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Extensional viscosity of microfibrillated cellulose suspensions

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ABSTRACT

The extensional properties of micro fibrillated cellulose (MFC)-suspensions at different fibril concentrations and with different amounts of added sodium chloride were evaluated. The MFC-suspensions were obtained by diluting a stock solution consisting of 0.95 wt.% cellulose with either deionized water or sodium chloride solution, giving a series of different concentrations and sodium chloride contents. The extensional viscosities of the suspensions were measured utilizing contraction flow geometry. Here the specimens were forced through a hyperbolic nozzle and the required pressure drop over the nozzle was measured. The extensional viscosity exhibited an extensional-thinning behaviour over the extensional strain rates used. Furthermore the extensional viscosity decreased with decreasing concentration of the suspensions, in similarities with the shear properties of the specimens. For the suspensions containing sodium chloride, the extensional viscosity appeared to increase when the concentration of sodium chloride was increased. But excessive amounts of added sodium chloride promoted an agglomeration of the suspensions.

1. Introduction

Extensional viscosity of fluids was first investigated by Trouton as early as 1906 but it was not until later the name extensional viscosity or elongational viscosity was coined. Extensional viscosity characterizes how a material (fluid) behaves when subjected to an extensional strain, for example when a fluid is pushed through a pipe contraction, or when it is used to coat a surface. Thus in a number of applications it is important to know the extensional properties of a given material. However, in contrast to conventional studies of the shear behaviour, there are fewer reports on the elongational deformation. The reason behind this is to some extent coupled to experimental difficulties. But since the extensional viscosity still is important in many situations, the extensional properties of several very different materials, such as polymer melts (Tzoganakis, Vlachopoulos, Hamielec, & Shinozaki, 1989) and food (Andersson, Öhgren, Johansson, Kniola, & Stading, 2011; Wikström & Bohlin, 1999a), have been investigated.

Depending on the type of material, different experimental methods have been employed for quantifying the extensional viscosity. For example, the filament stretching rheometer involves, as the name suggests, subjecting the material to an extensional strain and in order to obtain a constant extensional strain rate the distance between the clamps has to grow exponentially. With this method it is possible to measure the elongational properties of highly viscous samples such as polymer melts (Petrie, 2006). Spinline measurements can also be used to obtain extensional data, and the material in form of a fibre, is then drawn with a drum and the drawn profile of the material is captured by a camera. The required tensile force is measured and together with the captured shape the extensional viscosity can be evaluated (Ramanan, Bechtel, Gauri, Koelling, & Forest, 1997). Furthermore, contraction flow exerts extensional stress in a fluid by pushing it through a nozzle designed to give a constant extensional rate and by measuring the required pressure drop the extensional behaviour can be estimated (Wikström & Bohlin, 1999b). This is the method used in the present work.

The materials used here were suspensions of microfibrillated cellulose (MFC). There is an increasing interest in such suspensions which to some extent can be associated with the potentially very good mechanical properties of the fibrils (in the dry state) (Henriksson & Berglund, 2007; Iwamoto, Isogai, & Iwata, 2011; Walther, Timonen, Díez, Laukkanen, & Ikkala, 2011). Other possible applications involve transparent films and coatings with enhanced permeability properties (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009; Siró, Plackett, Hedenqvist, Ankerfors, & Lindström, 2011). To the authors' knowledge, the extensional properties of MFC-suspensions have not been reported on earlier.

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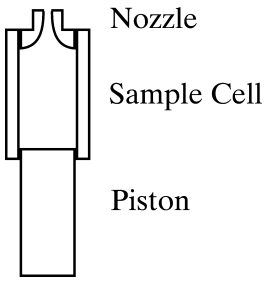

Fig. 1. Schematic picture of the experimental set-up used for measuring the extensional viscosity with a contraction flow. The piston at the bottom moves at a constant speed, pushing the sample in the sample cell through the hyperbolic nozzle where a force transducer measures the pressure drop over the nozzle.

2. Materials and methods

2.1. Materials

The micro-fibrillated cellulose (MFC)-suspensions were prepared by high-pressure homogenization of aqueous wood fibre suspensions and kindly supplied by Innventia AB, Sweden. The pulp was carboxymethylated before being passed through the high pressure homogenizer. Due to the carboxymethylation, the resulting fibrils were surface charged, corresponding to a substitution close to 0.1. The preparation and the properties of the MFC are described in more detail by Wågberg et al. (2008).

