

Technical Aspects on Rheological Characterization of Microfibrillar Cellulose Water Suspensions

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ABSTRACT

Microfibrillar cellulose water suspensions were tested in dynamic rotational rheometers using planar and cylindrical geometries. Within the sample sets, the results showed a clear correlation to measuring conditions, in particular to the geometry gap. This is mainly due to the boundaries of the measuring geometry affecting the flocculation process.

INTRODUCTION

Cellulose fibers can be divided into their structural nano-scale units by various chemical and mechanical means.¹ The results of such disintegration, so called micro-fibrils, have a lot of interesting properties. Their Young's modulus is very high (close to 140 GPa)² and they have a large surface area coupled with an aspect ratio that is also very high.³ Wood is a self-evident source for cellulose and wood pulp is a commonly used starting point in manufacture of microfibrillar cellulose (MFC). Due to this manufacturing route MFC is usually presented to the rheologist in a form of a water suspension.

MFC water suspensions may have a dry matter content varying from parts of a percent to few percents in weight of MFC.

At rest, already at markedly under one wt% concentrations, MFC water suspensions are gel-like substances, where

the gel network consists of sintered together fibre flocs.⁴

Upon shearing, the gel network disintegrates and fibrils start to flow in flocs.⁵ The size of the flocs is, excluding fibril size and surface properties, mainly dependent on the applied shear rate. In general, the higher the shear rate, the smaller the average size of the flocs is.⁶ This gives rise to pronounced shear thinning behaviour.

The changes in floc size resulting from changes in shear rate are often reversible but the adaptation time might be very long. The reversibility (detected on stress) and delayed response of the size of the flocs classify MFC suspensions in the category of thixotropic materials.^{6,7}

The reversibility of the flocculation process and network structure formation are not self-evident due to several possible reasons. The first comes back to the sometimes very slow growth rate of flocs — it is not always experimentally very feasible to follow a process that might take several days.⁸ Another case when full reversibility is not observed is, when something has happened to the sample during the test. If the used set up enables sample evaporation during the measurement, results are bound to be greatly affected as MFC suspensions are very sensitive to dry matter content. Furthermore, MFC forms a hard elastic film when it dries, which is a problem especially in planar geometries. Yet another possible occurrence is permanent aggregation of the

fibres that may happen under some conditions.

Already a number of studies have been performed on the rheological behaviour of MFC suspensions, but to the authors' knowledge, they have not considered the flocculated nature of the material much beyond casual notice.^{9,10,11,12,13} On the other hand, very thorough papers by eg. Björkman^{4,5,14,15,16} have been published, where the flocculated nature of fibre flow has been treated carefully. Compared to MFC suspensions, these studies have concerned fibers with larger diameters varying from 2 μm (Mycelial fibres) to 22 μm (fibres of soft wood pulp).^{4,14} Typical smallest fibril dimensions in MFC suspensions are in the range of 5 to 10 nm, i.e. one thousandth of what was used in Björkman's studies.¹² Björkman has demonstrated how the results of rheological tests on fibre suspensions are dependent on the geometry boundaries, most notably on the geometry gap. The gap limits the maximum size the flocs can achieve under any experimental conditions. In MFC the fibre dimensions are much smaller than in native cellulose pulp and therefore one might hope that the results are less affected by the chosen geometry. Unfortunately this hope is not completely fulfilled as shall be shown later.

The aim of this current paper is to present some of the anomalies observed in our standard type rheological tests of MFC water suspensions using typical run of the mill geometries. We hope that upon showing these examples we manage to increase the alertness of the reader and make her or him consider with care when making any direct comparisons between reported rheological results on MFC water suspensions type of materials recorded using different measuring set ups. Furthermore, we wish to point the reader into right direction to avoid the worst potholes, should the need arise to delve into the fascinating world of micro and nano scale fibre suspensions.

MATERIALS AND METHODS

Materials presented here represent MFC suspensions without any chemical pre-treatment's. The starting material, never dried hard wood pulp, was produced into MFC by mechanical disintegration of the fibres.

The first of the two alternative processing routes taken in this study started by pre-refining the pulp with a Voith-Sulzer refiner and was followed by actual disintegration of the fibres via several passes through a Microfluidizer[®] high-shear fluid processor (Microfluidics[®] M110Y). The details of the microluidized samples (F1 - Fn) are presented in Table 1 and microscopic and camera images in Fig. 1.

