements and attractive interactions exhibit higher viscosities due to the hindrance of relative movement of the involved entities. Systems having weak interactions or a collapsed structure typically exhibit low viscosities. Furthermore, systems with highly charged entities show low viscosities. The measurement of the viscosity as a function of decreasing shear rate gives further indicative information about the time dependence of recovery after a potential structural change.

In addition to dynamic shear, an oscillatory experiment was performed by fixing the frequency at 0.5 Hz and changing the oscillation amplitude (amplitude sweep). This was done by changing the response stress to the applied strain within the controlled region from 0.1 to 100 Pa with 50 point measurements made once a stable value reading was attained, followed by a controlled stress decrease ramp from 100 to 0.1 Pa, also with 50 point measurements.

The phase angle δ was chosen to be evaluated in more detail, as it contains information on the relative effects of the elastic and gel-like structure and the viscous behavior of a viscoelastic material, as well as on the eventual breakdown of the gel-structure:

$$\delta = \tan^{-1}\frac{G''}{G'} \quad (1)$$

with G´´ being the viscous loss modulus and G´ being the elastic storage modulus, respectively. The advantage of using the phase angle is that it is a relative, normalized parameter compared with the absolute values of the moduli. The point of equality between the storage and loss moduli sometimes is referred to as the flow point [17] and can easily be read out at $\delta = 45°$. An amplitude sweep measurement can thus give a deeper insight into the ratio of the potential change from an elastic solid to a viscous liquid as a function of deformation leading to the resulting stress. It is recalled that, up to the point where the solid-like structure (also often referred to as gel structure) is broken down, the predominant interaction is of an elastic nature (i.e., existing bonds in the form of potential energy wells are not broken), so one can refer to it as a "static" structure, which can be contrasted to the purely dynamic situation in a flow curve experiment.

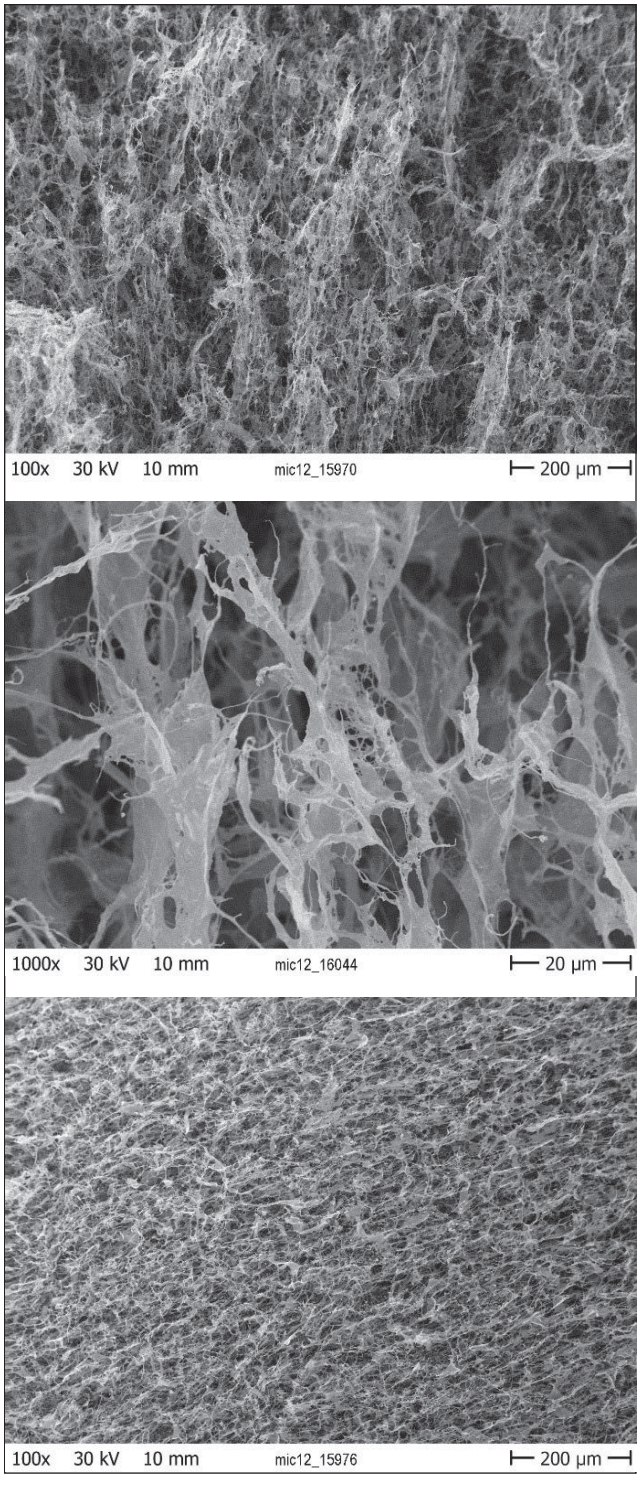
RESULTS AND DISCUSSION

MNFC morphology

As can be seen in the SEM images in **Figs. 1a-1b**, the MNFC material is an entangled network of fibrils of different diameters. Whereas some individual fibrils of only some nanometers diameter can be seen, larger fibrils and fibril aggregates are also present. The overall network of the MNFC suspension (Fig. 1a) appears to not be completely homogeneous, as areas of higher and lower fibril density can be identified. The dispersing effect of CMC on MNFC fibrils and the resulting change of the suspension network are obvious when comparing Figs. 1c and 1a.

Influence of solids content on MNFC rheology

Figure 2 shows the flow curves of the pure MNFC suspensions at different solids contents and of the tap water that was used to make the according dilutions. The well-known shear



1. Scanning electron miscroscope (SEM) images of freeze dried micro and nanofibrillated cellulose (MNFC) suspension (a,b) and MNFC + 5 w/w% carboxymethyl cellulose (CMC) suspension (c).

thinning behavior of the MNFC suspensions [3,11,18,19] as well as the overall reduction of viscosity with decreasing solids content [11,19] are apparent. It also can be seen that if the dilution becomes too great, then the MNFC suspension exhibits the viscosity of water, indicating the loss of interaction between MNFC entities. Furthermore, one can clearly see the hysteresis between the shear rate increase and decrease ramps for dilutions greater than 0.5 w/w%. This was also reported by Iotti et al. [11]. However, by comparing the hysteresis of the 1 w/w% dilution with the ones from the 2 and 3 w/w% dilutions, a reverse of the hysteresis can be seen that was not reported by Iotti et al. [11]. There also seems to be a trend that the hysteresis area becomes larger for higher solids contents, starting at 2 w/w%.