The homogenized suspensions were furthermore studied in cross-polarized light with an optical microscope. This revealed that there were still some unfibrillated cellulose fibres present, the largest was about 20 μm in diameter and 1 mm in length. Some agglomerates of microfibrils could also be distinguished. The amount of unfibrillated fibres and agglomerates was however considered to be quite low.

The initial MFC suspension had a cellulose content of 0.95 wt.% and a pH value of about 9.0. This starting MFC was used as a base for all other specimens. It was diluted to weight concentrations of 0.71 wt.% and 0.47 wt.% by adding deionized water to the suspension during sonication. In another series of experiment, a sodium chloride solution was added to the suspensions during mechanical stirring, giving a concentration of 0.71 wt.% MFC and final molarities of 0.005 M, 0.01 M or 0.02 M. The salt will screen the surface charges leading to a weaker repulsion between the individual fibrils in the suspension resulting in a stronger gel, as shown by Agoda-Tandjawa et al. (2010). At higher salt concentrations, the cellulose fibrils formed small agglomerates that did not break up during mixing; this was the reason for restricting the study to rather low salt concentrations.

2.2. Methods

The extensional viscosity was measured by using an contraction flow geometry (Wikström & Bohlin, 1999b). With this method, the sample is pushed through a contraction, and the sample will be subjected to an extensional strain. The experimental set-up is schematically shown in Fig. 1.

The sample cell is a metal cylinder where the sample initially is placed. At the top of the cell a nozzle is fastened and at the bottom there is a piston. The piston is moving at a constant speed pushing the material through the nozzle, and the required force (pressure drop over the nozzle) is measured with a force transducer. The extensional strain rate in the nozzle can be calculated from the volume flow rate, the nozzle geometry and the shear properties of the material as shown below. The profile of the nozzle has a hyperbolic shape in order to achieve a constant extensional strain along the length of the nozzle. This is the case assuming that the fluid is a power law fluid in shear (Wikström & Bohlin, 1999b). A power law fluid exhibits a shear viscosity described by $\eta_s = K\dot{\gamma}^{n-1}$ where η_s is the shear viscosity, $\dot{\gamma}$ is the shear rate and K and n are material parameters.

However the pressure drop over the nozzle cannot entirely be associated with the extensional deformation, there will also be shear flow present due to interactions with the wall of the nozzle (Wikström & Bohlin, 1999b). The contribution to the pressure drop from the shear flow can be calculated in the case of a power law fluid as

$$P_s = \frac{2H(3+1/n)^n(K/\pi)^n Q^n(1/r_0^{3n+1})2}{3n+3} \times \frac{(r_0^2/r_1^2)^{(3n+3)/2}-1}{(r_0^2/r_1^2)-1} \quad (1)$$

where H is the length of the nozzle, Q the volume flow rate of the fluid, r_0 is the entrance radius of the nozzle and r_1 its exit radius.

The material parameters are obtained from measurements of the shear viscosity as a function of strain rate. The shear contribution, Eq. (1), is then subtracted from the measured pressure drop giving the pressure losses associated with the elongational deformation.

The shear viscosity was measured with a ARES-G2 rheometer, TA Instruments, at shear rates from 0.1 s^{-1} up to 500 s^{-1} and at a temperature of 23 °C. A cone plate geometry with a diameter of 40 mm was used.

The extensional viscosity was measured at 23 °C with the set-up described earlier using three different speeds of the piston. The measurement was performed until the force reached a stable reading, and from each measurement two points on the stable plateau was chosen for calculating the extensional viscosity. This was repeated for at least three different runs with the same piston speed, and an average force value and standard deviations were calculated. The extensional strain rate was obtained from

$$\dot{\varepsilon} = \frac{2Q(3n+1/n+1)(1/r_i^2+1/r_o^2)}{2H\pi} \quad (2)$$

Here the volume flow rate, Q, is determined by the piston speed. The flow index n depends on the material, thus the extensional strain rate will differ somewhat between the samples. The extensional viscosity is then obtained as

$$\eta_e = \frac{P_m - P_s}{\dot{\varepsilon}} \quad (3)$$

where P_m is the measured pressure drop and P_s is the contribution from the shear, Eq. (1).

3. Results

The shear viscosity was, as already mentioned, measured at several shear rates in the region from 0.1 s^{-1} to 500 s^{-1}. The general trend for all samples was that the shear viscosity decreased with increasing shear rate, this was expected in view of earlier works (Agoda-Tandjawa et al., 2010; Iotti, Gregersen, Moe, & Lenes, 2010; Pääkkö et al., 2007). The coefficient of variation with regard to the viscosity was around 10%. Fig. 2 shows the shear viscosity as a function of the shear rate for MFC-suspensions with different concentrations of cellulose (no salt added).