The other alternative route included friction grinding in Masuko Supermasscolloider[®] (Model MKZA 10-15J, Masuko Sangyo Co. Ltd., Japan). Also this latter route included several passes through the instrument. The number of passes through the Microfluidizer or Masuko has a correlation with the level of fibril disintegration. In general, the more passes, the finer the average fibril and floc dimensions will be given the other parameters are kept constant.¹²

The rotational rheometers used in this study were Anton Paar Physica MCR 301 and TA Instruments AR 1500ex. Comparisons were made with the studied materials using different geometries as follows:

Physica MCR 301

Parallel plates geometry, diameter 50 mm (PP50) with various gaps.

Cone and plate geometry, 50 mm, 1° cone angle (CP50-1)

DIN concentric cylinders geometry with bob and cup diameters of 26.62 and 28.92 mm, respectively (CC 27).

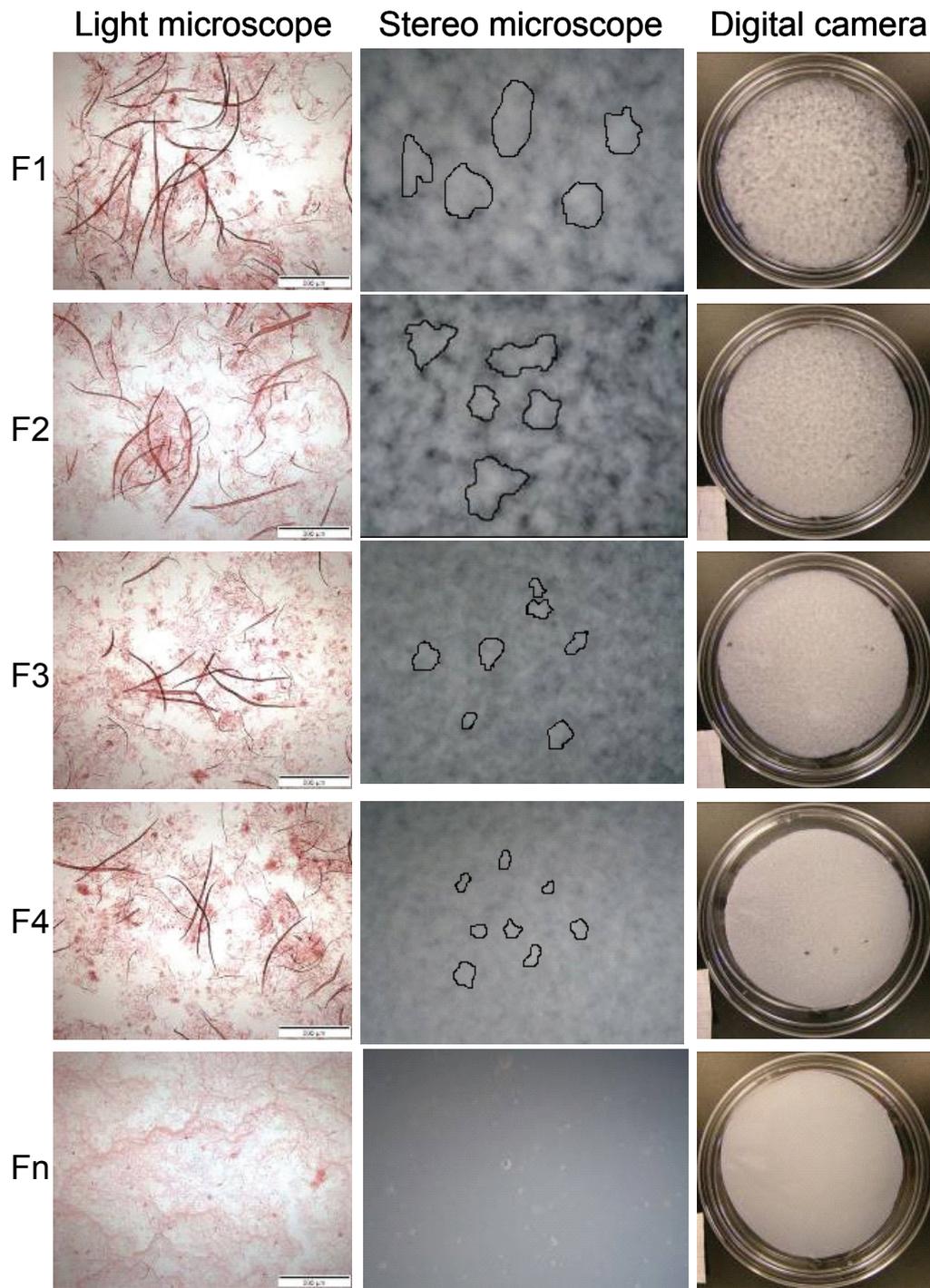


Figure 1. Light microscope, stereomicroscope and digital camera images of fluidiser processed cellulose samples: 1)F1, 2)F2, 3)F3, 4)F4, and 5)Fn. The number of passes through the fluidiser increased with increasing sample number and the average floc size decreases as the fibres are being disintegrated in the process. The samples are described in more detail in Table 1. The length of the scale bar in the light micrographs is 500 μm . Some examples of flocs are traced in the stereo microscope images to make the detection easier. The diameter of the lid of the Petri dish (outer vessel) in the last column is 9 cm.

Table 1. Description of the fluidiser treatments of samples F1-Fn. Numbers refer to chamber dimensions in the Fluidizer and to the number of passes through the chambers, respectively.

Sample ID	Processed with lab fluidiser	Dry matter content
F1	400 + 200 μm x 1	2,08 %
F2	400 + 200 μm x 1 200 + 100 μm x 1	2,06 %
F3	400 + 200 μm x 1 200 + 100 μm x 2	2,07 %
F4	400 + 200 μm x 1 200 + 100 μm x 3	2,07 %
Fn	400 + 200 μm x 1 200 + 100 μm x 4+~20	2,11 %

AR 1500 ex

20 mm stainless steel parallel plates with a gap of 1 mm.

MFC suspensions are very sensitive to the effects of shear history. Hence the sample handling prior to the measurements (storage time and possible shaking or mixing to improve homogeneity) plus loading into the geometry should be done as controllably as possible. Water separation from the gel during the storage was more visible with the coarser, less fluidized samples. In this study a waiting time of 120 s after loading the sample was followed throughout all the measurements.

