Evolution of Floc Structure as Function of Time

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ABSTRACT

Microfibrillated cellulose (MFC) was studied in a series of stepped flow measurements with varying point times. The point time had a clear effect to measured viscosities indicating that the suspension was not in a steady state. Presence of multivalent ions increased the difference between the point times. A hysteresis loop in viscosity-shear rate curve was observed when the suspensions were measured from high to low shear rates and back.

INTRODUCTION

Rheological properties of microfibrillated cellulose (MFC) suspensions have been under attention in several papers from different points of view. Dry matter content[1-4], degree of fibrillation[5], suspension ionic strength[1, 5, 6] and the effect of various modifications to the cellulose surface[7], and the effect of polymers[8] have all been studied with regard to basic rheological response in steady shear and oscillatory measurements. Mechanisms for the observed shear thinning behavior in steady shear have been discussed and a general conception is shear thinning is due to changes in the (floc) structure as a function of shear rate[3, 9].Thixotropic nature of the material has also often been noted, but seldom discussed beyond stating the obvious: adaptation of the floc structure to prevailing shear conditions requires time.

In this work, we present how varying point time during stepped flow measurement (flow curve) is reflected in the shear stress / viscosity, and the observed floc structure. From our earlier studies[5,10] we know that in a flow curve measurement, changes in the floc structure correlate with a change in the measured shear stress. Starting at low shear rates, a plateau in shear stress is seen. In this region, interfloccular network has sufficient time to form new contacts while others are being broken down. At high shear rates, the shear stress is increasing as a function of shear rate, and the fibrils flow in individual, detached flocs. In between lies a transition region, where the flocculated networks rate of recovery is not sufficient to retain the homogeneous structure but large flocs start to separate from each other.

In addition to changes in the floc structure, wall depletion and shear banding may also play important roles in the observed rheological results. Our current imaging is done in 2D and does not yield direct information of floc structure in the radial direction of the cylindrical geometry. In the future, we will expand our structural analyses to 3D techniques coupled with radial velocity profiling. In the meanwhile, shear banding is discussed from modeling point of view in a separate paper by Mohtaschemi et al.[10].

MATERIALS AND METHODS

Materials

Microfibrillated cellulose (MFC) was prepared from never dried birch pulp by mechanical disintegration in Supermasscolloider (Masuko Sangyo). Some of the pulp was washed to sodium form prior to disintegration ("washed MFC"), and rest was used as such ("unwashed MFC"). Solid contents of the materials were 2% (w/w).

Rheological measurements

The measurements were done using a dynamic rotational rheometer (TA Instruments AR G2), with a standard metal concentric cylinders geometry (bob and cup radii 14 and 15 mm, respectively). Stepped flow measurements were measured from shear rate of 500 s^{-1} to 10^{-3} s^{-1} and back. The same measurement was performed with point times 60, 6, and 1 s. Before each stepped flow measurement, the sample was sheared 10 min at 500 s^{-1}. The point time 600 s was measured in similar manner but with a fresh sample. In the beginning and at the end, a time sweep was measured at 0.5% strain for 10 min to control possible changes in the sample during the measurement.

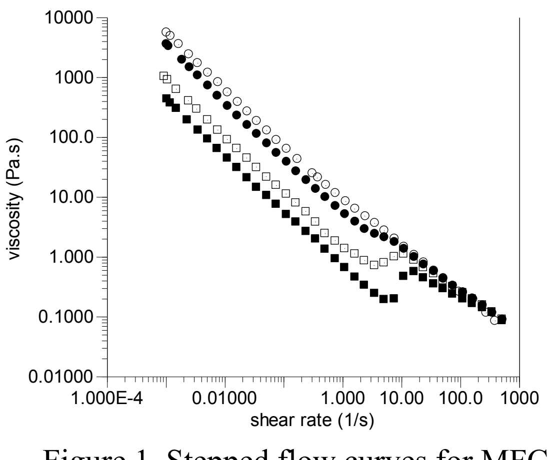

Figure 1. Stepped flow curves for MFC in process water and varying point times: 1 s (○), 6 s (●), 60 s (□), and 600 s (■). Measured from high to low shear rates.

RESULTS AND DISCUSSION

When unwashed MFC was measured in stepped flow measurement, the viscosity was drastically dependent on the point time at low shear rates (Fig. 1). The point time 1 s gave approximately 10 times higher viscosity than the point time 600 s. The same difference was observed for washed MFC but it was clearly smaller (Fig. 2). When MFC is washed to sodium form, all the counter ions on the fibers are changed to Na^{+} ion and there should not be any surplus ions present. Change of ions is performed prior to mechanical disintegration and it may also affect the grinding although significant differencies have not been observed. Without washing, MFC suspension contains multivalent ions that are present in tap water. This leads to the observed diffencenses in rheological behaviour between unwashed and washed samples originating in the mechanisms behind the repulsion between fibres. The repulsion is due to like electric charges on fiber surfaces[12]. The ions present in the suspending medium in unwashed MFC screen the charges allowing the fibrils to come closer to one another given enough time[12]. This facilitates stronger, longer

