Flow Behavior and Flocculation of MFC Suspension Measured in Rotational Rheometer

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ABSTRACT

We employed a dynamic rotational rheometer together with camera and optical coherence tomography (OCT) to study the rheology of microfibrillated cellulose suspensions. In the rheometer, concentric cylinders with transparent cup were used. Imaging with camera and OCT was used to analyze the flow across the rheometer gap. At the same time, we used normal digital camera to detect the macroscopic floc structure of the suspension.

INTRODUCTION

Wood pulp can be disintegrated by mechanical shearing to micro- or nanofibrillated cellulose (MFC or NFC, sometimes called nanocellulose), which has a diameter in nanoscale and length of several micrometers[1]. MFC has been studied, for example, as a reinforcing material in nanocomposites, in paper making, and as a rheology modifier. MFC has interesting rheological properties in water suspensions, like gel forming at very low concentration (~0.125%), thixotropy, and shear thinning behavior[2,3,4].

MFC fibers form an entangled, three-dimensional network[2], and the fibers tend to flocculate when they are in water. The structure is partly similar to macroscopic cellulose fiber suspensions[5], although MFC fibers have significantly smaller dimensions and a higher aspect ratio than pulp fibers. The floc strength is determined by number of contacts and cohesive forces present between the fibers[6]. The cohesive forces are in this case mechanical or colloidal. The fibers collide and entangle mechanically to form flocs under flow. On the other hand, flow may break down the flocs by eroding fibers from the surface or by splitting the floc in two[7,8].

Colloidal factors contributing to flocculation can be described by DLVO theory by Derjaguin and Landau[9] and Verwey and Overbeek[10]. The colloidal forces consist of van der Waals interactions and electrostatic double layer interactions caused by surface charges. In addition to these, flocculation can be affected by non-DLVO interactions like steric and electrosteric interactions caused by polymers and polyelectrolytes in the system[11]. All these forces and thus the floc structure can be changed, for example, by salt addition[12,5], polyelectrolyte addition[13,8,14] or by changing the pH[15]. The suspension structure and the related rheological properties are important for the processing of MFC and in some applications.

All in all, MFC is a complex material to study. In our study, we wanted to combine the rheological results with the information about the floc structure of MFC suspensions. Therefore, we made a set-up which consists of a transparent outer

geometry for the rheometer and a digital camera that is controlled by a computer, and photographed the suspension structure during the rheological measurements. Furthermore, we employed an optical coherence tomography (OCT) device, which is able to analyze the structure across the rheometer gap.

EXPERIMENTS

Materials

Microfibrillated cellulose was prepared from never-dried bleached kraft birch pulp by mechanical disintegration. The pulp was changed to its sodium form and washed with deionized water to electrical conductivity less than 10 µS/cm according to a procedure introduced by Swerin et al.[16] and subsequently ground five times in Supermasscolloider (Masuko Sangyo, Japan). The initial concentration of the MFC suspension was 2% (w/w). Similar MFC has been reported to have fiber diameters between 10-30 nm with some larger fibril aggregates[1]. Dilution of the suspension was made with deionized Milli-Q water in order to avoid excess electrolytes. The dilution was performed with propeller mixer (diameter 58 mm, RZR 2051 control, Heidolph Instruments, Germany) at the speed of 1400 rpm for 10 min in a beaker with a diameter of 70 mm.

Rheological measurements

The measurements were performed using a dynamic rotational rheometer (ARG2, TA Instruments), with a standard (ISO 3219/DIN 53 019) metal bob and transparent cup (bob and cup radii 14.00 and 14.87 mm). After a 20 min preshear interval at 500 s^{-1} and a subsequent 10 min recovery period (time sweep at 0.5% strain and 1 Hz frequency), a flow curve was measured strain-controlled from 0.01 to 1000 s^{-1}.

The tailor-made transparent polymethylmethacrylate (PMMA) outer geometry was used in order to detect the changes in the suspension structure during the measurements. The temperature in the water container was not controlled, but it was assumed to be close to the room temperature (23-25 ºC). The photographs were taken with Nikon D90 camera (Nikon Corporation, Japan) with a macro objective controlled by NKRemote software (Breeze Systems Limited, UK).

The floc sizes of the suspensions at various shear rates were determined from the images. A detailed description of the analysis can be found in our earlier publication[5].

OCT

Optical Coherence Tomography (OCT) is a non-invasive optical imaging technique capable of real-time access of both structural data and velocity information in an opaque scattering medium. In this study Telesto Spectral Domain OCT system by Thorlabs was utilized for imaging in radial direction from the transparent outer geometry boundary to the inner geometry boundary. Thereby OCT allows detailed observation of the suspension structure in 2D slices and the shear rate distribution throughout the gap.