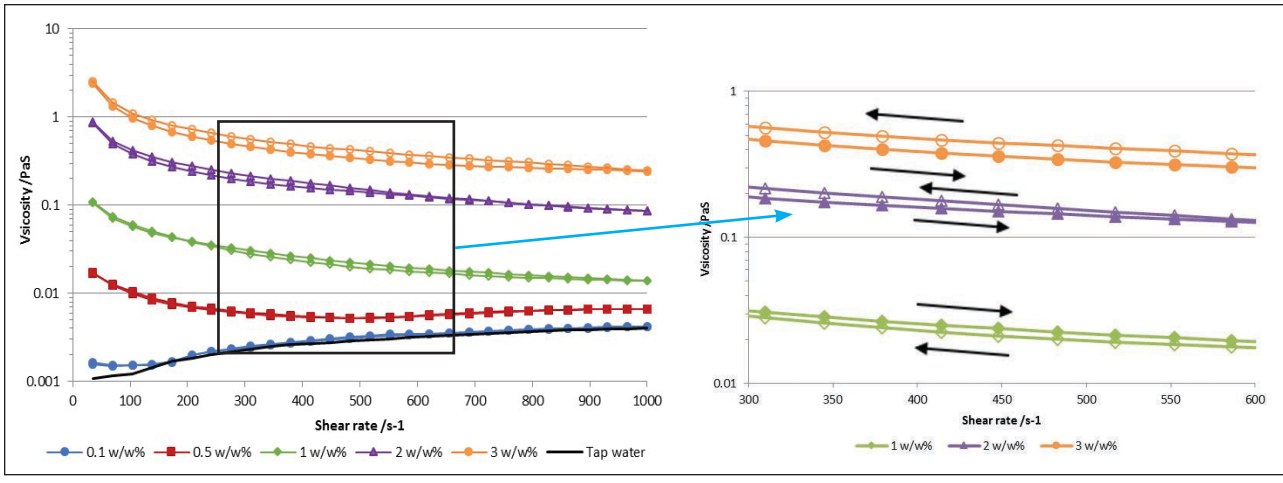
We hypothesize that shear leads to a structural change in the MNFC suspension with the two extreme conformations indicated in **Fig. 3** as highly entangled (low shear, Fig. 1a) and highly oriented (high shear), and that these structures need a minimal recovery time that is at least larger than the acquisition time for one measurement point, as also seen by Iotti et al. [11]. In this way, we can interpret the predominant conformation in the shear rate increasing ramp as being the entangled one, whereas in the shear rate decreasing ramp it is the highly oriented one. In a more diluted system (low solids content [s.c.]), the high shear conformation leads to an overall reduced interaction, leading to a lower viscosity in the shear rate decreasing ramp at a given shear rate value. In the case of a less diluted system (high s.c.), however, the high shear conformation leads to an overall stronger interaction related to re-entanglement similarly compared with the low shear conformation, and therefore exhibits higher viscosity values at a given shear rate in the shear rate decreasing ramp. This model is generally in agreement with the one proposed by Horvath and Lindström [14], so their model can be used to identify the nature of the previously mentioned interactions in the low shear conformation regime. In the case of low consistencies, the dominating interactions are of a colloidal nature, whereas in the case of high consistencies they are considered to be fiber interlocking.

The amplitude sweep measurement shows that the yield point increases with increasing solids content of the MNFC suspension (**Fig. 4**). It also seems that some secondary structure is formed temporarily, as all curves show characteristic "shoulders" in the amplitude increase ramp.

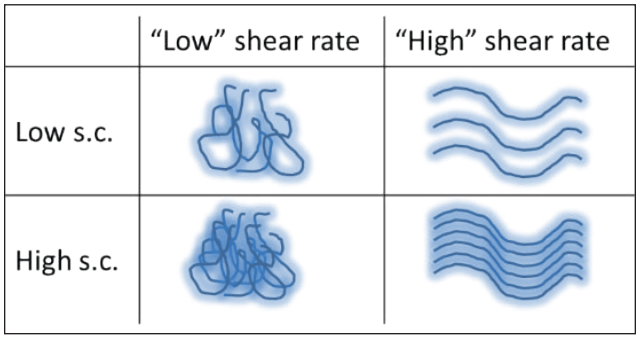
It is not surprising that higher solids contents of MNFC suspensions lead to increased flow points, as there are more cellulose entities that form interactional "bonds" (i.e., situated within a potential energy well) and therefore more force (shear stress) is required to break them. Again, the observed data here are also in good agreement with the data presented by Horvath and Lindström [14]. Also, note that the phase angle is the same (10°) for all solids contents before the gel structure breakdown.

Influence of the degree of fibrillation on MNFC suspension rheology

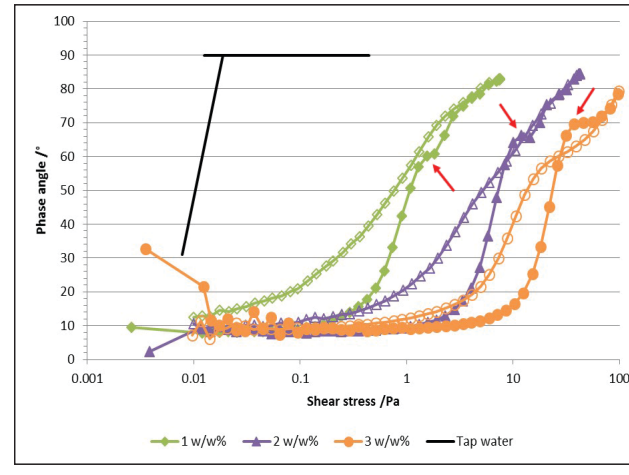
As the degree of fibrillation (DoF) increases, the overall viscosity becomes greater, as is apparent in **Fig. 5**. An increasing DoF seems to have an effect like that of increasing solids content. However, the hysteresis apparently becomes smaller



2. Flow curves of MNFC samples at different solids contents and the tap water that was used to make the various dilutions. The filled symbols represent the measurement points of the shear rate increase ramp, whereas the open symbols represent the measurement points of the shear rate decrease ramp. The extracted picture is the enlarged region indicated in the main plot, with arrows indicating the shear rate increasing and decreasing ramps.



