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ORIGINAL PAPER

Carboxymethylated nanofibrillated cellulose: rheological studies

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Abstract The rheological properties of carboxymethylated nanofibrillated cellulose (NFC), investigated with controlled shear rate- and oscillatory measurements, are reported for the first time. It was shown that the rheological properties of the studied system are similar to those reported for other NFC systems. The carboxymethylated NFC systems showed among other things high elasticity and a shear thinning behaviour when subjected to increasing shear rates. Further, the shear viscosity and storage modulus of the system displayed power-law relations with respect to the dry content of the NFC suspension. The exponential values, 2 and 2.4 respectively, were found to be in good agreement with both theoretical predictions and published experimental work. Furthermore, it was found that the pulp consistency at which NFC is produced affects the properties of the system. The rheological studies imply that there exists a critical pulp concentration below which the efficiency of the delamination process diminishes; the same adverse effect is also observed when the critical concentration is significantly exceeded due to a lower energy input during delamination.

Keywords Nanofibrillated cellulose · Carboxymethylation · Gel · Rheology · Viscosity · Homogenization

Introduction

In recent decades, the interest in nanoscaled materials has surged, and numerous applications have been investigated in laboratories around the world. Among these materials, nanocellulose stands out as being a cheap, renewable, biodegradable, and sustainable material made from cellulose, presumably the most abundant biomaterial on earth. Potential applications of nanocellulose range from large-scale papermaking applications (as a dry strength agent and in sizing and coating formulations), food and emulsion/dispersion applications, various nanocomposite materials, and medical/pharmaceutical/cosmetic and hygienic applications, to applications in flexible electronics, to mention but a few application areas. The reader is referred to some of the many reviews and books (Lucian and Rojas 2009; Eichhorn et al. 2010; Siquiera et al. 2010; Klemm et al. 2011; Isogai et al. 2011; Siro and Plackett 2010; Moon et al. 2011; Lindström et al. 2014) on the subject of nanocellulosic materials.

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There are at least three main domains of nanocellulosic materials (Klemm et al. 2011), i.e., NFC, nanocrystalline cellulose, and bacterial nanocellulose, all with different potential applications. NFC, earlier known as microfibrillated cellulose, traces its origins to developments at ITT Rayonier (Turbak et al. 1983; Herrick et al. 1983) in the late 1970s. Investigators there found that processing fibrous materials such as wood fibres using high-pressure homogenizers formed a gel-like material containing fibril aggregates. The early generations of delaminated fibres were coarser than those produced today using various chemical pre-treatment procedures, but the name did not actually reflect the true size of the produced fibrils.

A major impediment to the commercial exploitation of NFC has been the high energy consumption during production and the complex rheology of NFC. Procedures involving various chemical/enzymatic pre-treatments of the fibre material subsequently lowered (Klemm et al. 2011; Sandquist 2013) the high energy consumption in NFC production. Although the high viscosity of NFC is a key advantage in emulsion/dispersion applications, high viscosity can pose problems in many industrial applications involving for example mixing, pumping, and extrusion. Therefore, controlling the rheology is crucial to commercial NFC applications. The basic rheological features of NFC, such as shear thinning and thixotropic behaviour, were identified by the original investigators (Herrick et al. 1983) and have been confirmed more recently (Iotti et al. 2011; Pääkkö et al. 2007; Tatsumi et al. 2002; Lasseuguette et al. 2008). Though the basic properties are clear, the mechanisms governing NFC rheology are not fully understood at this point in time. In addition, the various procedures and conditions used during manufacturing are expected to affect NFC rheology, adding to the complexity. Despite awareness of this, to our knowledge, no published work addresses the effects of various process parameters on the rheological properties of the NFC product. The present paper reports the effects of pulp consistency in the manufacturing process on the rheological properties of the obtained products. This information is important, as NFC production at much higher consistencies than are currently achievable, i.e., ≤ 3 % (w/w), may be a prerequisite for commercializing NFC in many applications. It is noted that though some research groups (Pääkkö et al. 2007; Tatsumi et al. 2002) have already treated this issue, their studies used NFC systems prepared by concentrating and/or diluting a pre-existing NFC product; as such, these investigated systems differ from those presented here.

The NFC-system chosen in this investigation was a carboxymethylated NFC, which during delamination forms more individualized fibrils (Wågberg et al. 2008) than those from low-charged NFC-systems (Pääkkö et al. 2007; Karppinen et al. 2012), which contain more non-separated fibril bundles, which is expected to add to the complexity of the system. Further, this system has never been subjected to any previous rheological analysis. The rheological properties of this system were studied using a combination of oscillatory and shear rate measurements.

