Rheological Study of Microfibrillar Cellulose and Dynamic Mechanical Analysis of Paper Sheet

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ABSTRACT

Rheological study of microfibrillar cellulose suspension and dynamic mechanical analysis of paper sheet were done. Different polymers were used as strengthening agents in model suspensions containing MFC. Dynamic mechanical behaviour of paper sheet could be predicted from viscoelastic behaviour.

INTRODUCTION

The purpose of the study is to present a new way to consider paper wet strength and evaluate if rotational rheometry could be used as a simple tool to predict which polymers would be suitable as wet strength agents. To be able to predict wet strength properties, it is important to know how polymers behave in dilute suspensions. Microfibrillar cellulose (MFC) was chosen to be studied in this study. Surface of wood fiber consists of microfibrillar part, which MFC represents. MFC is relative homogeneous compared to wood fiber and suitable for rheological studies in dilute suspensions.

This study consists of two parts. The main part is extensive rheological study. The other part is dynamic mechanical analysis, where we compare viscoelastic properties of the microfibrillar cellulose with different polymers in water suspensions and dynamic mechanical properties of the paper sheets prepares from wood fibre and polymer. The purpose of the study is also to predict how rheological properties of a suspension correlate to dynamic mechanical properties.

EXPERIMENTAL

Materials

In this study, four different polymers were studied: Cationic starch (CS), cationic polyacrylamide (CPAM), carboxymethyl cellulose (CMC) and poly(ethylene oxide). Suspensions for rheological measurements were prepared by mixing 1% solutions of MFC and polymer. Solutions were done in water containing $NaHCO_3$. Paper sheets for DMA measurements were prepared in lab scale as manual sheets. Polymers above were used as additive in suspending water of fibre mass.

Rheological measurement

Viscoelastic properties of suspensions of MFC and polymer were measured with stress controlled rotational rheometry (Rheometric Scientific). Measuring geometry used was bob and cup geometry. Two runs were performed: steady and dynamic shear stresses. Stress sweeps were run from 0.02 Pa up to 10 Pa and dynamic run was done at 1 Hz. Focus in data analysis was in viscocity and moduli.

Dynamic mechanical analysis

DMA measurements were done with TA Instruments DMA Q800 equipment. The maximum force was 18 N and maximum frequency 200 Hz. Cooling of the equipment was done with liquid nitrogen. The measurements were done in ambient pressure using Film/Tension measuring head. Stress sweep of the samples were done between 0 and 30 MPa or until they broke down. Frequency used was 1 Hz. Dimensions of the samples were w * t * l = 3 mm * (0.12 – 0.17) mm * (11.8 – 17.6) mm. Length was measured automatically by the equipment, whereas other dimensions were measured manually before each run.

Humidity of the measuring chamber was stabilized with external humidity element connected with the measuring chamber (Kep Technologies Wetsys Setaram Instrumentation). The samples were stabilized for 30 min. Stabilization time was adjusted so that time required was enough to get stabile humidity content in the sample. Targeted humidity levels were 10, 40 and 70 % relative humidity. Measurements were carried out at three different temperatures, 30, 50 and 70 ºC, except at highest humidity content at highest temperature, where stabile atmosphere could not be reached and humidity had tendency to concentrate on the walls of the chamber.

RESULTS AND DISCUSSION

Rotation Rheometry

MFC has gel like properties[1] over the whole region of tested frequencies inside the linear viscoelastic region (LVE) and when concentration is high enough. MFC is gel like system even at very low concentrations, 0.125 mass-%. That means that MFC itself is strongly yielding material. This study does not concentrate only on linearly viscoelastic region. Focus is rather on yielding behaviour and in sensitivity to changes under stress.

Relative viscosity of the suspension is determined by the ratio between viscosities of matrix solution and fiber suspension in matrix. It has typically been used to describe interaction between fibers usually in some polymeric matrix.[2] In this study it is used as a tool to study how different polymeric matrices affect viscosity of MFC suspension. In this study, relative viscosity is determined in Eq. 1.

$$\eta_{rel} = \frac{\eta_{susp}}{\eta_{sol}} \tag{1}$$

where *susp* consists of 0.5 % polymer + 0.5 % MFC and *sol* 0.5 % polymer solution.

Relative viscosity of four different polymers is presented in Fig. 1. Salt level in water environment is stabilized, because salt affects rheological properties of both cellulose and water soluble polymers.

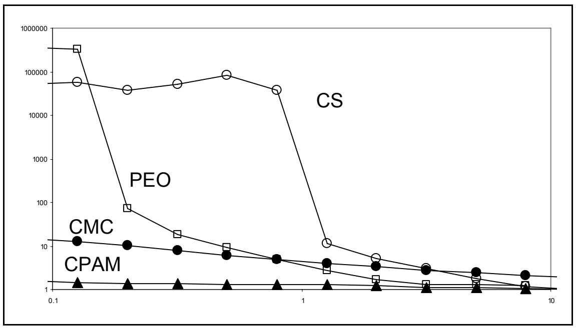

Figure 1. Relative viscosity of MFC suspension at 0.5 mmol salt level.