3. Schematic of the proposed conformations at high and low shear rate for higher and lower solids contents (s.c.). The "halos" around the fibers indicate their interaction potential. At high enough solids concentration, the aligned structure is suspected to transit into an entangled matrix, similar to the low shear rate state, but in this case induced by the forced proximity of the fibrils.

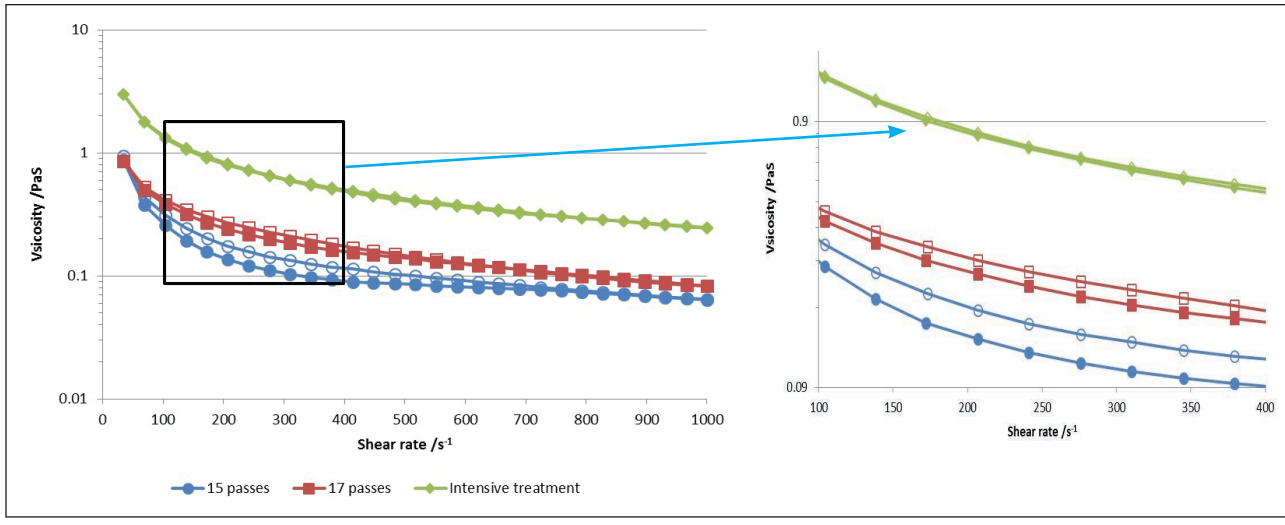


4. Amplitude sweep curves of MNFC samples at different solids contents and the tap water that was used to make the different dilutions. The filled symbols represent the measurement points of the shear rate increase ramp, whereas the open symbols represent the measurement points of the shear rate decrease ramp. The inconsistent starting phase angle is considered here to be an artefact of the measurement. The red arrows are marking the characteristic shoulders in the increasing shear stress ramp.

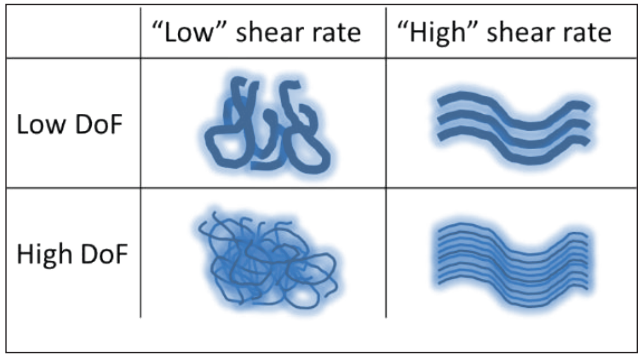
with the increasing degree of fibrillation as opposed to the trend with increasing solids content.

If we again hypothesize the same structural situation as described earlier, then the change of the hysteresis area can be explained accordingly: at low DoF, there is not much interaction between the cellulose entities, as there are only few surface features and the main structural body is relatively stiff, so not many interaction points are present in the low shear conformation (**Fig. 6**). In the high shear alignment conformation, however, there is much more interaction due to the alignment, as long as the solids content is high enough. Therefore, a large hysteresis can be seen between the shear rate increasing and decreasing curves, that is, once again, assuming the already proposed predominant conformations in the respective sweeps. But if the degree of fibrillation is high, then there is already a high level of interaction in the low shear conformation because more individual entities are present that are probably more flexible compared with the dimensionally thicker less fibrillated entities. Overall, this leads to many more interaction points. In this case, the alignment in the high shear conformation does not lead to substantially more interactions, so the difference in the viscosity curves for the increasing and decreasing shear rate ramps is small, indicating only slight hysteresis. The overall increase of viscosity with increasing degree of fibrillation can probably be attributed to the lesser amount of free water. The increase of water retention by an increasing degree of fibrillation was already described by Herrick et al. using the water retention value as characteristic [20].

