On the Viscoelastic Properties of Microfibrillated Cellulose (MFC) Suspensions

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ABSTRACT

In this work the viscoelastic properties of microfibrillated cellulose (MFC) suspensions have been studied. Three different types of MFC were here used. Two of these were prepared by subjecting wood pulp to an enzymatic treatment and subsequently a homogenization, performed by passing the pulp through a high pressure fluidizer. These two MFC suspensions differed by the number of passes used in the homogenization step; one pass or five passes. The third suspension was prepared in a similar way but instead of treating it with enzymes this pulp was carboxymethylated, and then homogenized one time, using the same method as described above. The concentration of the final suspension was kept at 2 %.

The viscoelastic characterization of the MFC -suspensions was carried out using a dynamic stress rheometer. The rheological measurements showed that the enzymatically treated sample subjected to only one homogenization step exhibited the lowest shear storage modulus of the three, almost three times lower than the two other. This suspension had also the lowest critical stress, marking the onset of non-linear behaviour. The frequency dependence of the storage modulus was quite insignificant in the frequency range covered indicating a network structure in all the suspensions. The creep-recovery measurements showed a large increase in strain when an external stress was applied to the sample corresponding to an elastic response, after this first elastic deformation a viscous "flow" took place. When the stress was released then some of the strain was recovered but not all, implying that the material cannot recover totally after being subjected to stress. Further differences in the creep behaviour between the suspensions are described.

INTRODUCTION

During recent years the interest in microfibrillar cellulose (MFC) has increased quite dramatically. As a starting point of the interest the work performed by ITT Rayonier[1,2] is often referred to. When producing MFC, a homogenization treatment is often employed in order to disintegrate or delaminate cellulose fibrils from the cell wall[3,4]. It has been pointed to that an enzymatic pretreatment can greatly reduce the required energy consumption during this processing[3,5]. Carboxymethylation is reported to have a similar effect[4,5]. There are certainly a vast number of publications dealing with properties and production of MFC and a significant part of the interest stems from the potentially very good mechanical properties of the fibrils (in the dry state)[6–8]. As examples of products or applications (mainly on a laboratory scale) could be mentioned the use of MFC and similar materials as reinforcing elements in composites[5,6], forming of nanopaper with high toughness[9], for transparent films[10,11] and for coatings/films with good permeability properties[10–12].

It is well known that a MFC-suspension can form a gel-like structure, even at low concentrations, and that its rheological behaviour can be quite complex. Generally, these suspensions exhibit a shear-thinning behaviour, at least at not too high shear rates, and the viscosity increases with increasing concentration of MFC[3,13–15]. At very high shear rates (> 105 s^{-1}), however, a dilatant behaviour has been reported[15] as well as hysteresis effects[15] and a transition region[14] (at lower shear rates) in the viscosity-strain rate relations. A transition region of this kind can possibly be associated with a change in flow structure of the suspensions[14]. It has also been shown that additives, for example salt, carboxymethylcellulose, cationic starch and polymethacrylates, can influence the viscosity of the MFC-suspensions[13,14]. As shown in several publications, MFC-suspensions are not only viscous, but also exhibit elastic characteristics (which is not surprising in view of their gel-like behaviour). The storage modulus G' (as determined from dynamic mechanical measurements) is not appreciably affected by the frequency (at least in the lower end of the frequency region) which is to be associated with its network (or gel-like) structure consisting of entangled fibrils[3,14]. The magnitude of the storage modulus can be affected by additives as shown by Karppinen et al.[14]. Measurements of the storage modulus as a function of the stress (or strain) amplitude provide information on the extent of the linear viscoelastic region. Exceeding a critical stress (or strain) amplitude then will result in a decrease of the storage modulus[13], which can be interpreted as a break-down of the network structure. The storage modulus of cellulosic microfibril networks also appears to be rather insensitive towards moderate changes in temperature[3,16], which would point to a rubber-elastic behaviour. It may also be noted that Hill[17] could reasonable well describe the concentration behaviour of the storage modulus using a scaling theory.

In this work, the viscoelastic properties of two different types of MFC are compared, one based on a pulp that was enzymatically treated before the homogenization and the other subjected to carboxymethylization before the disintegration. The interest is focused on the strength of the network as revealed by dynamic mechanical measurements and the creep behaviour of the suspensions.