It can clearly be seen in Fig.1 that MFC suspensions with CMC follows viscosity of CMC, and strongly shear thinning behaviour of MFC disappears. Also PEO decreases yielding tendency, but relative viscosity remains quite low. CS and CPAM maintain strongly yielding character of the suspensions. It is also remarkable that relative viscosity is about 1 at high shear stresses. That means that adding fiber to the suspension, viscosity does not increase at all. The reason may be that suspension becomes more unstable and the organized structure breaks down.

Yielding properties of MFC suspensions can be seen in dynamic stress sweep at 1 rad/s in Fig. 2. Behaviour of the materials in dynamic stress sweep varied a lot depending on the polymer. It can be seen how strongly yielding material pure MFC is, but when a polymer is added, yielding behaviour of the suspension changes dramatically depending on the associating polymer. PEO compatibilization leads to most strongly yielding polymer suspension.

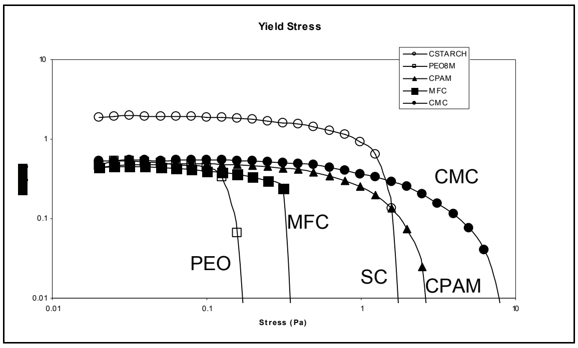

Figure 2. Yielding behaviour of the MFC suspension at 0.5 mmol salt level.

Tan delta values in Fig. 3 also show the evidence how differently suspensions are stabilized depending on the associating polymer. Tan delta of MFC is smaller tan 1 over the whole LVE region. However, it can clearly be seen, that MFC soon looses its properties when stress is applied. Viscotic properties of CMC and CPAM are dominant over the whole region. CMC stands most stress of all of the materials. Elastic properties are dominant in SC suspensions, but it is also strongly yielding material, like pure MFC.

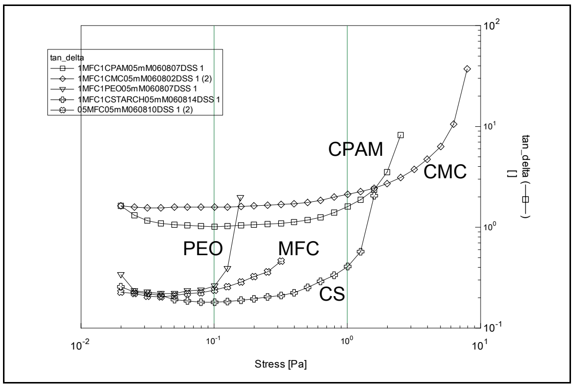

Figure 3. Tan delta of MFC suspension at 0.5 mmol salt level.

Focus in literature has been in elasticity. However, comparison between CStarch and CMC shows that the situation is much more complicated than that. It can be seen that starch has very high elasticity module even though its yield stress is lower than CMC:s. CMC seems to change rheological behaviour of MFC suspension toward more viscous direction. The same phenomena can be realized also when CPAM is added, even though not as strong. Cationic starch seems again to have a completely different effect. It strengthens MFC suspension, but it remains still strongly shear thinning. That means, that it maintains gel-like behaviour of MFC.

<u>Dynamic Mechanical Analysis</u>

Two of the polymers, CS and CMC, were chosen to DMA studies due to their different viscoelastic behaviour. Fig. 4 shows stress-strain behaviour of these materials in DMA. Measurements were done with three different relative humidity levels, 10, 40 and 70%. Both of the materials weaken when humidity is increased. Weakening is not the most important phenomena observed since it has widely been studied[3] but the profile of the curves. CMC seems to strengthen under implied stress which is not seen with CS. This effect is seen more clearly at higher humidity contents. This phenomenon is further evidence for the viscotic nature of

CMC that could already be seen in rheological study.

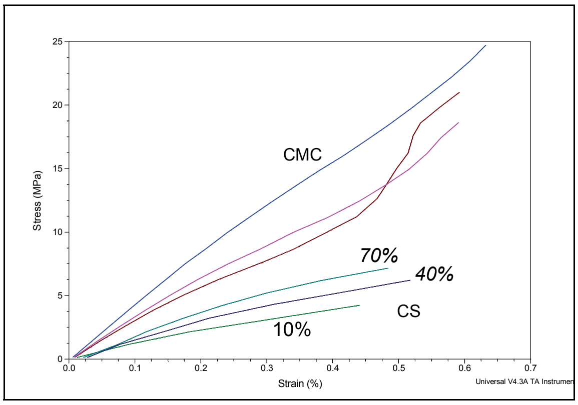

Figure 4. Stress-Strain behaviour of CS and CMC with different humidity levels at 30 ºC. Humidity levels are 10, 40 and 70 % of relative humidity.

CONCLUSION

MFC is very elastic, but outside the LVE linear viscoelastic region it is strongly yielding. Adding polymer into a MFC suspension changed yielding behaviour of MFC by bringing viscotic nature to the suspension. Carboxymethyl cellulose (CMC) had most significant effect whereas cationic starch did not increase elasticity very much. Behaviour of these polymers as strengthening agents in paper sheets in DMA corresponded to their rheological behaviour. Viscosity of CMC was seen as strain hardening behaviour of paper sheet in oscillating tensile measurement of DMA.

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