Frequency sweeps in this kind of material exhibit rather constant loss and storage modulus levels across the practically measurable frequency range.¹² An amplitude sweep (or a stress sweep) has a potential to give out information on both the modulus levels (G' and G'') at rest conditions and also show how big stresses and strains are required for the gel to deform plastically. Therefore we chose to make the comparisons based on amplitude sweeps (MCR 301) and stress sweeps (AR 1500 ex). Measurements were recorded at 23°C.

RESULTS

Displayed in Fig. 2 are comparisons of results measured using different geometries. The apparent storage modulus level is clearly higher with the cone and plate geometry than with the other geometries. Figs. 3 and 4 exhibit the results of two different fluidized samples, samples F4 and Fn, correspondingly. Here is obvious how sample Fn, having more homogeneous and finer structure, is less affected by the gap setting than sample F4. Finally, Fig. 5 reveals how G' decreases by consecutive passes through the Microfluidizer.

DISCUSSION

With particle filled systems, and fibre suspensions in particular, the proximity of geometry walls raises at least three different issues.

First is wall slip (wall depletion). It is well known that in particulate filled systems there is a particle free layer at the boundary.^{17,18} Thickness of the depleted layer depends on the thickness of the particles. The thicker the particles are in relation to the geometry gap, the thicker the relative depleted layer and the more severe the effect of wall slip on the results.¹⁷ In the cases presented here, the modulus levels tend to be higher with narrower gap, which is opposite of what would be observed if wall slip was the dominant factor in the measurements. Therefore, even if wall slip cannot be ruled out, its effect on the result is lost under other issues discussed in the following paragraphs.

Second issue related to the closeness of the geometry boundaries, is the geometrical constraint caused by the boundaries to the movement of the elastic, thick fibers that remain in the suspension.