RESULTS

Fig. 1 shows flow curve for 0.5% MFC suspension. The suspension is drastically shear-thinning, as has been reported in the literature[2,3,4,17]. The viscosity curve can be divided into two shear thinning regions with a small plateau between them. The same regions were observed in the shear stress curve, where the shear stress was constant at low shear stress, and at higher shear stresses, after a small transition, the shear stress started to increase with increasing shear rate.

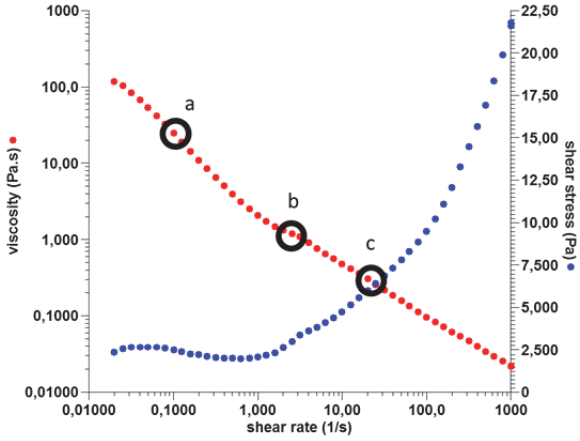

Figure 1. Shear stress (blue circles) and viscosity (red circles) as a function of shear rate for 0.5% MFC suspension. The letters in the rheograph show the shear rates at which the images in Fig. 2 were taken.

Fig. 2 shows the floc structure of MFC suspension during the flow curve measurement shown in Fig. 1. The images in Fig. 2 were selected from the two shear thinning regions in the flow curve and from the transition region between them. At the lowest shear rates (Fig. 2a), the suspension was very even after the previous high shear interval, and the floc formed a continuous three dimensional network. At intermediate shear rates, where a subtle bend in viscosity was observed, the flocculated fiber network broke and structures with large flocs and voids between them appeared, shown in Fig. 2b. The voids appeared parallel to the direction of greatest compression while flocs remained chained to each other between the voids at this region. After the transition region (Fig. 2c), the chains were broken, and the structure consisted of separate, small flocs. The schematic drawing in the Fig. 2 shows the floc structure at different shear rates. At low shear rates, we have network of the fibers, and flocs are more concentrated areas within that network. When the shear rate is increased and we exceed the yield stress of the suspension, the fibers flow as individual flocs, which are able to move relatively to each other.

The average floc sizes at each shear rate for the 1% MFC suspension were analyzed. At low shear rates, the floc size did not change but when the shear stress started to increase, the floc size increased as well and the floc size distribution was broad. This is the shear rate where we saw the breakup of the network in the images. After the breakup, the floc size starts to decrease as a function of shear rate. At these shear rates, the shear that starts to disrupt the large flocs and break floc chains. On the other hand, increasing shear rate may also increase the collision frequency between the fibers and flocs, forming new contacts. The balance between new contact points and disruption of the flocs determined the floc size at each shear rate. In this region, the flocs were rolling and moving relatively to each other, which enabled them to orientate themselves in the direction of flow. The decreasing floc size and orientation of the flocs caused the shear thinning behavior at the high shear rates[18].

