A method to correlate floc size to rheological characteristics of microfibrillated cellulose water suspensions

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ABSTRACT

Microfibrillated cellulose (MFC) water suspensions were characterized in a rheometer using transparent geometry which allowed the observation of the suspension's flocculated structure and the structural changes. The shear rates 500, 30, and 5 1/s induced different floc structures, whereas shear rate 0.5 1/s preserved the structure from the previous shear rate. MFC's degree of fibrillation was reflected in the coarseness of the floc structure. The viscosity of the suspension at a given shear rate was dependent on the floc structure.

INTRODUCTION

Microfibrillated cellulose (MFC) water suspensions have been under intensive rheological research during the last few years[1,2,3,4]. This is due to their excellent usability in thickening fluids and suspending particles in e.g. foodstuffs and paints, correspondingly. These studies, so far, have concentrated mainly on fibre dimensions, and concentration and the way in which the fibrils are structured within the suspension volume has received less attention. Based on papers[5,6,7] dealing with macroscopic fibre suspensions, it is known that fibres tend to arrange in flocculated formation and that it bears a great significance in the suspension rheology. Therefore, we have launched an effort to investigate the role which flocculation plays in the rheological characteristics of MFC suspensions. This paper presents a method for imaging of the sample during the rheological measurements. The viscosity and floc size are dependent on shear rate and the fibril dimensions. This has been investigated in a series of peak hold tests at different shear rates and different degrees of microfibrillation.

MATERIALS AND METHODS

Materials

Microfibrillated cellulose was obtained from UPM-Kymmene Corporation. The material was prepared from never dried birch pulp by mechanical disintegration. The pulp was ground three, four, or five times in Supermasscolloider (Masuko Sangyo) to get varying fibre disintegration levels. Solid contents of the materials were 2% (w/w). The materials are called M3, M4, and M5, where the number refers to the number of grinding cycles.

Rheological measurements

The measurements were done using a dynamic rotational rheometer (TA

Instruments AR G2), with a standard metal DIN concentric cylinders geometry (bob and cup diameters 14 and 15 mm, respectively). After a 20 min preshear interval at 500 1/s and a subsequent 30 min recovery period, frequency sweep was measured from 0.02 to 200 rad/s at 0.5% strain. The viscosities of the suspensions were measured at four shear rates (500, 30, 5, and 0.5 1/s) for 10 min. After each shear rate, a time sweep was measured at 0.5% strain for 10 min. In addition to standard metal outer geometry, a self-made transparent PMMA outer geometry was used in order to photograph the changes in the suspension structure during the measurements. The cup was placed into a transparent water container to prevent the reflections. The photographs were taken with Nikon D90 (Nikon Corporation, Japan) camera controlled by NKRemote software (Breeze Systems Limited, UK).

RESULTS AND DISCUSSION

The frequency sweeps of the MFC suspensions in Fig. 1 are typical for a gel. Storage modulus is clearly higher than loss modulus for every sample and both increase only slightly over the investigated angular frequency range. The gel-like behavior originates from the three-dimensional fiber network structure. The links between the fibers are physical and chemical in nature. The degree of fibrillation is expected to raise the moduli levels but deviations occur in the frequency sweep data due to remaining ungrounded thick fibrils in the suspension.[8]

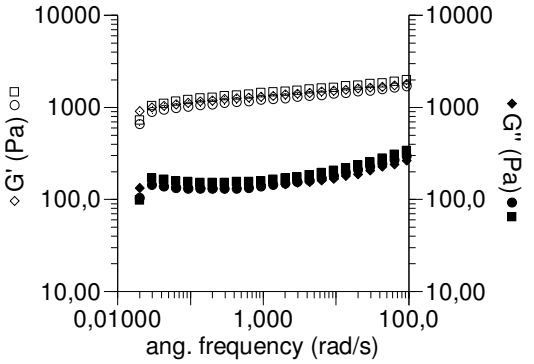

Figure 1. Frequency sweep for the suspensions. Symbols: circles – M3, squares – M4, and diamonds – M5.

The viscosities of the suspensions measured with normal metal cup and self-made PMMA cup are shown in Fig. 2. MFC suspensions are highly shear-thinning. The viscosity increases at every shear rate when the suspension is further microfibrillated even though the difference between M4 and M5 is small. In flow measurements, the remaining thick fibrils contribute less than in a frequency sweep being aligned in the shear.

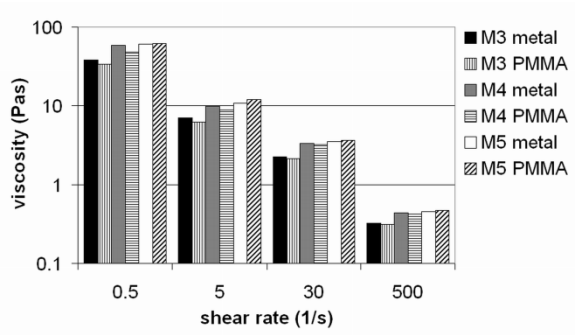

Figure 2. Viscosity at four shear rates after 10 min shearing.

When the results obtained with PMMA outer geometry are compared to the standard metal cup results, it is seen that the viscosities at higher shear rates are very close to each other (shear rates 30 and 500 1/s). Instead, small deviation from the metal cup results occurs at lower shear rates (shear rates 0.5 and 5 1/s). The PMMA cup seems to give lower viscosity than the metal cup,

which could be due to some wall slip between the suspensions and PMMA surface. The difference, however, is quite small.