Experimental section

Materials

The studied NFC was prepared at Innventia AB, Sweden, from a softwood sulphite dissolving pulp (Domsjö Dissolving Plus, Domsjö Fabriker, Sweden) that was subsequently carboxymethylated; the carboxymethylation process is described in detail, for example by Wågberg et al. (1987, 2008). Basically, water swollen pulp was ion-exchanged to ethanol, after which the fibres were transferred to isopropanol, containing monochloroacetic acid. Finally the reaction was carried out under alkaline conditions. The total charge of the fibre (and hence the resulting NFC) was determined by means of conductometric titration to be 590 μeq g^{-1} (DS $\approx$ 0.1). It is noted that the strong electrostatic repulsion forces among the grafted charges onto the fibrils result in a strong swelling of the fibre. This leads, in the subsequent mechanical processing of the fibres (see below) to an enhancement of the efficiency of the delamination process, and the production of NFC with smaller widths (5–15 nm) (Wågberg et al. 2008), as compared to when fibre systems with lower charge densities are used (Pääkkö et al. 2007; Karppinen et al. 2012). The pre-treated fibres with dry contents in the range of $\approx$0.2–6 % (w/w) were homogenized once in their sodium form. The homogenization process was conducted at ca 1,750 bars using a Microfluidizer M-110EH high-pressure fluidizer (Microfluidics Corporation, Westwood, MA, USA) employing two serially coupled

Z-shaped interaction chambers with diameters of 200 and 100 μm, respectively. Deionized water was used throughout the studies reported here.

Preparation of diluted NFC systems

Nanofibrillated cellulose samples of different concentrations were prepared by first blending appropriate amounts of the concentrated NFC with water for 30 min by using a laboratory propeller mixer at a speed of 1,000 rpm. Thereafter, the diluted systems were homogenized at 300 bars using serially coupled Z-shaped interaction chambers with diameters of 400 and 200 μm, respectively. The idea behind the lowering of the pressure and the change of the interaction chambers was to dilute the NFC systems with as low applied shearing as possible, as a mean to preserve the structure of the produced NFC systems.

Preparation of nanofibrillated cellulose films

Nanofibrillated cellulose samples, 0.1 % (w/w), were prepared by first blending appropriate amounts of the concentrated NFC with water for 30 min. The diluted systems were then homogenized once at 300 bars using two serially coupled Z-shaped interaction chambers with diameters of 400 and 200 μm, respectively, after which the systems were degassed under vacuum for 2 h. Films were prepared by vacuum filtration, using 0.65 μm DVPP filters (supplied by Millipore), and then oven drying for 7 h at 50 °C.

Tensile strength measurements

An MTS tensile strength machine with a Teststar IIS controller (MTS, USA) was used in the investigations. The samples were kept at 50 % Rh/23 °C, for at least 3 days, before conducting the measurements. The samples were weighted after strips were cut out. The length and width of the strips were 45 and 6 mm, respectively; the distance between the grips holding the strips was 30 mm. The strips were then mounted into a tensile strength machine and the mechanical properties were measured with a speed of 100 %/min.

Rheological studies

The rheological studies were conducted on samples that had been stored in a fridge at 5 °C for at least 3 days after their manufacturing, and then equilibrated overnight at room temperature.

The investigations were performed using a Kinexus stress-controlled rotational rheometer (Malvern Instruments, Malvern, UK) together with iSpace software (Malvern Instruments, Malvern, UK). A standard (ISO 3219/DIN 53019) metal concentric cylinder (bob and cup geometry) was used in the studies. Note that the surface of the bob and cup were serrated to minimize slippage effects (Dzuy and Boger 1983; Yoshimura et al. 1987; Buscall et al. 1993). These are believed to occur when a thin layer of fluid forms next to the test geometry (the wall), when colloidal systems viz. NFC suspensions are studied. At sufficiently high shear rates, the velocity of the fluid next to the wall is higher than that of the bulk material; which in the extreme case leads to a particle-free fluid near the walls, while the bulk material remains virtually intact (Walls et al. 2003). The height and distance between the serrations were 300 and 1,000 μm, respectively (supplier information, Malvern Instruments, Malvern, UK).

The diameter and length of the used bob were 25 and 37.5 mm, respectively; the diameter and wall height of the cup were 27.5 and 62.5 mm, respectively. A working gap of 9.15 mm was employed in the measurements.

The samples, as prepared and without any preshearing, were loaded into the device and allowed to equilibrate for 2 min before the measurements began. The experimental temperature was 25 °C; a protective hood was used during the measurements to minimize possible effects from the drying of the samples.

Controlled shear rate measurements

The controlled shear rate measurements were conducted in the range of 0.01–1,000 s^{-1}. Integration time per measuring point was set to 30 s.

Strain sweep measurements

The studies were made in the 0.01–100 % range. The measurement frequency was set to 1.592 Hz; the minimum integration time per measuring point was 10 s.

Frequency sweep measurements

The strain value was set to 0.05 % for samples with concentrations of <2.6 % (w/w); a strain value of 5 %

Table 1 The dry contents of NFC systems prepared by homogenizing carboxymethylated pulp suspensions of different dry contents

NFC system	Dry content (% (w/w))
NFC-0.3	0.26
NFC-0.6	0.57
NFC-1.0	1.05
NFC-1.3	1.32
NFC-2.6	2.56
NFC-3.2	3.22
NFC-4.9	4.87
NFC-6.2	6.22

was used for systems with higher dry contents. As will be shown (Fig. 4), the given strain values lie within the so-called linear viscoelastic region (LVR). The frequency range used in the studies was 0.1–100 Hz; a minimum integration time of 10 s was used for each measuring point.