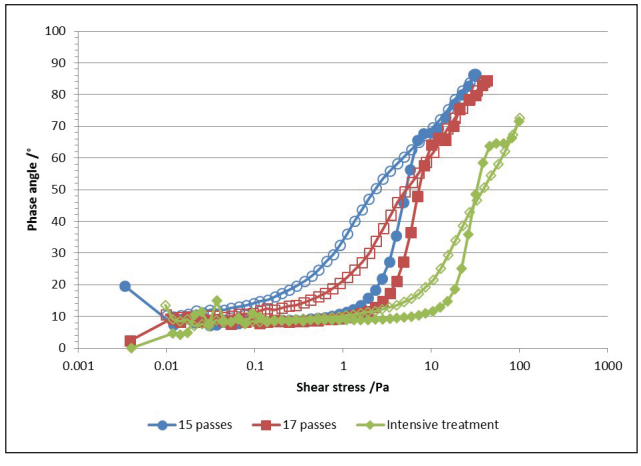
Alternatively, it could be assumed that the relaxation time



5. Flow curves of MNFC suspensions at different degrees of fibrillation. The dilution for these samples was set to 2 w/w%. The neighboring plot shows the enlarged region outlined in the main diagram.



6. Schematic of the proposed conformations at high and low shear rate for greater and lesser degrees of fibrillation (DoF). The halos around the fibers indicate their interaction potential, which here is seen to have a greater penetration into the water phase than that shown in Fig. 2 due to the greater zeta potential, causing more interaction potential overlap.

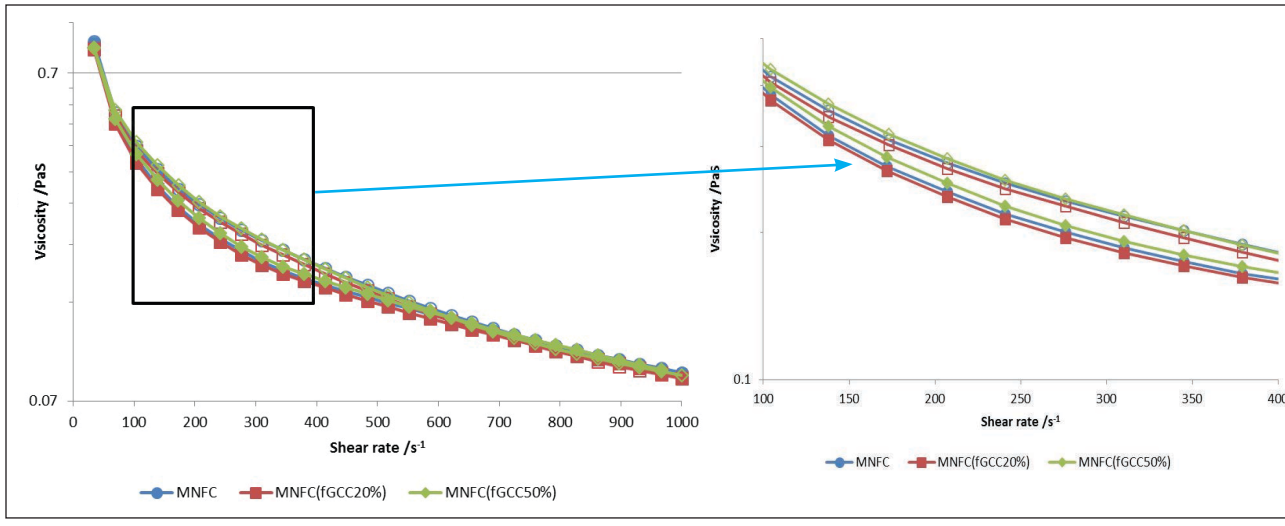


7. Amplitude sweep curves of MNFC suspensions at different degrees of fibrillation. The dilution for these samples was set to 2 w/w%.

is changing with the degree of fibrillation, in respect to the diameter of the cellulose entities: the smaller the diameters are, the faster a given conformation can rearrange, and the hysteresis therefore becomes smaller or disappears when the relaxation time becomes shorter than the point measurement time. This then would mean that the effect is no longer dependent on the predominant conformation as a function of the direction of the shear rate change, but just an equilibrium conformation that is only depending on the actual shear rate. Alternative time dependent measurements could reveal which hypothesis applies better to the current situation, or if it is probably a combination of many.

The trend of an increased overall viscosity with an increasing degree of fibrillation was also seen, for example, by Sneck [21], who investigated the viscosity dependence of mechanically fibrillated MFC on the amount of passes through an ultrafine friction grinder. However, one also finds publications where an opposite trend is seen, for example a finer (TEMPO oxidized) NFC having a lower viscosity than a coarser MFC [15,22], or an increased amount of passes through an ultrafine friction grinder led to an MFC with lower viscosity [23], or at least not to an increased viscosity as the difference was quite small. In the latter case, it was argued that a cutting of the fibers/fibrils can probably lead to a reduced viscosity. In the other case, Horvath and Lindström's [14] explanation can be applied, in respect to increased charge on the fibers leading to a decrease in internal friction, as the TEMPO oxidation typically leads to an increased surface charge density [5]. However, it cannot be attributed to the generally decreased fibril dimensions (increased DoF), as in this case it is not the surface charge density which is increased, but rather the overall charge in the system by exposing new charged surface. It is very probable that the overall viscosity of an MNFC suspension is the result of an interplay of different, opposing effects that are changed differently upon changing the degree of fibrillation.

The flow point also increases with increasing degree of



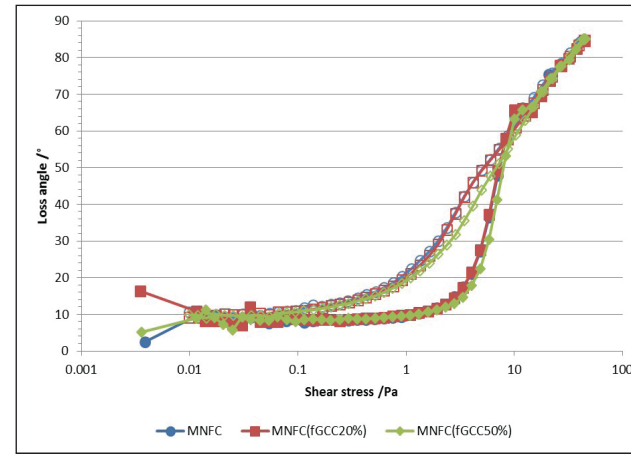
8. Flow curves of MNFC suspensions at different pigment filler loadings. The indicated filler levels are based on the total dry amounts. The cellulosic solids content was 2 w/w% for all samples. The neighboring plot shows the enlarged portion outlined in the main figure.

fibrillation, as can be seen in **Fig. 7**. The same explanation for the increasing flow point as was applied to increasing solids content can also be used here, i.e., increased degree of fibrillation results in a greater number of individual nanofibrillar entities, and thus more connection/interaction points per unit volume are present, and, therefore, more force (shear) is needed to break down the attendant gel structure.