MATERIALS

As already mentioned, microfibrillated cellulose (MFC) is prepared by high-pressure homogenization of aqueous wood fibre suspensions. Two different types of MFC-suspensions were used in the present case, both based on bleached sulphite-softwood-dissolving pulp (Domsjö Fabriker AB, Sweden). The first one, denoted MFC 1, was obtained by beating the pulp, followed by an enzymatic treatment and then beating again before being passed through the homogenisator. The width of the fibrils was typically of the order of 20 nm and the surface charge of the fibrils was relatively low. The suspensions were either passed once or five times through the homogenisator (fluidizer), denoted MFC 1:1 and MFC 1:5, respectively. The detailed procedure for preparing MFC 1 as well as its characteristics is described in the article of Pääkkö et al.[3]. The second type of MFC, denoted MFC 2, was carboxymethylated before the homogenization step. Here only one pass through the fluidizer was used. Due to carboxylation, the resulting fibrils were surface charged, corresponding to a degree of substitution close to 0.1. These fibrils were somewhat thinner than MFC 1, about 5-10 nm. The preparation of MFC 2 and its properties are described in detail in the article of Wågberg et al.[4]. The weight concentration of the cellulose was 2 % for all three suspensions. The prepared MFC suspensions were kindly supplied by Innventia AB, Sweden.

EXPERIMENTAL

Optical microscopy

The three different materials were examined in a stereo microscope (Zeiss, Discovery V20). The measurements were performed by viewing the samples squeezed between two slides of glass.

In the samples that were subjected to only one homogenization step, some less defibrillated fibres could be seen. With five passes through the fluidizer, the further defibrillation led to a significantly enhanced homogeneity of the suspension Fig. 1 shows an optical micrograph of the MFC 1:5 suspension.

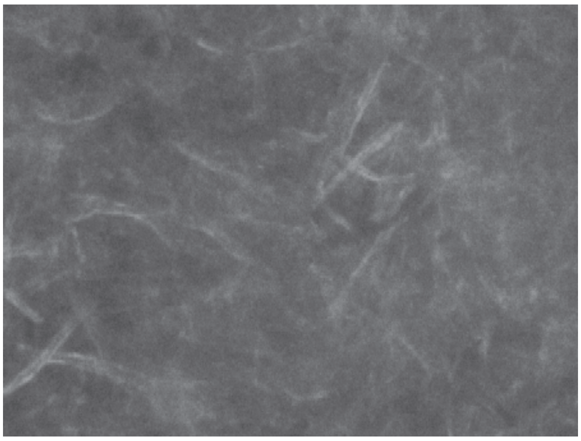

Figure 1. Optical micrograph of the 2 % MFC 1:5 suspension. Magnification 150X.

Dynamic-mechanical analysis

The dynamic-mechanical properties of the suspensions were measured with a controlled stress rheometer (Rheometrics Inc., DSR) at 25°C using a cone-plate configuration. A cone-and plate geometry was chosen with the diameter 25 mm, cone angle 0.1 radians and a gap distance of 58 μm. The linear viscoelastic region of the MFC suspensions was determined from dynamic stress sweep tests performed at a frequency of 1 Hz. The storage modulus was followed as function of the applied stress; the lowest shear stress being 0.5 Pa. The upper stress level used depended on the suspension studied, but could be up to 100 Pa or more Pa. To determine the onset of non-linearity was obtained by finding for what stress the storage modulus was 90% of the maximum storage modulus for the sample.

The frequency dependence of the viscoelastic parameter was determined at 25° C in the frequency range 0.1 to 10 Hz. The applied stress was set to 5 Pa, which is within the linear range for all the suspensions.

Creep and recovery of the suspensions

The creep behavior of the suspensions was measured with the same rheometer as given above and at the same temperature. A constant shear stress was applied to the specimen for 200 seconds (in some cases the loading time was extended to 1000 s). After this time, the stress was removed and the recovery of the strain followed as a function of time. The creep-recovery experiments were performed with different applied shear stresses.

RESULTS AND DISCUSSION

Linear and non-linear behaviour

Fig. 2 shows the shear storage modulus G' at 1 Hz as a function of the applied stress for one measurement on MFC 1:1 (one pass through the fluidizer). The onset of non-linearity is revealed as a clear decrease of the modulus as the applied stress increases. In the case of MFC 1:1, the corresponding stress was quite low; calculated to be around 10 Pa (using the 90 % rule) using the method described earlier. This value can be regarded as a critical stress. Exceeding above this value disrupts the network or gel structure of the suspension. The decrease in modulus above the critical stress is quite rapid indicating a quick and rather complete rupture of the structure. At lower stress levels, i. e. in the linear viscoelastic region, the storage modulus is of the order of 1000 Pa.