Results

Table 1 presents the dry contents of NFC systems prepared by homogenizing a carboxymethylated pulp system at different consistencies, while Fig. 1 shows representative images of the systems. As can be seen, the consistency and appearance of the various systems gradually changes from weak, jelly-like, and nearly clear for NFC systems with the lowest dry contents to stiff, gel-like, and turbid for systems with the highest dry contents.

Repeatability and reproducibility of the rheological investigations of this report has been exemplified by the rheological response of NFC-1.0 in Fig. 2. The scattering in repeated measurements on the same sample was ≤ 10 %; the scattering between 2 independently prepared samples (of the same system) was < 20 %. These values should be regarded as low and acceptable considering the processes that are involved for preparation of the samples (see "Experimental section").

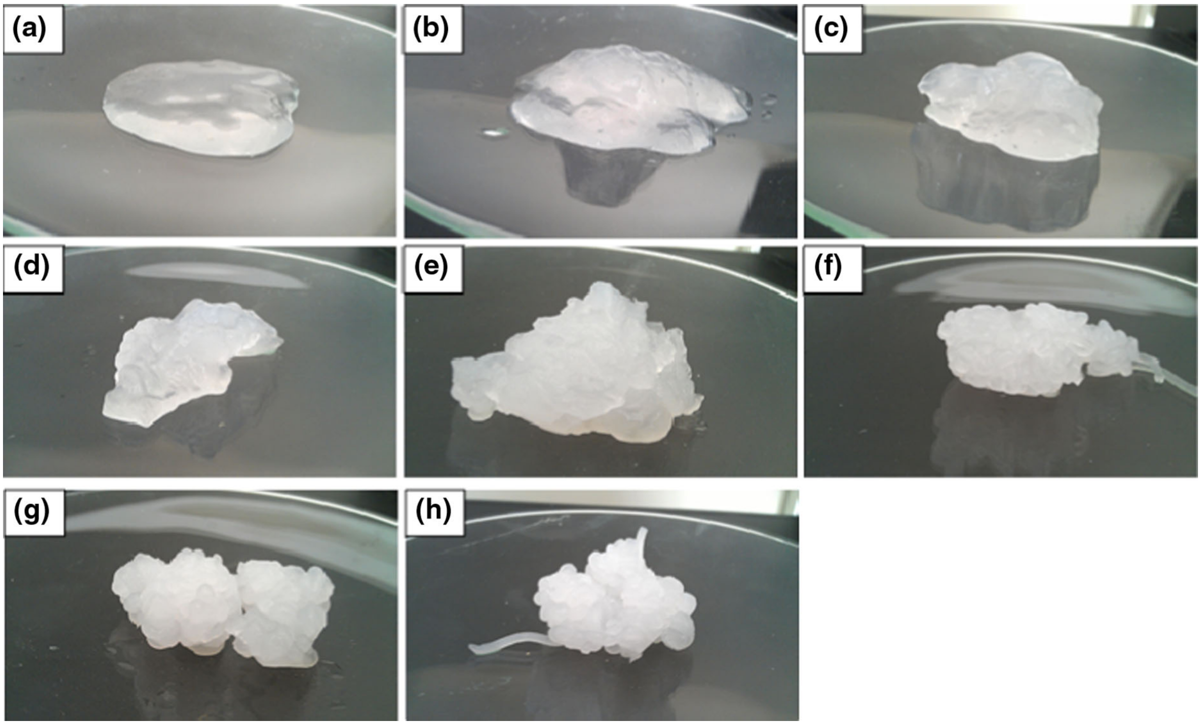

Fig. 1 Images of NFC-gels processed at different dry contents: **a** NFC-0.3, **b** NFC-0.6, **c** NFC-1.0, **d** NFC-1.3, **e** NFC-2.6, **f** NFC-3.2, **g** NFC-4.9 and **h** NFC-6.2