Influence of additives on MNFC suspension rheology

As can be seen from the flow curves (**Fig. 8**) and the amplitude sweep measurements (**Fig. 9**), the addition of pigment filler, even at substantial amounts of 50 w/w% of the total dry mass (MNFC(fGCC50%)) does not have a strong influence on the rheological response of the MNFC suspension. There is only a small lift of the flow curve to higher viscosity values, but no change of the curve shape, and only a slight increase of the flow point seen in the amplitude sweep measurement.

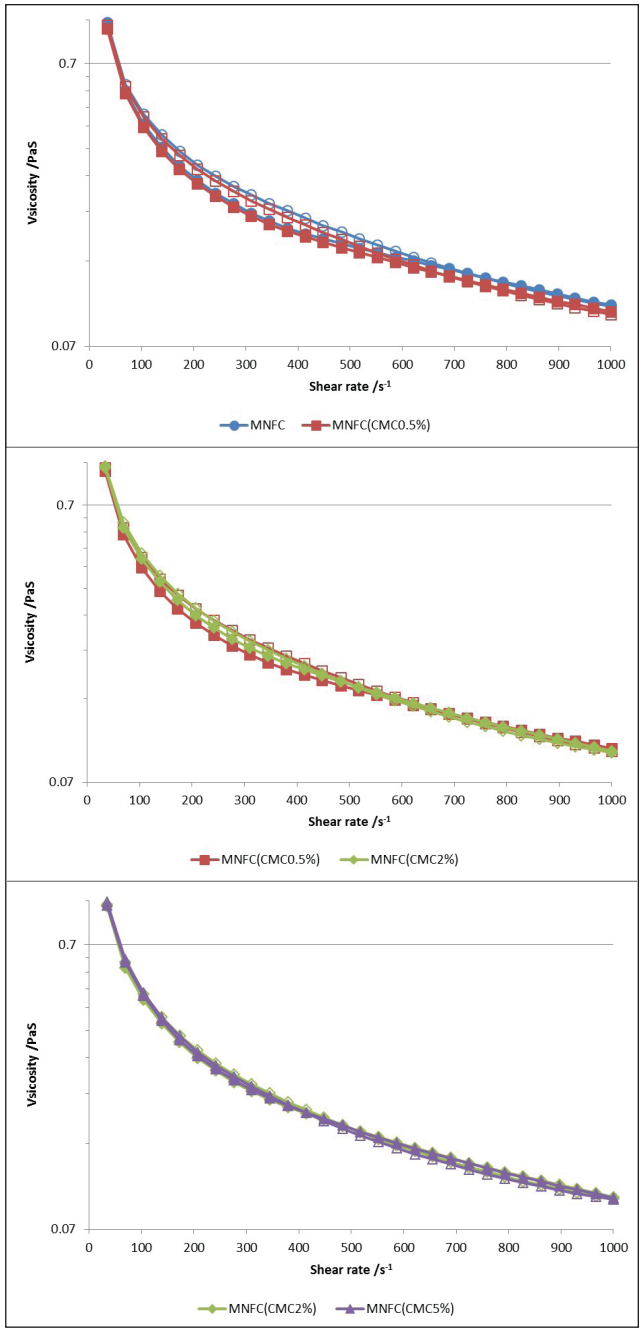
The absence of significant changes of the MNFC suspension rheology indicates that there is little to no interaction of the pigment particles with the MNFC entities. This may be attributed to the low surface charge and lack of reactivity of undispersed calcium carbonate pigment particles, with its ζ potential value of -8.2 mV. The relative inertness could perhaps have already been foreseen indirectly, as it is known from traditional papermaking that untreated ground calcium carbonate particles behave relatively independently of the fibers in a paper sheet and during the forming process, unless retention chemicals are used or the solids content has risen high enough to create enforced physical contact. Also, Dimic-Misic et al. [15] concluded in their investigation of different coating color formulations that the pigment they used, even though it was anionically dispersed and the system was more complex, did not effectively interact with the added MFC or NFC. In a later publication [22], they also provide a schematic



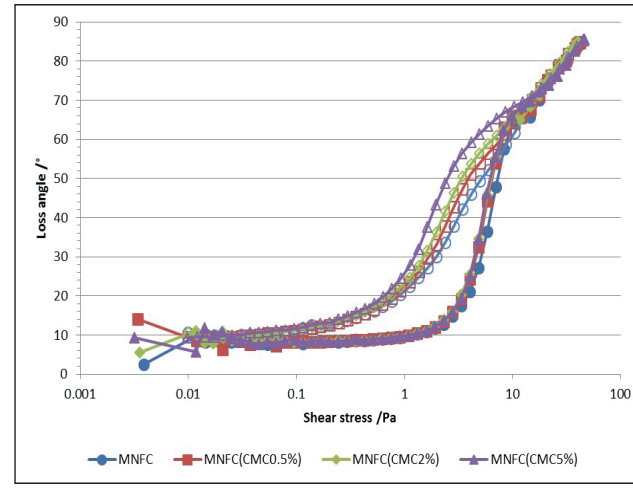
9. Amplitude sweep curves of MNFC suspensions at different pigment filler loadings. The indicated filler levels are based on the total dry amounts. The cellulosic solids content was 2 w/w% for all samples.

model and assign a more critical role to the addition of CMC to a system containing MFC or NFC and pigment particles and further coating color components. On one hand, it is mentioned that the CMC has a dispersing effect on the MFC or NFC material by reducing the cellulose particulate interactions, as indicated earlier, for example, by Vesterinen et al. [24], or shown visually by Xu and Roussière in their work [25,26]. On the other hand, they also mention that in the presence of CMC, flocculation of the dispersed filler and the latex is only induced in the case where MFC/NFC is absent. The influence of CMC on the rheology of MNFC suspensions, and in those containing pigment filler, is hereby further investigated in this current work.