From these measurements the consistency K and the flow index n can be evaluated for the different samples, see Table 1.

It is to be noted that the degree of shear-thinning (as given by the flow index n) decreased with decreasing concentration.

When adding sodium chloride to the MFC-suspensions the cellulose concentration was kept constant at 0.71 wt.%. This concentration was chosen since at lower cellulose concentrations agglomerates were more easily formed when adding the salt. The effect of sodium chloride on the shear viscosity is shown in Fig. 3.

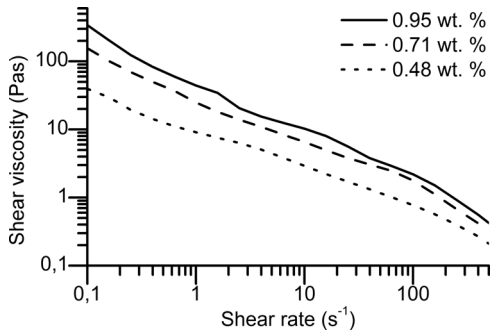

Fig. 2. The shear viscosity as a function of the shear rate for MFC-suspensions with weight concentrations of 0.48, 0.71 and 0.95 wt.%.

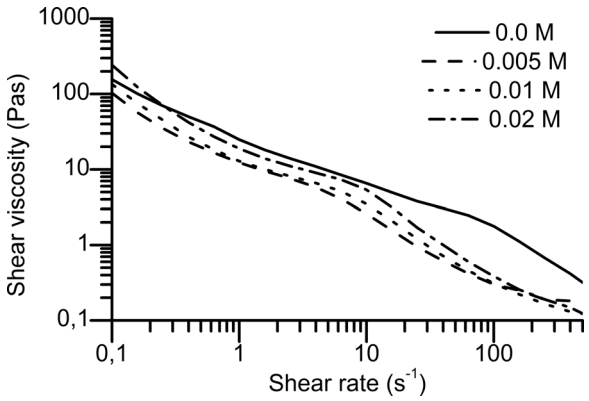

Fig. 3. The shear viscosity as a function of shear rate for different salt concentrations. The MFC concentration was 0.71 wt.%.

With the salt concentrations used, there was no strong effect on the shear viscosity. For the three samples with salt there was a trend towards increasing viscosity with increasing sodium chloride concentrations. It is to be expected that the viscosity increases with increasing salt concentration as shown by others (Agoda-Tandjawa et al., 2010; Lowys, Desbrières, & Rinaudo, 2001). This is believed to be due to that the sodium chloride screens the electrostatic repulsion between the fibrils and thus increase the fibril-fibril interactions associated with hydrogen bonds. Interestingly, the sample without any added salt had the highest viscosity at higher shear rates. In this case, this can be an effect of the preparation of the suspensions, since the non-salt-containing suspension was not processed in exactly the same way as the others. The power law provides no perfect description of the shear flow of the salt-containing suspensions, since there was a change in the slope of the curves at approximately 10 s^{-1}. The values for K and n given in Table 2 were calculated from the low shear rate region.

Table 1
Power-law parameters for MFC-suspensions.

Sample (wt.%)	K (Pa s^n)	n
0.95	49.0	0.30
0.71	28.6	0.37
0.48	9.9	0.45

Table 2
Power-law parameters for the salt-containing MFC-suspensions.

Sample (M)	K (Pa s^n)	n
0.0	28.6	0.37
0.005	14.1	0.27
0.01	16.4	0.23
0.02	24.2	0.18

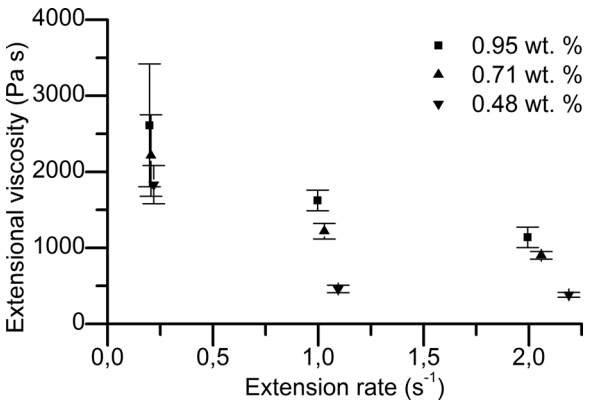

Fig. 4. The extensional viscosity as a function of the extensional strain rate. The bars indicate the standard deviations.