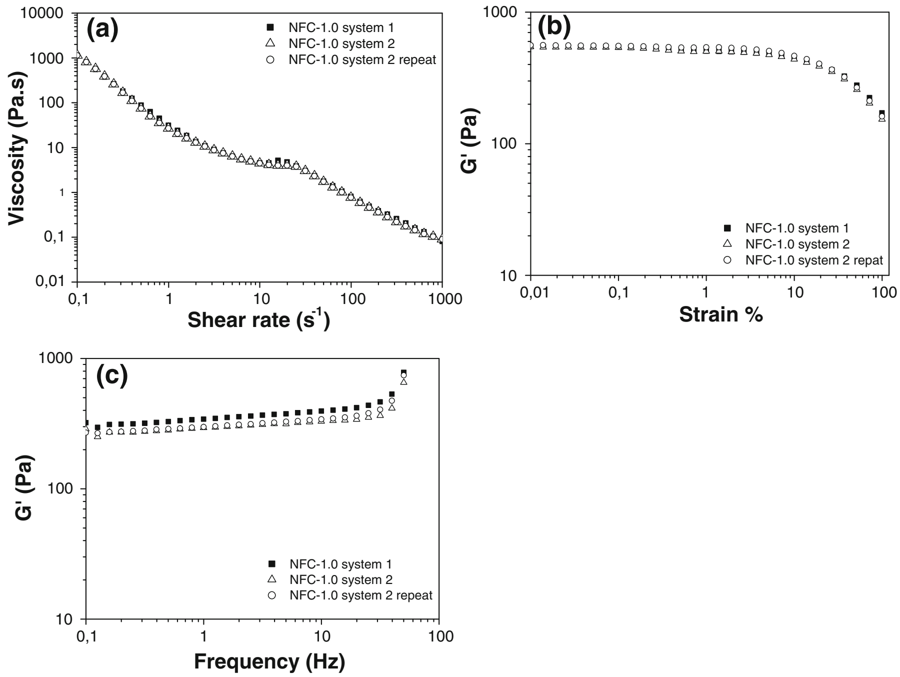

Fig. 2 Repeated measurements conducted on NFC-1.0: **a** Shear rate measurements, **b** Strain sweep measurements, and **c** Frequency sweep measurements. System 1 and 2 denote measurements conducted on NFC-1.0 systems prepared and measured at different times; "repeat" denotes repeated measurements on the same system

The high gel stiffness of the samples with the highest investigated dry contents, i.e., > 2.6 % (w/w), constituted a problem, as it did not allow the bob to be inserted into the samples, which was necessary for an even distribution of the samples within the measurement gap. Note that changing the geometry from bob and cup to parallel plates was (due to the earlier stated reason) equally fruitless.

Figure 3a shows the evolution of shear viscosity (η) as a function of shear rate ($\dot{\gamma}$) for the various measurable systems. These investigated systems display the well-known (Lasseuguette et al. 2008; Herrick et al. 1983; Iotti et al. 2011; Karppinen et al. 2012) shear-thinning behaviour with increasing shear rate associated with NFC systems; the observed increasing shear viscosity with increasing dry content is another recognizable (Pääkkö et al. 2007; Tatsumi et al. 2002) feature of NFC systems. A plateau region is noted in the viscosity curves in the $10\ \mathrm{s}^{-1} \leq \dot{\gamma} < 100\ \mathrm{s}^{-1}$ range, a region that becomes more pronounced with an increasing dry content of the NFC systems. Note that Karppinen et al. (2012) have related the plateauing tendency to a significant increase in floc size and floc size distribution. Notable, is also that in the same shear rate range ($10\ \mathrm{s}^{-1} \leq \dot{\gamma} < 100\ \mathrm{s}^{-1}$) Iotti et al. (2011) report a dilatant-type effect, which the authors postulated to be caused by a net-work formation process. Finally, it is noted that the "apparent" rheological response (Fig. 3a) is highly dependent on measuring parameters such as the gap width, the geometry, measuring times and rates (Saarikoski et al. 2012).

The shear viscosity of the studied systems at $0.1\ \mathrm{s}^{-1}$ (when measurable) as a function of the dry content is summarized in Fig. 3b. The power-law relationship ($\eta \sim c^{\beta}$) between the viscosity and concentration (c), and the value of 2 obtained for the exponent are in agreement with the findings of Tatsumi et al. (2002), who in their report actually plotted the shear stress ($= \eta \times \dot{\gamma}$) versus the NFC concentration. The authors proposed that the value obtained for the exponent ($\beta = 2$) indicated that the stress was caused by "two-body" collisions. It should be recapitulated (see "Introduction") that the NFC systems investigated by Tatsumi et al. (2002) were based on the dilution of a concentrated NFC system to lower consistencies, in contrast to the preparation procedure used in this investigation.

The viscoelastic properties of the studied NFC systems, as registered using strain sweep measurements, are summarized in Fig. 4. The viscoelastic properties of the NFC-2.6 system were measurable starting from a strain value of approximately 1 %. Beyond the apparent LVR, the rate of deterioration of the storage modulus (G') increases with increasing dry

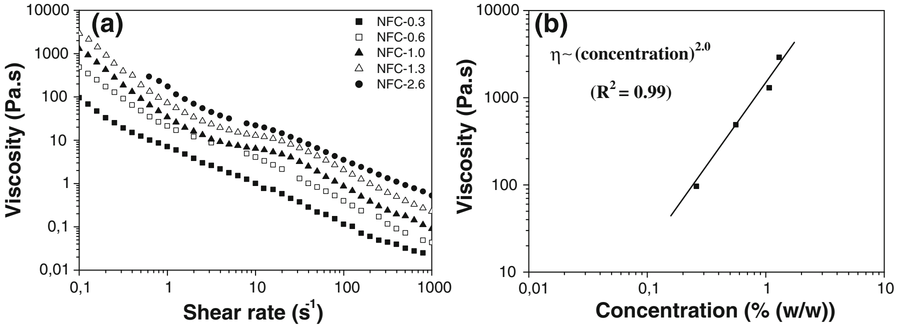

Fig. 3 **a** Shear viscosity versus shear rate of NFC systems with different dry contents. **b** The power-law evolution of the shear viscosity (measured at 0.1 s^{-1}) as a function of NFC consistency

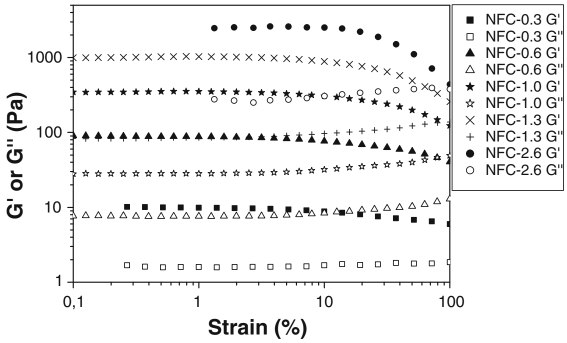

Fig. 4 The viscoelastic properties of NFC systems with different dry contents as registered using strain sweep measurements. G' denotes storage modulus and G'' denotes the loss modulus

content. This is due to the stiffening of the network (Benhamou et al. 2014), due to the increasing number of fibril–fibril interactions with NFC concentration.