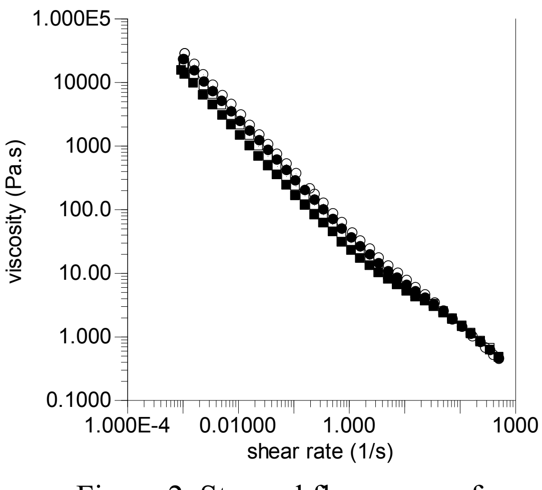

Figure 2. Stepped flow curves for washed MFC and varying point times: 1 s (○), 6 s (●), 60 s (□), and 600 s (■). Measured from high to low shear rates.

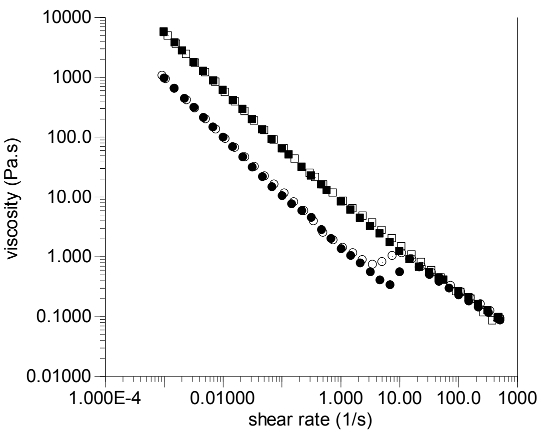

Figure 3. Stepped flow curves for MFC in process water with point time 1 s from shear rate 500 to 10^{-3} s^{-1} (○) and back (●), and with point time 60 s from shear rate 500 to 10^{-3} s^{-1} (□) and back (■).

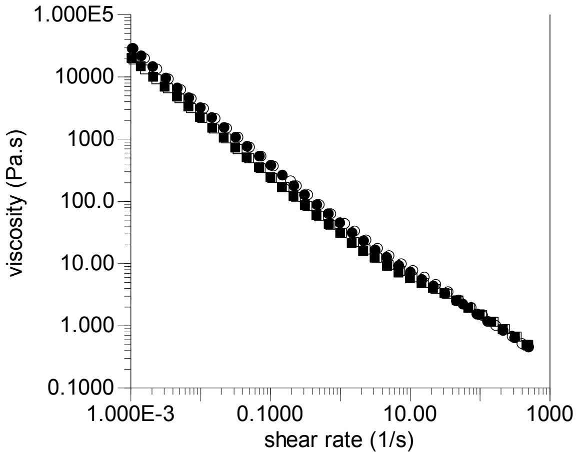

Figure 4. Stepped flow curves for washed MFC with point time 1 s from shear rate 500 to 10^{-3} s^{-1} (○) and back (●), and with point time 60 s from shear rate 500 to 10^{-3} s^{-1} (□) and back (■).

lasting contacts between the fibrils which equate to a more compact flocs in the network. The longer the suspension is sheared at low shear rates, the more time fibrils have to collide and form contacts and thus flocs, causing lower viscosity in Fig. 1.

Fig. 3 and 4 present the stepped flow measurements measured from high to low shear rate and back for washed and unwashed MFC. Hysteresis is clearly observed in the unwashed MFC suspension (Fig. 3) with point time 60 s but with shorter point time (1 s), the curves lie on top of each other (Fig. 4). For the washed MFC, hardly any hysteresis is detected at point times 1 or 60 s. This is in line with the results in Fig. 1 and 2 - it takes more energy (higher shear rate) for the flocs to come loose with higher ionic strength and longer point time.

CONCLUSIONS

Based on our findings, point time used in the characterization of MFC suspension bears great significance on the observed results. The effect is particularly evident when ions are present in the suspension medium. Ions screen the repulsive charges on fibre surface and thus allow fibres to come into closer contact increasing the probability for flocculation and increasing the friction between interfibrillar contact points. These factors cause denser flocs to appear with the higher ionic strength, unwashed sample at longer point times as seen from the lower viscosity and more pronounced hysteresis. In the future, we will further elaborate the relative contribution of shear banding, wall depletion and changes in the floc structure on the rheological response by means of radial velocity profiling and 3D structure imaging.

ACKNOWLEDGMENTS

This research is part of EffNet project established by the Finnish Forest Cluster.

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