Summarizing, with higher amounts of added salt, the material became more viscous and the shear-thinning became more pronounced.

The extensional viscosity obtained from Eqs. (1)–(3) for the different samples without salt is shown in Fig. 4.

The extensional viscosity decreased with increasing extension rate, and it also decreased with decreasing MFC-concentration. For the lower concentrations, the difference between the viscosities at the two highest extension rates was quite small; this might indicate the appearance of a plateau level. Worth noting is that the extensional viscosity was much higher than the shear viscosity at all rates used here, i.e. the Trouton ratio was significantly higher than 3. The samples were allowed to recover for one minute between different applied extensional strain rates in order to minimize memory effects. These memory effects were observed as a non-zero load at the beginning of the measurement, but after one minute of recovery the load was negligible. Such effects were more pronounced at higher rates as a result of the higher stresses.

As shown in Fig. 5, the salt-containing specimens exhibited a higher extensional viscosity than the samples without any added salt at the lowest extensional strain rate. However, the former showed a more pronounced strain-thinning reversing the situation at higher strain rates. In this rate region, a higher salt concentration tended to yield a higher extensional viscosity, but the difference was actually quite small. In case of the highest salt concentration 0.02 M, a stable force reading was not obtained and the force readings increased with increasing time. These problems were possibly associated with a combination of fibril agglomeration (which was visible) and dewatering of the sample. The latter was evident as a pool of water was formed at the bottom of the piston during the measurements. The suspension was thus not homogenous.

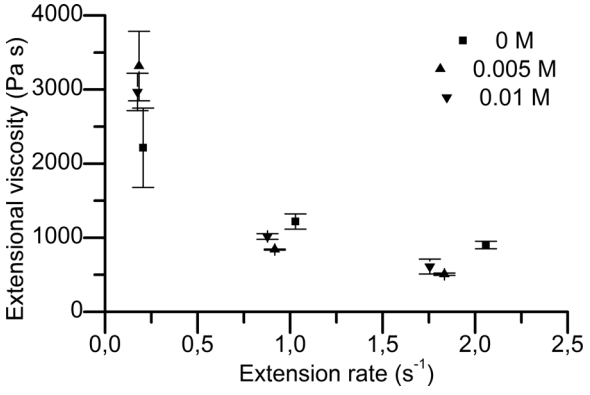

Fig. 5. The extensional viscosity as a function of the extensional strain rate for the MFC-suspensions when adding salt. The MFC concentration was 0.71 wt.%.

4. Discussion

It was demonstrated that the MFC-suspensions exhibited a rather high extensional viscosity which is coupled to the concentration of the fibrils. It is also clear that the suspensions were strain-thinning and that screening of the surface charges resulted in an increase of the extensional viscosity. The latter obviously is a result of the decreased repulsion between the fibrils possibly leading to a more enhanced entanglement of the fibrils and thus a higher viscosity, both in shear and in extension.

It may be remarked that it was quite difficult to determine η_e for MFC-suspension. An attempt to measure the elongational viscosity of MFC-suspensions based on fibrils produced using another technique, giving a lower surface charge, was less successful. These suspensions were somewhat more prone to aggregation and phase separation giving an unstable force measurement although they clearly exhibited an elongational viscosity.

It may be of interest to compare the magnitude of the extensional viscosity obtained here with results for other materials. Based on Cogswell's approach, polypropylene was found to exhibit an extensional viscosity in between 250 Pa s and up to 6000 Pa s at 230 °C depending on the molecular weight (Tzoganakis et al., 1989). The extensional rates were in this case in the region 50–250 s^{-1}. Polymer melts of low density polyethylene had an extensional viscosity of around 9000 Pa s at a temperature of 220 °C (Toft & Rigdahl, 2002). These results were also based on Cogswell analysis and obtained at extensional strain rates between 30 and 200 s^{-1}. Both mentioned studies thus employed extensional strain rates that were higher than used here for the MFC-suspensions but the values of the extensional viscosities were of the same order of magnitude. Measurements using almost the same strain rates as in this work have been performed on doughs (Andersson et al., 2011). These were performed on wheat dough and zein-starch dough with a hyperbolic contraction flow at 40 °C. These materials exhibited an extensional-thinning behaviour and the extensional viscosity at strain rates of 1 s^{-1} was about 70 Pa s for the wheat dough and 200 Pa s for the zein-starch dough. The viscosities of these doughs were thus about 5 times lower than that of the MFC-suspensions.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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References