Figure 5a summarizes the viscoelastic properties of the NFC systems obtained using frequency sweep measurements. Figure 5b shows the evolution of the storage modulus as a function of dry content (c). The system displayed power-law behaviour ($G' \sim c^{\alpha}$), as has been observed by several groups (Pääkkö et al. 2007; Tatsumi et al. 2002; Rezayati Charani et al. 2013; Saito et al. 2011). Note that the obtained α-value (2.4) is somewhat higher than the theoretical value, $\alpha = 2.25$, as proposed by De Gennes (1979) and Doi and Edwards (1978), which was derived for polymer systems in the semidilute regime and in good solvent conditions; the magnitude of the α-value is hence dependent on the solvent quality of the system. A similar α-value ($\approx$2.5) as found for the investigated carboxymethylated NFC in this contribution has, however, been reported by Saito et al. (2011) for a TEMPO-based NFC system. The α-values reported in other contributions (Pääkkö et al. 2007; Rezayati Charani et al. 2013) are however significantly higher.

The results presented in Figs. 3, 4, 5 clearly indicate the well-known impact of the dry content on the rheological response of the systems. Hence, for a meaningful comparison, different systems have to be studied at the same dry content level. Figure 6 shows the rheological responses of NFC systems diluted to the same dry content as that of NFC-1.0 ($\approx$1 % (w/w)). NFC-1.0 was also homogenized in the same manner as the other systems during the dilution process to ensure that all samples were subject to the same handling, which also affects the rheology of the systems.

Figure 6a–c, shows how the pulp concentration (c_{pulp}) during NFC production affects the rheological properties. A close examination of the curves reveal that there seems to be an optimum in the rheological response at a specific pulp concentration interval ($2.6 > c_{pulp}\%$ (w/w) > 1.0); the magnitude of the rheological properties (obtained by shear-, strain- and frequency sweep measurements) decreases on either side of this pulp concentration. This has been visualized by summarizing the rheological responses for the different systems in Fig. 6d.

Interestingly, despite the difference in the magnitude of the rheological response, the gels seem to display similar rheological characteristics. This conclusion is based on the observed small differences in shear viscosity (at low and high shear rates, Fig. 6a) and in the ratio between G' and G'' (Figs. 6b–c, summarized in Table 2). This observation can also be made by another route (Eq. 1) often employed in the literature to evaluate the strength of the NFC gels, which employs the study of the frequency (f) dependency (Kim and Yoo 2006; Jampala et al. 2005) of the storage modulus of systems. In Eq. 1, where G'_0

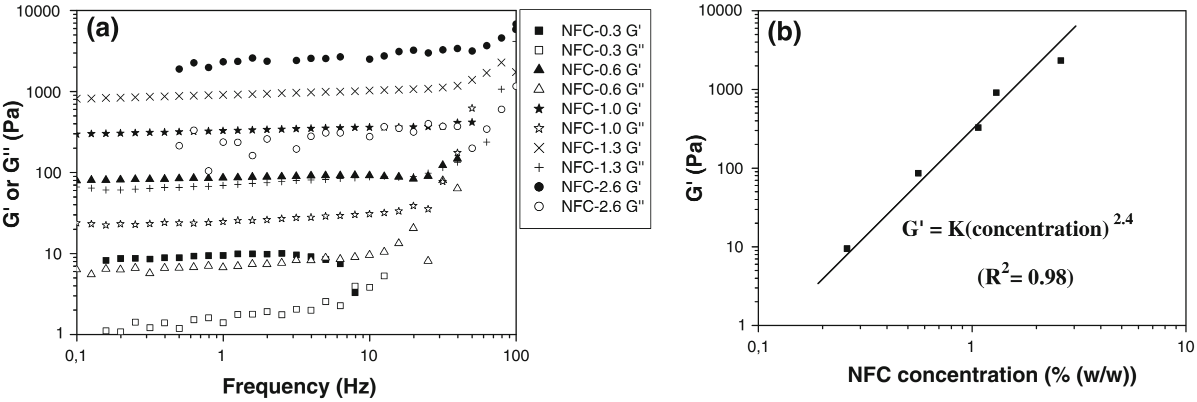

Fig. 5 **a** The viscoelastic properties of NFC systems with different consistencies as registered using frequency sweep measurements; **b** Storage modulus (G') versus concentration of the produced NFC; the G'-values were measured at 1 Hz