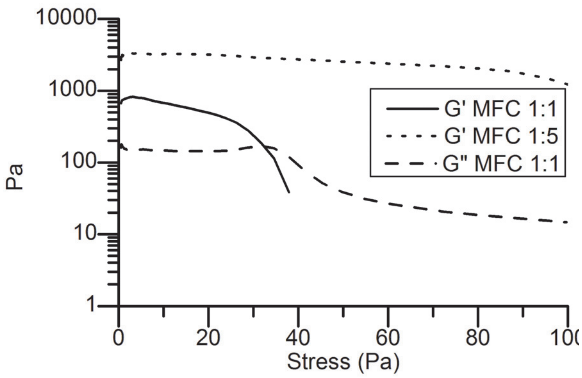

Figure 2. The storage shear modulus *G'* at 1 Hz for MFC 1:1 and MFC 1:5 as a function of the applied shear stress. The stress dependence of the loss shear modulus *G"* for MFC 1:1 is also included.

Fig. 2 also includes the corresponding curve in case of MFC 1:5 (five passes through the homogenizator). The improved homogenization obviously had quite a drastic effect on the mechanical behavior of the suspensions. The critical shear stress is now measured to be around 30 Pa, which is at least three times higher than that of MFC 1:1. The network or gel structure becomes obviously stronger with increasing number of passes through the fluidizer. The degree of fibrillation is improved, and the structure more homogeneous with less fibre fragments, and well-connected. This can also be seen in the images taken with the optical microscope; these indicate a more homogeneous structure of MFC 1:5 compared to that of MFC 1:1. The stronger network structure, as reflected in the higher critical stress, also corresponds to an increase of the stiffness in the linear region. The shear storage modulus in that region is approximately 3000 Pa for MFC 1:5. The decrease in modulus with increasing applied stress is furthermore not as dramatic as in the case of MFC 1:1. Included in Fig. 1 is also the loss shear modulus *G"* for MFC 1:1. There was a gradual and rather slight decrease in the loss modulus in the low stress region and here the loss modulus was lower than the storage modulus. There was also a slight increase in *G"* in the vicinity of the stress level where the storage modulus decreased steeply. If the viscoelastic behaviour would be depicted in terms of the mechanical loss factor tan δ, the behaviour shown in Fig. 2, would correspond to an increase of tan δ at higher applied stresses. Such a behaviour has been reported for other types of suspensions as well. Up to the critical stress *G'* is always larger than *G"* pointing to that the suspensions exhibit primarily an elastic character rather than a viscous one.

The carboxylated grade MFC 2 exhibited a behaviour which was intermediate between those of the two other grades (see Fig. 3).

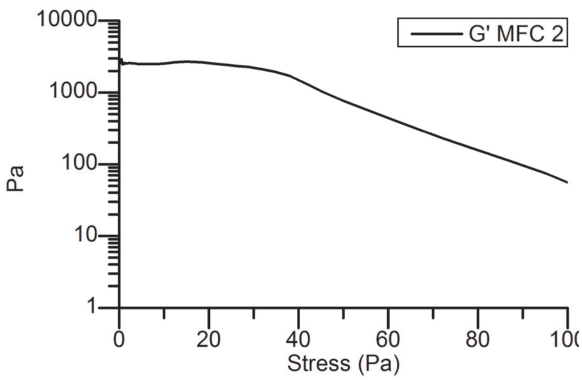

Figure 3. The storage shear modulus *G'* at 1 Hz for MFC 2 as a function of the applied shear stress.

The shear storage modulus in the viscoelastic region was of the order of 3000 Pa whereas the critical stress for onset of non-linearity was relatively low being around 20 Pa. The decrease in *G'* with increasing applied stress above the critical stress value is not as marked as that in case of MFC 1:1, but it is more pronounced than noted for MFC 1:5.

The steeper decrease for MFC 2 compared to MFC 1:5 might be that the strength in MFC 1:5 comes from the many microfibrils that has been liberated from the larger cellulose fibre, and these forms a network that gives the suspension its strength, in the MFC 2 the surface of the fibrils are charged and this charge may prevent the fibrils from coming in closer contact with each other, they might instead form an entangled network that is more easily destroyed than the network in MFC 1:5. This is in line with that the MFC 1:5 appeared to be more fibrillated than MFC 2 when examined through a microscope.