Images from the M3 suspension during the measurements are seen in Fig. 3. The images are taken immediately after the shearing at each shear rate for 10 min. It should be noted that the measurements were performed from high shear rate to low shear rate although the images are presented from low shear rate to high shear rate. Fig. 3d after shearing at 500 1/s shows an even suspension where the flocs are almost too small to see with bare eye. Some ungrounded fiber aggregates are detectable (white spots). During shearing at 30 1/s, the flocs grow and they are better seen in the image (Fig. 3c). Shearing at 5 1/s causes divisions to appear between separate flocculated regions and the inner cylinder (black) is easily visible between the flocs (Fig. 3b). Shearing at 0.5 1/s for 10 min does not seem to alter the structure much (Fig. 3a) although the viscosity is clearly higher for the lower shear rate.

M4 suspension in Fig. 4 shows similar structures than M3 suspension. However, there are less fiber aggregates (white spots) in M4 suspension than in M3 suspension, and the flocs seemed to be smaller in M4 suspension. M5 suspension in Fig. **Fel! Hittar inte referenskälla.** does not contain any aggregates but otherwise exhibits analogous floc structures but again with smaller floc size than the less disintegrated M4 and M3. In general, the coarser the fibrils are in the suspension, the coarser is also the floc structure at a given shear rate but otherwise similar transitions are observed. As a side note, a way to avoid the changes observed in the floc structure could be via addition of various hydrophilic polymers eg. carboxymethyl cellulose and xanthan gum. These have also an added benefit of preventing water bleeding from the gel during both shear and storage.

CONCLUSIONS

We were able to see flocs, their structural changes during the measurements, and the response in rheological parameters. The shear rates 500, 30, and 5 1/s induced different floc structures. Shear rate 0.5 1/s preserved the structure from the previous shear rate (5 1/s). The degree of fibrillation was reflected in the coarseness of the suspension floc structure.

ACKNOWLEDGMENTS

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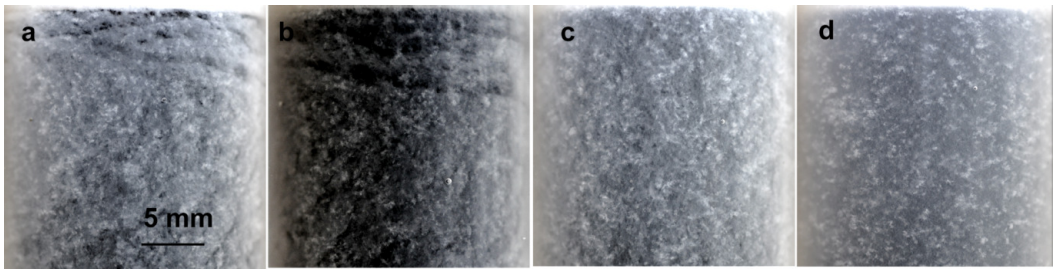

Figure 3. Images from the M3 suspensions immediately after shearing for 10 min at different shear rates. a) after 0.5 1/s, b) after 5 1/s, c) after 30 1/s, and d) after 500 1/s.

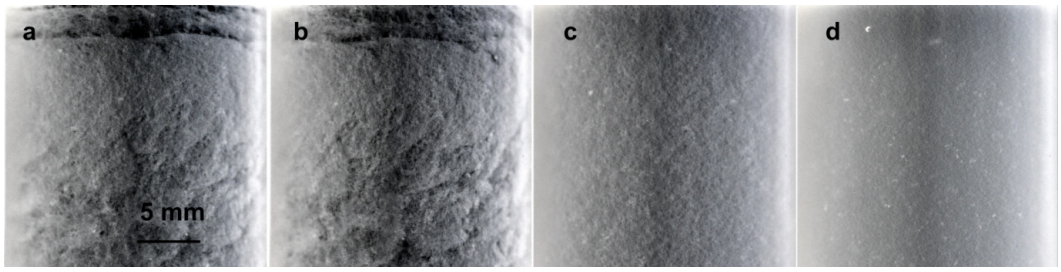

Figure 4. Images from the M4 suspensions immediately after shearing for 10 min at different shear rates. a) after 0.5 1/s, b) after 5 1/s, c) after 30 1/s, and d) after 500 1/s.

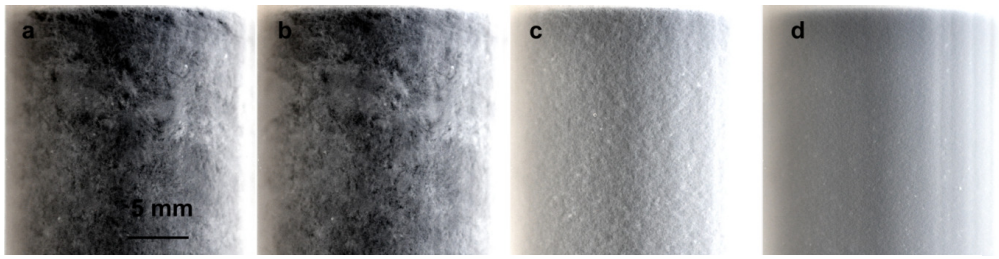

Figure 5. Images from the M5 suspensions immediately after shearing for 10 min at different shear rates. a) after 0.5 1/s, b) after 5 1/s, c) after 30 1/s, and d) after 500 1/s.