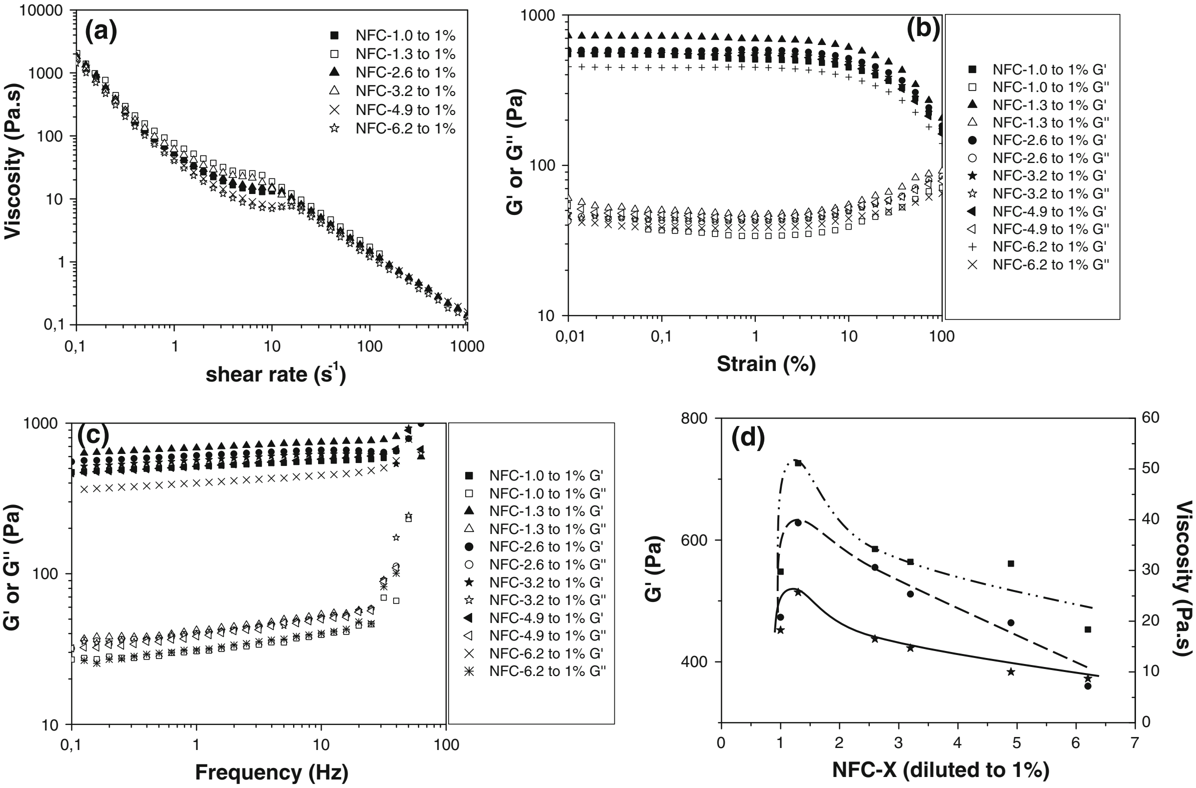

Fig. 6 Rheological properties of concentrated NFC systems (NFC-X, X = 1.0–6.2) diluted to the same concentration, i.e., ≈1 % (w/w): **a** Shear viscosity; **b** G' and G'' obtained using strain sweep measurements; **c** G' and G'' obtained using frequency sweep measurements; **d** Viscosity-values measured at 5 s^{-1} (*stars*, Fig. 6a) and G'-values obtained at 0.1 % (*squares*, Fig. 6b) and 1 Hz (*circles*, Fig. 6c). The *lines* indicate trends in the results

denotes the intercept of the G' curve with the y-axis, a lower n-value is indicative of a more elastic system. As it can be seen in Table 2, and judged by the corresponding n-values, the different NFC systems have similar properties.

$$G' = G'_0 f^n \tag{1}$$

The impact on the fibre concentration, in the homogenization step, on the mechanical properties of NFC films was also investigated; the properties of 3

Table 2 Characteristics of the various systems as obtained from rheological measurements

	Conc. % (w/w)	G'/G'' strain-sw[a]	G'/G'' freq-sw[b]	G'^{c}_{0}	n^{c}
NFC-1.0	1.1	18	14	514	0.04
NFC-1.3	1.1	18	14	683	0.04
NFC-2.6	1.1	17	14	605	0.04
NFC-3.2	1.1	15	12	566	0.04
NFC-4.9	1.1	15	12	517	0.05
NFC-6.2	1.0	14	12	402	0.05

[a] Strain sweep measurements; measured at 0.1 %

[b] Frequency sweep measurements; measured at 1 Hz

[c] See Eq. 1

Table 3 Mechanical properties of NFC films

System	Tensile Strength Index (kNmkg^{-1})	Tensile Stiffness Index (MNmkg^{-1})	TEA Index (kNmkg^{-1})	Strain (%)
NFC-1.3	203 ± 19	9.5 ± 0.5	8.9 ± 1.5	6.6 ± 0.8
NFC-2.6	178 ± 11	10.1 ± 0.3	6.7 ± 1.2	5.5 ± 0.8
NFC-6.2	191 ± 17	9.7 ± 0.6	7.8 ± 1.7	6.1 ± 1

different systems have been summarized in Table 3. As it can be seen, and as observed in the rheological properties, there are no significant differences between the systems.