A reduced attractive interaction between the cellulose entities due to the addition of CMC can be observed as a reduction of the overall viscosity at increased shear rates in **Fig. 10**. Apparently, the addition of only 0.5 w/w% CMC is



10. Flow curves of MNFC suspensions at different CMC loadings. The indicated addition levels are based on the cellulose dry amounts. The cellulosic solids content was 2 w/w% for all samples.

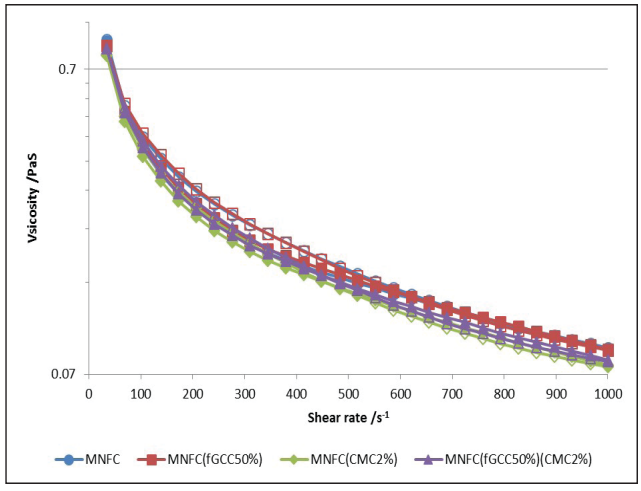


11. Amplitude sweep curves of MNFC suspensions at different CMC loadings. The indicated addition levels are based on the cellulose dry amounts. The cellulosic solids content was 2 w/w% for all samples.

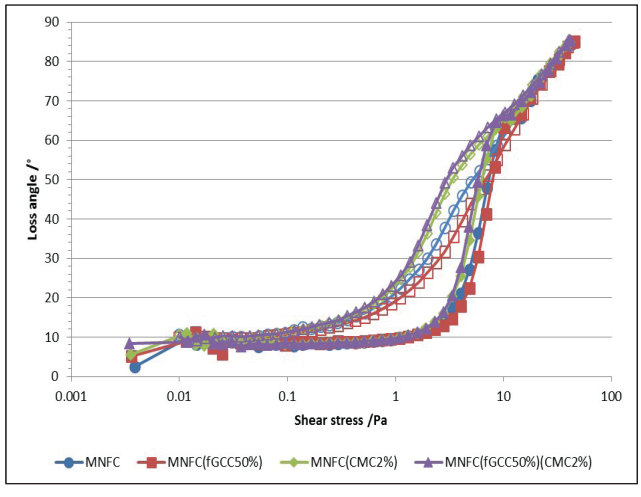
enough to reduce the viscosity at increased shear rates (cf. MNFC vs. MNFC(CMC0.5%) above 600 s^{-1}). Interestingly, even higher amounts of CMC do not further reduce the overall viscosity, but reduce the hysteresis area, and also tend to invert the hysteresis at increased shear rates (MNFC(CMC5%) above 500 s^{-1}). From the amplitude sweep curves, one can see that the gel structure is broken down at slightly decreased shear stresses when CMC is added to the MNFC suspension (**Fig. 11**), but independent of the CMC amount over this range of addition levels, as the measurements for 0.5, 2 and 5 w/w% CMC content are having an identical upsweep curve. However, as the hysteresis of the flow curves is becoming smaller and even inverted, the excess CMC probably has a more complex effect. Following the previously proposed argumentation, the effect of "excess" (= "free") CMC might be explained by the dispersing effect of CMC: as more entities get dispersed, the MNFC suspension appears as a more fibrillated material, and therefore, as hypothesized previously, the low and high shear state do not differ that much in interaction. Therefore, the hysteresis between the shear rate increasing and decreasing curves disappears. Alternatively, the hysteresis might be lost due to an increased mobility of the finer entities, effectively reducing the time constant of the structure reorganization. These results clearly indicate that the state of CMC, either bound to the cellulose particulate surface, as described by Horvath and Lindström [14], or present as free polymer, has an influence on the rheological response of the MNFC system. Whereas bound CMC reduces the flow point and the general viscosity by adding to the electrostatic repulsion, thus reducing internal friction, free CMC on the other hand may change the apparent degree of fibrillation, thus reducing relaxation time of the MNFC suspension.

The decrease of yield stress of pulp suspensions due to addition of CMC was also reported by Liimatainen et al. [27]. On one hand, they found that the yield stress keeps decreasing with increasing CMC amount, as opposed to the data presented here and to those of Horvath and Lindström [14]. On the other hand, they also saw that an increasing amount of non-adsorbed CMC led to a further reduction of the yield stress. It may be that the yield stress determination method used by Liimatainen et al. [13] is confused by viscosity and time dependent effects that lead to a misinterpretation of the yield stress.

It is also worth noting that the plateau phase angle before

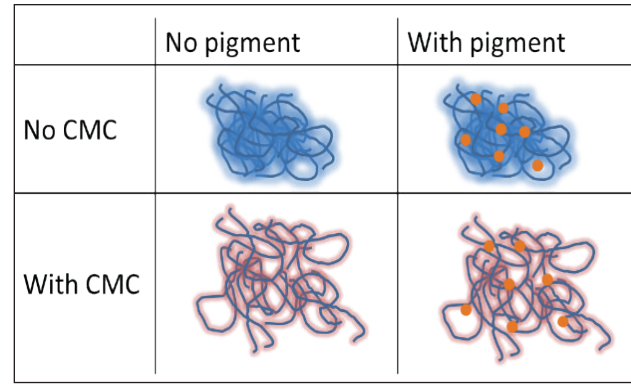


12. Flow curves of MNFC suspensions containing zero, one, or two additives (CMC and/or dispersant free calcium carbonate [fGCC]). The indicated CMC addition levels are based on the cellulose dry amounts, whereas the filler levels are based on the total dry amount. The cellulosic solids content was 2 w/w% for all samples.