Different Geometries

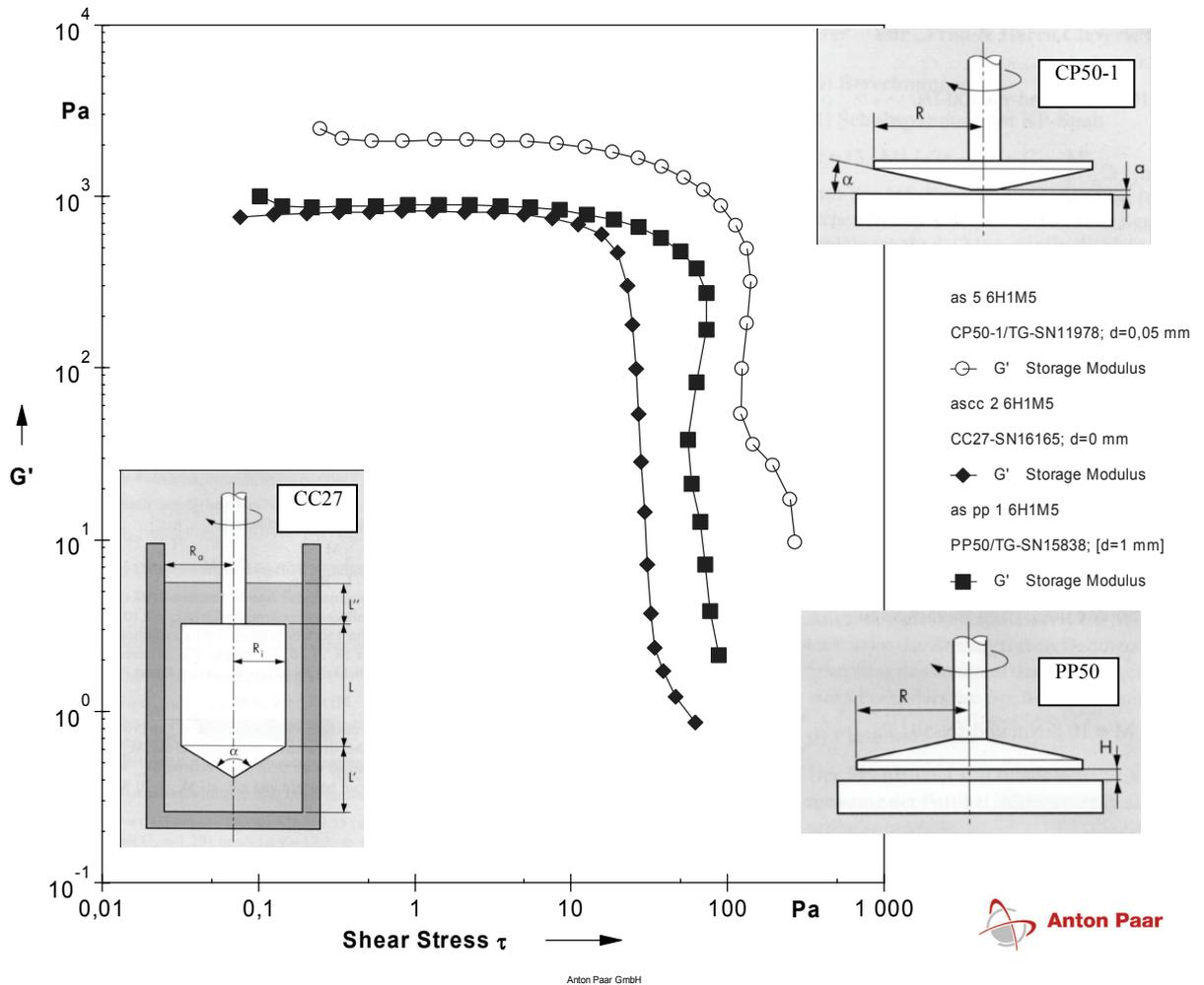


Figure 2. The geometry dependence of amplitude sweeps presented as function of stress. The most deviant result is obtained with cone and plate geometry (CP50-1) and is due to the gap being on the average much smaller than in the other geometries and especially diminutive near the tip of the cone. This constrains the fibre movement and results in apparently higher modulus levels.

Thick fibers might also affect the flocculation by slowing down the movement of the flocs.

Third is the effect the boundaries have on the flocs — the maximum floc size is limited by the size of the gap.

Particle sedimentation depends on the coarseness of the fibrils and the corresponding gel properties and might be an issue in coarser suspensions. In any case, it is more problematic in parallel plates geometry than in concentric cylinders geometry.¹⁷

Barnes¹⁸ has presented a scheme for assessing a safe gap size for rheological measurements based on the size of the filler particles and their corresponding phase volume fraction.

In non-colloidal suspensions filler loadings can be rather high without an adverse effect on rheological results. Flocculated systems, however, pose a far more problematic case.

The floc phase volume is much larger than the phase volume of the fibres. Flocs bind water to their surface and to their interstices¹³ and the number and volume of the flocs are, as mentioned, time and shear rate depend as well as affected by the geometry boundaries. That the effect of gap on G' in Fig. 3, sample F4 is more pronounced than that of Fig. 4, Fn has probably more to do with the geometrical constraint of thick fibres than differences in flocculation per se.