Discussion

According to the theoretical work of De Gennes (1979) and Doi and Edwards (1978), the exponent (α) in the power-law relation ($G' \sim c^{\alpha}$), between the storage modulus (G′) versus dry content (c) of highly swollen gels is 2.25. The α-value for the investigated carboxymethylated NFC system was found to be slightly higher ($\alpha = 2.4$). This discrepancy might be understood by the notion that the theoretical work deals with ideal (uncharged) systems (i.e., gels) without heterogeneities in the constituent size or in the distance between the crosslinking points. Furthermore, these ideal gels are expected to be "well above" their gelling points and to exist in "good" solvent conditions. The latter condition can be assumed to hold in the studies of this report due to the highly charged nature of the entities. However, as expected, the NFC systems studied here are not ideal. Homogenization, like most industrial processes, is expected to lead to a heterogeneous distribution of the constituents. Furthermore, as the turbid appearance of the NFC systems (see Fig. 1) indicates, the system constituents are characterized by a broad size distribution. Finally, a discrepancy between the theoretical expectations and the system properties can be expected when the magnitude of the dry content of the NFC systems approaches the order of the critical overlapping concentration (gelling point) (c_0) of the systems, at which point the systems start to form 3D networks. Note that Pääkkö et al. (2007) have identified $c_0 \leq 0.1$ % (w/w) for an enzymatically pre-treated NFC system, while Tatsumi et al. (2002), studying a commercially available NFC, have suggested $c_0 < 0.1$ % (w/w). Attention is drawn to the dry content of NFC-0.3, which is in the vicinity of the mentioned critical overlapping concentrations. Notably, despite the non-ideality of the studied NFC systems, Tatsumi et al. (2002) reported an α-value of 2.25.

It was already realized from the pioneering work of Herrick et al. (1983) that the key to successful NFC production is the input of a certain specific amount of energy per processed amount of pulp. Therefore, the logical expectation would be that reducing the amount of pulp to be processed (using, for example, homogenization) while keeping the energy consumption constant would lead to a more efficient delamination process, and thereby the formation of stronger gels. The investigations reported here somewhat support this view.

The outcome of our investigations of NFC systems with similar concentrations (summarized in Fig. 6) indicate that the magnitudes of the rheological properties (G' and η) are optimum when the pulp concentration is in the range of $2.6 > c_{pulp}\%$ (w/w) > 1.0. On either side of this interval the magnitudes of the rheological properties diminish. Taken together, these observations indicate that the homogenization process requires a critical pulp concentration below which the delamination process becomes inefficient, and that at pulp concentrations significantly exceeding this critical pulp concentration, the energy input per processed amount of pulp becomes too low, in agreement with the earlier-mentioned expectations. It must, however, be emphasized that the delamination process may also

Table 4 Slope (K) and exponent (α) of storage modulus (G') versus concentration plots for three NFC systems

System	α	K
NFC-1.3	2.2	600
NFC-2.6	2.2	489
NFC-6.2	2.1	413

The measurements were made on diluted systems in the 0.5–1.2 % (w/w) range

be dependent on the specific equipment used for homogenization.

The magnitude of the storage modulus increases with the aspect ratio, defined as the ratio between fibril length and diameter (see e.g. Tatsumi et al. (2002)). This is understandable considering the large excluded volume and entangling effects involved in suspensions with highly anisotropic entities. For charged systems the aspect ratio is calculated from the fibril diameter, incorporating the thickness of the electrostatic double layer. However a closer examination of the strength of the produced NFC gels (Fig. 6) by comparing the G'/G'' and the frequency dependency of G' of the systems revealed no dramatic differences (Table 2) or unambiguous trends in the properties.

Tatsumi et al. (2008, 2002) have proposed that power-law relationships fitted to plots of G' versus concentration (see Fig. 5b) enable the aspect ratio (AR) to be estimated. According to Tatsumi et al. the slope (K) of the fitted curve is defined by the AR and the elastic modulus (E_0) of the fibrils (Eq. 2). Furthermore, the exponent (α) reflects the properties of the existing network, $\alpha \approx 2$ being indicative of a 3D random network. Table 4 summarizes the characteristics (K and α) of NFC-1.3, NFC-2.5, and NFC-6.2. Note that the systems represent different parts of the rheological scale (i.e., the high, mid, and low ranges), as seen in Fig. 6b, c.

$$K \sim E_0 (AR)^2 \tag{2}$$

As seen in Table 4, the α-value presupposes the existence of 3D networks; there is also a clear decreasing trend in the K-values.

Equation 2 states that the K-parameter is dependent on both the elastic modulus (E_0) and the aspect ratio (AR). Hence, for evaluation of the relative magnitude of the AR of different systems, the E_0 of the various nanofibrils has to be estimated. Obviously, the modulus of individual wet NFC fibrils is difficult to determine. Instead, the dry modulus was used as an indicator of the modulus in the wet state; this property can be estimated from the film properties of the NFC film. According to Cox (1952) the E_0 of a highly oriented polymeric fibre is related to the modulus (E_{film}) of randomly oriented fibres in film networks by the following equation:

$$E_0 = 3E_{\mathrm{film}} \tag{3}$$

Therefore, preparation of NFC films and the analysis of their mechanical properties in combination with Eq. 3 should allow for estimation of the relative magnitudes of the elastic moduli of the various nanofibril systems. However, this assumes that the relative magnitudes of the elastic moduli of the various systems remain the same in both the wet and dry states. The elastic moduli of the three tested films are summarized in Table 3; as can be seen, the systems differ very little. It can be concluded, based on the K-values presented in Table 4, that the delamination efficiency and, hence, the aspect ratio of the produced NFC decreases somewhat with increasing pulp concentration in the homogenization process.