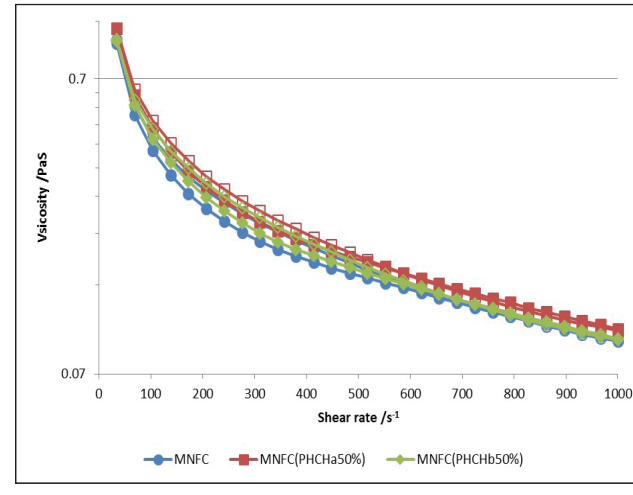


13. Amplitude sweep curves of MNFC suspensions containing zero, one, or two additives (CMC and/or fGCC). The indicated CMC addition levels are based on the cellulose dry amounts, whereas the filler levels are based on the total dry amount. The cellulosic solids content was 2 w/w% for all samples.

the gel structure breakdown is not changed upon the addition of CMC nor throughout the increasing addition levels. This indicates that the static interaction is still predominantly determined by the MNFC entities themselves. However, as the flow point is slightly reduced by the presence of CMC, the ultimate stress that can be borne by the system before losing the gel structure is reduced. It also should be mentioned that when pigment filler and CMC are both added together to an MNFC suspension, the property-determining component is clearly the CMC, as can be seen in **Fig. 12** and **Fig. 13**, as the curves of the filler and CMC containing sample (MNFC(fGCC50%)(CMC2%)) are following the respective curves of the CMC-only containing sample



14. Schematic of the proposed conformations for MNFC suspensions with and without CMC and/or pigment. The blue halos around the fibers indicate their interaction potential, and the red halos indicate the general altering of the fiber-fiber interaction potential related to the presence of CMC.

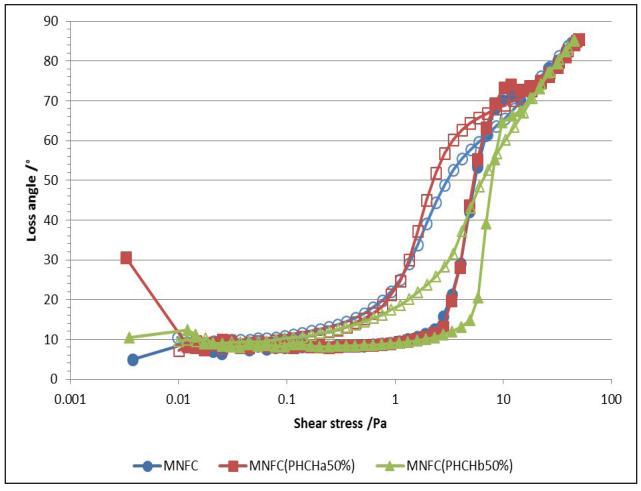


15. Flow curves of MNFC suspensions containing no and the two different PHCH filler pigments, PHCHa and PHCHb. The indicated filler levels are based on the total dry amount. The cellulosic solids content was 2 w/w% for all samples.

(MNFC(CMC2%)).

The general effects of the previously discussed additives are summarized in **Fig. 14**. CMC (red) disperses the cellulose entities by being initially adsorbed on their surface, and, when in excess, remaining partly in solution. The pigment particles (orange) do not interact with the cellulose fibrils. A significant adsorption of CMC onto the pigment particles is not expected, because of the low reactivity of their undispersed surface. The data presented in the following paragraph will support these conclusions.

By co-grinding CMC with the calcium carbonate pigment filler (PHCHa), as also with further addition of cationic polymer (PHCHb), the CMC (and cationic polymer) is bound to the pigment filler surface. This "immobilization" of the polymer(s) on the surface has an effect on the MNFC suspension rheological behavior when such pigment fillers are mixed into it. Looking at the flow curves (**Fig. 15**) reveals that the CMC-only co-processed pigment filler (PHCHa) leads



16. Amplitude sweep curves of MNFC suspensions containing no pigment additive versus the two different PHCH pigments. The indicated filler levels are based on the total dry amount. The cellulosic solids content was 2 w/w% for all samples.

to a generally increased viscosity, a reduced hysteresis area and even a slight hysteresis reverse at increased shear rates (> 650 s^{-1}). The cationic polymer additionally co-processed PHCH (PHCHb) pigment filler also leads to an increase of the viscosity, but less pronounced and only at lower shear rates (< 700 s^{-1}).

Interestingly, the gel structure breakdown (flow point) is affected (increased) only by the cationic polymer containing PHCH (PHCHb), as can be seen in **Fig. 16**. This might be expected due to the Coulombic attraction of the anionic MNFC and partly amphoteric pigment.

As there is no reduction of the flow point in the PHCHa-containing MNFC suspension, but the addition of CMC (as also together with fGCC) does reduce the yield point, it can be concluded that most of the CMC is actually bound to the pigment filler particles in the case of PHCH. Furthermore, it can be hypothesized that the static structure of the cellulose entities is not altered by the CMC covered particles, but, interestingly, those particles have an influence on the dynamic structure flow curve. First, there is an increased viscosity, indicating a stronger interaction between the involved entities during initial collisions. As this was not seen for untreated calcium carbonate particles (fGCC), it can be assumed that a specific CMC-cellulose interaction may be attributed to the development of this stronger interaction. We hypothesize that the increase of anionicity of the pigment filler particle seems not to be the reason for an increased viscosity, as this most probably would lead to overall less internal friction and therefore even lower viscosities. Second, the hysteresis becomes smaller, and this, then, may be attributed to free CMC (see previous explanation). This finding is contradictory to what is observed in the amplitude sweep measurement, as in the case of free CMC, in that the flow point would be expected to decrease, too. So, it may be that the observed flow point is determined by several counteracting effects. Further investigations are needed to clarify this situation.