Frequency sweep

For all the three different MFC-suspensions, the frequency dependence of the storage modulus was quite weak over the range of frequencies used here. This is shown in Fig. 4 in case of MFC 2. The modulus only exhibited a minor increase as the frequency was raised, i. e. *G'* attains more or less a plateau value. This indicates that a network structure was formed in the suspension. The only difference between the suspensions is the magnitude of the modulus, which was already discussed in conjunction with the stress sweep measurements above.

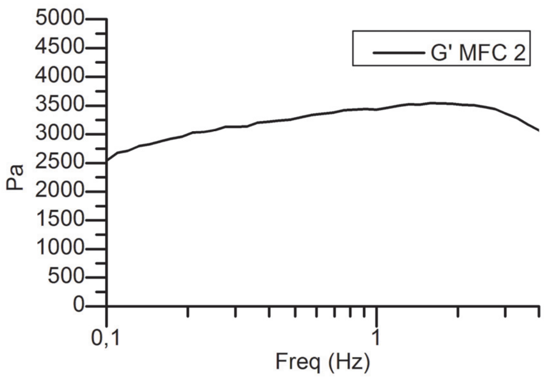

Figure 4. The shear storage modulus *G'* as a function of the frequency for MFC 2.

Fig. 5 shows the absolute value of the complex viscosity $|\eta^*|$ as a function of the angular frequency ω in case of MFC 1:5. The complex viscosity decreases strongly with increasing frequency and the slope of the line in the double logarithmic plot is close to -1. This indicates that the suspensions have a yield stress in shear corresponding to the plateau value of *G'* shown in Fig. 4.

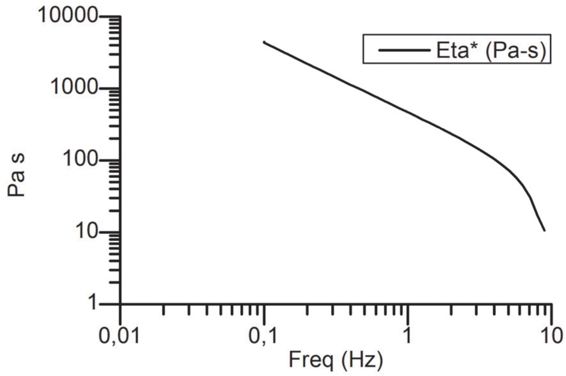

Figure 5. The complex viscosity as a function of the angular frequency, for MFC 1:5 in a double logarithmic plot.

Creep and recovery

The creep-recovery measurements show an initial elastic response when applying the stress and followed by a slower viscous response. An example is shown in Fig. 6 in the case of MFC 2. Here the stress (15 Pa) was applied for 200 seconds, then removed and the strain was allowed to recover.

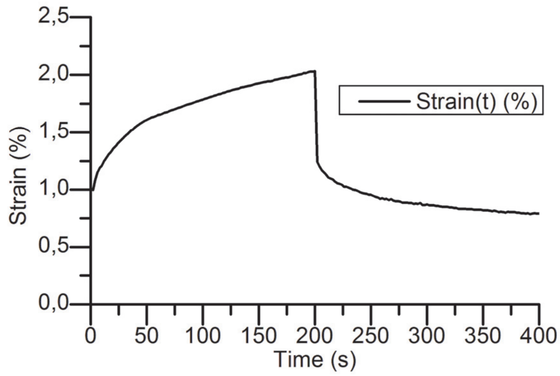

Figure 6. Creep and recovery of MFC 2. The applied stress was 15 Pa which is in the linear viscoelastic region according to the earlier measurement.

The experiments performed within the frames of this study do not indicate that the creep deformation will fully recover when releasing the load. Furthermore, the strain during the creep stage does not seem to approach any plateau value where the material seizes to creep; there is only a monotonous increase in the deformation, i.e. the material “flows”. This is even more noticeable when extending the creep time to 1000 seconds as shown in Fig. 7 in the case of MFC 1:5 with an applied stress of 15 Pa. After the initial deformation, there was an almost linear increase in strain with increasing time, the slope being of the order of $4 \cdot 10^{-4}$ s^{-1}.