Agoda-Tandjawa, G., Durand, S., Berot, S., Blassel, C., Gaillard, C., Garnier, C., et al. (2010). Rheological characterization of microfibrillated cellulose suspensions after freezing. *Carbohydrate Polymers*, *80*(3), 677–686. http://dx.doi.org/10.1016/j.carbpol.2009.11.045

Andersson, H., Öhgren, C., Johansson, D., Kniola, M., & Stading, M. (2011). Extensional flow, viscoelasticity and baking performance of gluten-free zein-starch doughs supplemented with hydrocolloids. *Food Hydrocolloids*, *25*(6), 1587–1595. http://dx.doi.org/10.1016/j.foodhyd.2010.11.028

Fukuzumi, H., Saito, T., Iwata, T., Kumamoto, Y., & Isogai, A. (2009). Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. *Biomacromolecules*, *10*(1), 162–165. http://dx.doi.org/10.1021/bm801065u

Henriksson, M., & Berglund, L. A. (2007). Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. *Journal of Applied Polymer Science*, *106*(4), 2817–2824.

Iotti, M., Gregersen, Ø. W., Moe, S., & Lenes, M. (2010). Rheological studies of microfibrillar cellulose water dispersions. *Journal of Polymers and the Environment*, *19*, 137–145. http://dx.doi.org/10.1007/s10924-010-0248-2

Iwamoto, S., Isogai, A., & Iwata, T. (2011). Structure and mechanical properties of wet-spun fibers made from natural cellulose nanofibers. *Biomacromolecules*, *12*(3), 831–836. http://dx.doi.org/10.1021/bm101510r

Lowys, M.-P., Desbrières, J., & Rinaudo, M. (2001). Rheological characterization of cellulosic microfibril suspensions. Role of polymeric additives. *Food Hydrocolloids*, *15*(1), 25–32. http://dx.doi.org/10.1016/S0268-005X(00)00046-1

Petrie, C. J. S. (2006). Extensional viscosity: A critical discussion. *Journal of Non-Newtonian Fluid Mechanics*, *137*(1–3), 15–23. http://dx.doi.org/10.1016/j.jnnfm.2006.01.011

Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., et al. (2007). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*, *8*(6), 1934–1941. http://dx.doi.org/10.1021/bm061215p

Ramanan, V. V., Bechtel, S. E., Gauri, V., Koelling, K. W., & Forest, M. G. (1997). Exploiting accurate spinline measurements for elongational material characterization. *Journal of Rheology*, *41*(2), 283–306. http://dx.doi.org/10.1122/1.550856

Siró, I., Plackett, D., Hedenqvist, M., Ankerfors, M., & Lindström, T. (2011). Highly transparent films from carboxymethylated microfibrillated cellulose: The effect of multiple homogenization steps on key properties. *Journal of Applied Polymer Science*, *119*(5), 2652–2660.

Toft, N., & Rigdahl, M. (2002). Extrusion coating with metallocene-catalysed polyethylenes. *International Polymer Processing*, *17*(3), 244–253.

Trouton, F. T. (1906). On the coefficient of viscous traction and its relation to that of viscosity. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, *77*(519), 426–440. http://dx.doi.org/10.1098/rspa.1906.0038

Tzoganakis, C., Vlachopoulos, J., Hamielec, A. E., & Shinozaki, D. M. (1989). Effect of molecular weight distribution on the rheological and mechanical properties of polypropylene. *Polymer Engineering & Science*, *29*(6), 390–396. http://dx.doi.org/10.1002/pen.760290607

Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M., & Axnas, K. (2008). The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir*, *24*(3), 784–795. http://dx.doi.org/10.1021/la702481v

Walther, A., Timonen, J. V. I., Díez, I., Laukkanen, A., & Ikkala, O. (2011). Multifunctional high-performance biofibers based on wet-extrusion of renewable native cellulose nanofibrils. *Advanced Materials*, *23*(26), 2924–2928. http://dx.doi.org/10.1002/adma.201100580

Wikström, K., & Bohlin, L. (1999a). Extensional flow studies of wheat flour dough. II. Experimental method for measurements in constant extension rate squeezing flow and application to flours varying in breadmaking performance. *Journal of Cereal Science*, *29*(3), 227–234. http://dx.doi.org/10.1006/jcrs.1999.0252

Wikström, K., & Bohlin, L. (1999b). Extensional flow studies of wheat flour dough. I. Experimental method for measurements in contraction flow geometry and application to flours varying in breadmaking performance. *Journal of Cereal Science*, *29*(3), 217–226. http://dx.doi.org/10.1006/jcrs.1999.0251