The differences in G' levels between samples F1 to Fn (results in Fig. 5) clearly manifest the large elastic contribution of thick fibres, which is also evident in the large variation of the G' of the least processed sample F1.

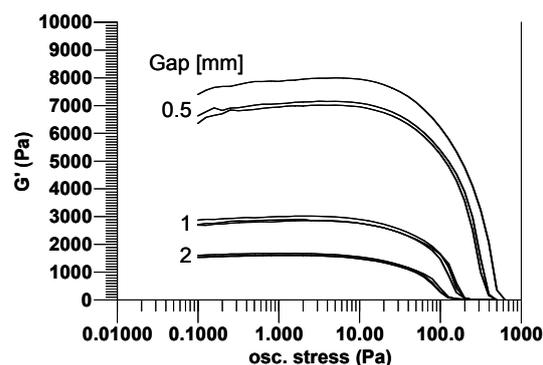


Figure 3. The effect of gap size on the stress sweep result of the fluidiser processed cellulose sample **F4**. The measurements were performed with the AR 1500ex rheometer. All samples were measured in triplicate.

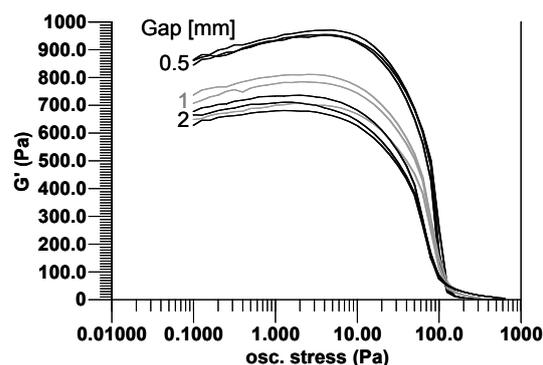


Figure 4. The effect of gap size on the stress sweep result of the fluidiser processed cellulose sample **Fn**. The measurements were performed with the AR 1500ex rheometer. All samples were measured in triplicate.

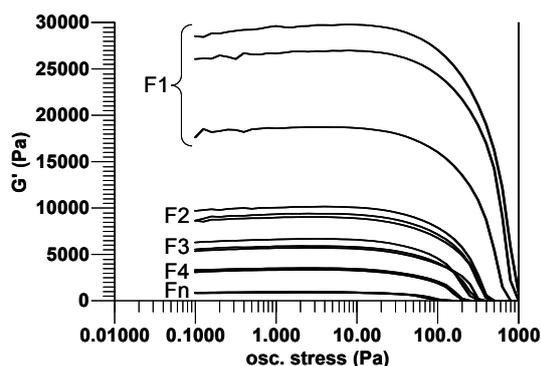


Figure 5. Stress sweeps of lab fluidiser processed cellulose samples. The measurements were performed with the AR 1500ex rheometer. All samples were measured in triplicate.

CONCLUSIONS

As has been repeatedly demonstrated before with fibre suspensions having more macroscopic fibre dimensions,^{4,5,7,14,15,16} and here with MFC water suspensions, making meaningful rheological characterizations with this kind of flocculating materials is not without challenges.

To be better able to do so, we have suggestions of things to consider.

First of all, it is advisable to combine other characterization techniques with rheological measurements, especially microscopic imaging. Even a simple visualization between squeezed together Petri dishes will help to give an idea of the coarseness of the system. The coarser the fibre dimensions are, the more dependent the results are on the measuring set up.

Regarding rheological measurements, because floc sizes depend on the shear rate, which is non uniform in parallel plates geometry, concentric cylinders geometries are perhaps better suited for characterizing flocculated systems than planar geometries. The effect of measuring gap should be confirmed with parallel plates measurements, however, before settling to a concentric cylinders geometry. In general, a concentric cylinders geometry with a gap of at least 1 mm seems advisable with MFC

suspensions over a geometry with narrower gap.

Moreover, dilute suspensions are less affected by the gap setting than more concentrated suspensions as the phase volume of the flocs remains smaller. Therefore, unnecessarily high dry matter contents should be avoided in the measurements. An added benefit of more dilute suspensions is also that they are less tormented by air bubbles which in concentrated suspensions get easily trapped in the gel network and induce unwanted variance into the results.

Finally, the effect of large fibres could in part be alleviated by using a vane geometry where applicable. Vane allows larger fibers and fibrils to settle in the larger gap between the blades which will lessen the effect the thick fibers have on the measurements.^{17,19} One alternative might be to filter out larger fibres so that their elastic contribution is removed from the system.

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