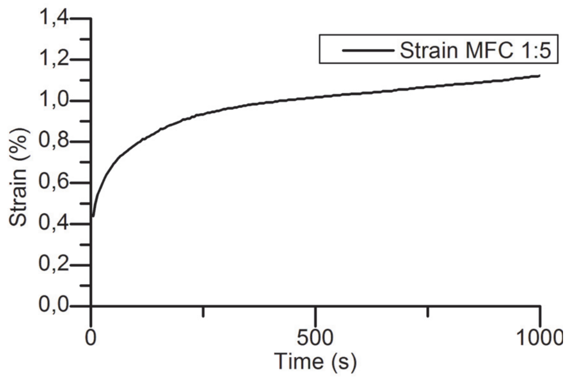

Figure 7. Creep of MFC 1:5 during 1000 seconds when a stress of 15 Pa was applied.

The above observations indicate that it may not be straightforward to describe the creep behaviour using simple viscoelastic models. In fact, attempts to fit the deformation behaviour to a standard linear solid model were unsuccessful, even at shorter creep times. Probably a Burger model would be more suitable at the price of introducing more fitting parameters.

The viscoelastic character of the suspensions can be further investigated by evaluating the creep compliance *J(t),* i.e. the strain divided by the stress, at different applied stress values. This is shown in Fig. 8 for MFC 1:1. In the stress range 1-10 Pa the compliance is fairly independent of the applied stress (recognising the somewhat inhomogeneous character of the suspensions), whereas *J(t)* is markedly higher when applying a stress of 15 Pa, i.e. a non-linear behaviour is observed at higher stress levels. This is also in good agreement with the critical stress determined from the stress sweep measurements described earlier.

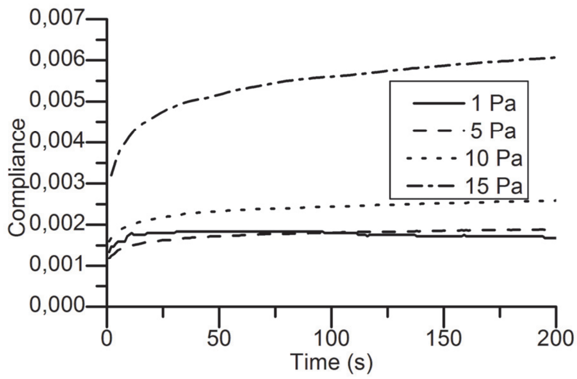

Figure 8. The compliance for MFC 1:1 for four different applied stresses.

Fig. 9 compares the creep strain of the three suspensions used in this study. The applied stress was 5 Pa which is within the linear viscoelastic range for all materials according to the stress sweep experiments. Obviously the deformation of MFC 1:1 was significantly larger than that of the other suspensions which is in line with its lower storage modulus.

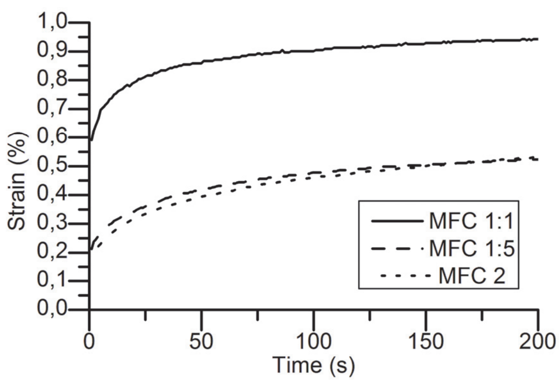

Figure 9. Creep deformation of the three suspensions at an applied stress of 5 Pa.

If a too high stress is applied to the specimen, the network structure will be more or less completely destroyed (combined with a loss of contact with the cone in the rheometer) and an excessive deformation will result as shown in Fig. 10.

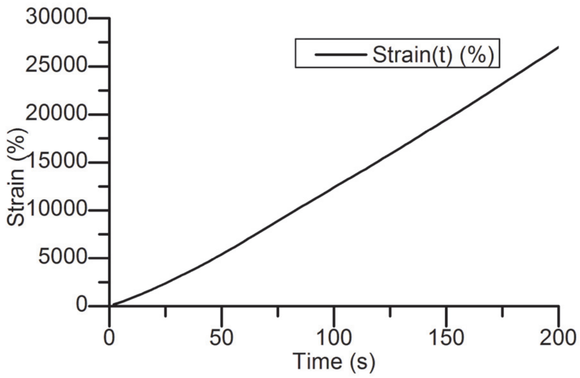

Figure 10. Creep for MFC 2 during 200 seconds at an applied stress of 55 Pa. Here the strain is almost linear with the time.

Here it can be noted that derivative of the creep curve actually was lower in the earlier part of the curve than at longer times.

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