As the flow curve is less changed when PHCHb is added compared to PHCHa, it can be concluded that there is less dynamic interaction. As the PHCHb pigment particles are also covered by cationic polymer, it might be concluded that there is less specific CMC-cellulose interaction as a part of the CMC interacting with the cationic polymer. On the other hand, as the flow point is increased, the situation must be different in the static configuration. Probably a stable, but weak, (electrostatic) structure is formed between the cellulose entities and the PHCHb particles that are destroyed during shearing, and they are not re-formed rapidly enough in the flow curve measurement. As a result, the cellulose entities and the pigment particles are not hindered anymore in their relative movement, and the viscosity is not much different from that of a pure MNFC suspension. Further (rheological) investigations are needed to test this hypothesis.

It was shown that the localization of CMC (and polyDADMAC) on pigment fillers does have a significant influence on the rheological properties of MNFC suspensions compared with direct addition of those polymers to pigment filler containing MNFC suspensions. Earlier work in the field of MNFC-pigment nanocomposites already indicated that the localization of CMC (and additional polyDADMAC) on the pigment filler surface leads to a beneficial behavior compared with their direct addition when fillers are used with MNFC [9]. It was specifically shown that such surface treated PHCH pigments lead to a significant increase in mechanical strength properties in an MNFC-pigment composite compared with when they contain non surface-treated pigment filler, with or without the free addition of CMC. The present work thus confirms those proposed increased interactions of the PHCH pigment filler particles with the cellulose fibrils, as manifest here by the increased gel strength, for example.

Further work needs to be done, but using this knowledge looks promising as a tool for tailoring MNFC suspension properties, and also for manufacturing economic and well performing pigmented MNFC composite materials.

CONCLUSIONS

The influence of MNFC suspension properties on its rheological behavior was investigated. The typical shear thinning behavior was observed, and existing mechanistic models were applied and extended for interpretation of the data. Apparently contradictory data were critically discussed in the light of competing mechanisms of charge repulsion, particle entanglement, and gel formation, which highlights the need for further clarifying investigation. Also, the influence of additives on MNFC suspension rheology, namely CMC and pigment particles, was investigated. Additionally, some existing data could be confirmed and explained by mechanistic models. Finally, it was found that the localization of CMC on pigment filler particles by adsorption during pigment co-pro-

cessing produces pigment filler particles that change the MNFC suspension rheology in a way that has not been previously reported. Such pigment hydrocolloid hybrid (PHCH) particles can increase either the gel strength or the apparent viscosity of an MNFC suspension, whereas regular pigment particles and CMC typically show no or opposite effects. The further development of such PHCH pigment particles may be a versatile tool to specifically influence the rheological behavior of an MNFC suspension, and thereby ultimately impact the properties of composites made from them. **TJ**

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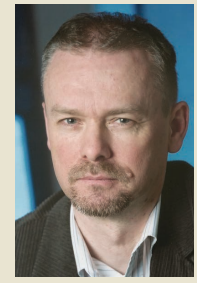
Schoelkopf


Mangin


Gane

Micro nanofibrillated cellulose (MNFC) is a very versatile material with a great potential in very different applications. However, the handling of MNFC in its suspension form may be challenging — on one hand because of its high water binding potential, and on the other hand because of the related complex rheological properties. A better understanding of MNFC's rheological behavior may help to find solutions like specific additives or processing conditions. Additionally, we wanted to enhance the interactional properties between filler pigment and the fibrillar material, which has been achieved, to enable further potential to be derived from MNFC-filler pigment composites and coatings.

One part of this work confirms previously presented data and hypothesized mechanistic interaction models. However, some data also indicate that we do not yet have a model general enough to be able to explain all the observed effects. This can be seen, for instance, when we encounter controversial findings. Finally, some previously unreported effects are also reported here by changing the additive chemical and particulate surface properties, the latter point being rarely described in literature.

When working with MNFC materials, one is typically already challenged with achieving an accurate or precise material characterization. Sometimes, it can be found that MNFC is characterized by techniques typically used for pulp. However, most of these techniques are not able to give reliable results and therefore may lead to misleading results. On one hand, we avoid any measure of potentially misleading MNFC characteristics. On the other hand, the work itself hopefully contributes to the development of a more reliable characterization by using, for example, rheological properties in combination with other more suitable data.

Even though already indicated by the literature, it was somewhat surprising that the standard pigment filler particles had basically no interactive influence on the form of the rheological properties of the MNFC suspension, even though the weight ratio was quite high. However, we could show that the fixation of polysaccharide, in the form of carboxymethyl cellulose (CMC), on the pigment filler particle surface (pigment hydrocolloid [PHCH] pigments) changes the yield point or the viscosity of the MNFC suspension-dependent surface properties. This is all the more interesting, because free addition of CMC itself has a different effect on those properties.

Recently, it was shown that MNFC can be used as a strength additive in paper applications at industrial scale. In this case, the MNFC is applied at the wet end of a paper machine. To fully exploit the benefits of MNFC, different application, such as in coatings, might be a valuable alternative. When it comes to such applications, this work might possibly help to address issues that are related to the coating process and final coating strength and stiffness based on composite properties.

More work is needed in order to better understand the colloidal interactions, which could be of benefit in MNFC-filler pigment composites and coatings, as well as a composite additive for fiber product strength, as exemplified here by the MNFC-PHCH combination. Some of the hypotheses developed here must also be challenged by further experimental work.

As it was seen in other work that the co-processing of pigment filler during the manufacturing of MNFC leads to enhanced mechanical properties of composite materials made from them, it will also be of interest to investigate pigment filler coprocessed MNFC suspensions in more detail rheologically.

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