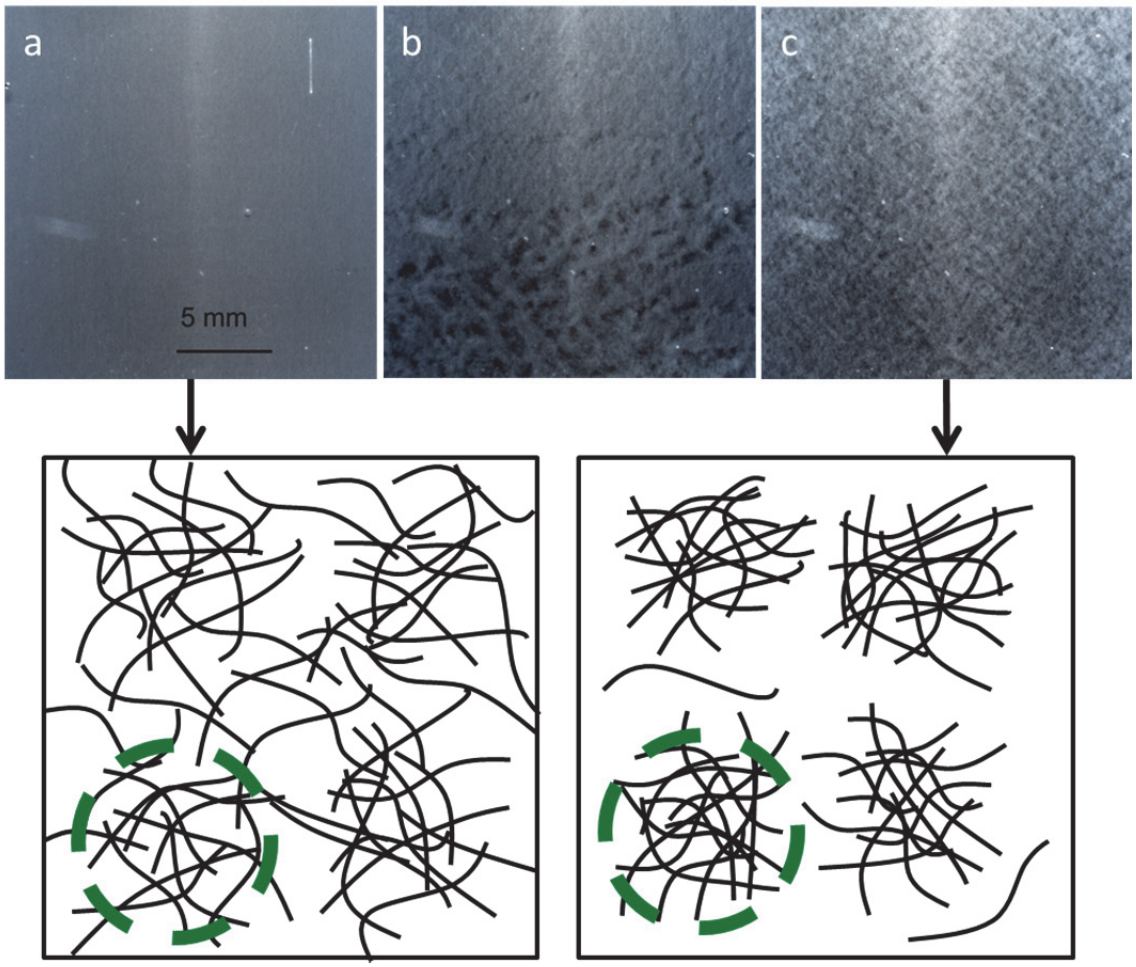

Figure 2. Images from the flow curves for washed MFC suspensions at a concentration of 0.5%. The images are from three different regions from the flow curve: a) shear rate 0.1 s^{-1}, constant shear stress, b) shear rate 5 s^{-1}, transition region, and c) shear rate 63.1 s^{-1}, increasing shear stress. The inner cylinder rotates to the left. Below is schematic presentation of the floc structure at low and high shear rates.

Using OCT with rheological experiments, we were able to detect the flow of the suspension through the rheometer gap. Fig. 3 shows the suspension structure just before the fiber network break-up. Similar floc structures as in the images in Fig. 1 were observed in the OCT imaging as well. However, the results also showed that wall depletion can be a severe problem in the stepped flow measurement. The flow profile was not linear over the gap, and the suspension seemed to slide on the outer geometry wall.

CONCLUSIONS

MFC suspension rheology is dependent on the floc structure of the suspension at different shear rates and measuring conditions. Heterogeneous structure causes nonlinear flow profile to the gap of the rheometer, depending on flow conditions. This then gives skewed results. In this study, we combined two imaging methods, photographing and OCT with conventional rheometer.

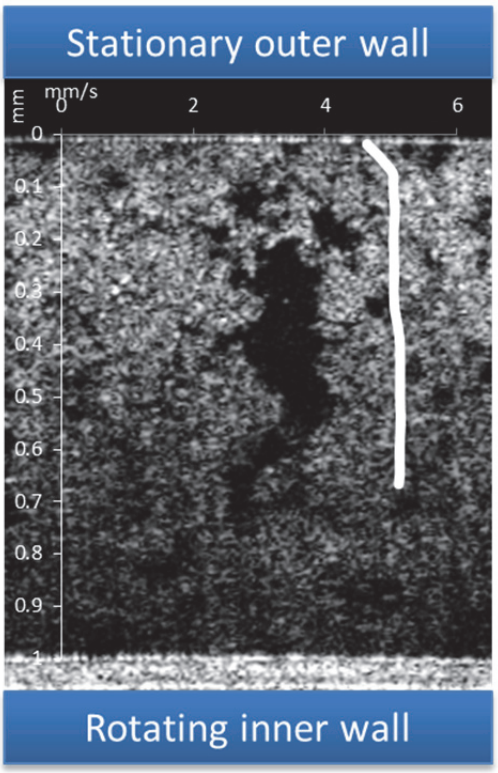

Figure 3. Image taken with OCT of the 1% MFC suspension at shear rate 7 s^{-1} with mean velocity profile overlaid.

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