Notably, the differing AR-values have no dramatic impact on the mechanical properties of the NFC films (Table 3). These results are also in accordance with the findings of Fukuzumi et al. (2012).

Conclusions

The rheological properties of carboxymethylated NFC were investigated using oscillatory and rotational measurements. It was demonstrated that carboxymethylated NFC exhibits properties similar to those of other NFC systems described in the literature. The shear viscosity (η) and the storage modulus (G') were found to scale with concentration (c) as $\eta \sim c^{2.0}$ and $G' \sim c^{2.4}$, respectively.

The outcome of these trials indicates that the consistency at which NFC is produced, while keeping the shearing energy in the homogenization step constant, influences the rheological properties of the system. The investigations imply that there is a critical concentration below which the efficiency of the delamination process diminishes. The same adverse effect is also observed when the critical concentration is significantly exceeded, which is postulated to be caused by lowering the amount of shearing per amount of processed fibre.

Surprisingly, even though the degree of delamination was found to affect the magnitude of the storage modulus of the systems, the strength of the different NFC-networks, as studied by oscillatory measurements, displayed little difference. Finally, the results indicate that the degree of delamination has little effect of the mechanical properties of NFC films.

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References

Benhamou K, Dufresne A, Magnin A, Mortha G, Kaddami H (2014) Control of size and viscoelastic properties of nanofibrillated cellulose from palm tree by varying the TEMPO-mediated oxidation time. Carbohydr Polym 99:74–83. doi:10.1016/j.carbpol.2013.08.032

Buscall R, McGowan JI, Morton-Jones AJ (1993) The rheology of concentrated dispersions of weakly attracting colloidal particles with and without wall slip. J Rheol 37(4): 621–641. doi:10.1122/1.550387

Cox HL (1952) The elasticity and strength of paper and other fibrous materials. Br J Appl Phys 3(3):72

De Gennes PG (1979) Scaling concepts in polymer physics. Cornell Univ Press, Ithaca

Doi M, Edwards SF (1978) Dynamics of rod-like macromolecules in concentrated solution Part 1. J Chem Soc Faraday Trans 2(74):560–570. doi:10.1039/f29787400560

Dzuy NQ, Boger DV (1983) Yield stress measurement for concentrated suspensions. J Rheol 27(4):321–349. doi:10.1122/1.549709

Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, Weder C, Thielemans W, Roman M, Renneckar S, Gindl W, Veigel S, Keckes J, Yano H, Abe K, Nogi M, Nakagaito AN, Mangalam A, Simonsen J, Benight AS, Bismarck A, Berglund LA, Peijs T (2010) Review: current international research into cellulose nanofibres and nanocomposites. J Mater Sci 45(1):1–33

Fukuzumi H, Saito T, Isogai A (2012) Influence of TEMPO-oxidized cellulose nanofibril length on film properties. Carbohydr Polym 93:172–177

Herrick FW, Casebier RL, Hamilton JK, Sandberg KR (1983) Microfibrillated cellulose: morphology and accessibility. J Appl Polym Sci Symp 37:797–813

Iotti M, Gregersen OW, Moe S, Lenes M (2011) Rheological studies of microfibrillar cellulose water dispersions. J Polym Environ 19:137–145. doi:10.1007/s10924-010-0248-2

Isogai A, Saito T, Fukuzumi H (2011) TEMPO-oxidized cellulose nanofibers. Nanoscale 3(1):71–85. doi:10.1039/c0nr00583e

Jampala SN, Manolache S, Gunasekaran S, Denes FS (2005) Plasma-enhanced modification of xanthan gum and its effect on rheological properties. J Agric Food Chem 53:3618–3625. doi:10.1021/jf0479113

Karppinen A, Saarinen T, Salmela J, Laukkanen A, Nuopponen M, Seppälä J (2012) Flocculation of microfibrillated cellulose in shear flow. Cellulose 19(6):1807–1819. doi:10.1007/s10570-012-9766-5

Kim C, Yoo B (2006) Rheological properties of rice starch-xanthan gum mixtures. J Food Eng 75:120–128. doi:10.1016/j.jfoodeng.2005.04.002

Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, Dorris A (2011) Nanocelluloses: a new family of nature-based materials. Angew Chem Int Ed 50(24):5438–5466. doi:10.1002/anie.201001273

Lasseuguette E, Roux D, Nishiyama Y (2008) Rheological properties of microfibrillar suspension of TEMPO-oxidized pulp. Cellulose 15(3):425–433. doi:10.1007/s10570-007-9184-2

Lindström T, Aulin C, Naderi A, Ankerfors M (2014) Microfibrillated cellulose. In: Encyclopedia of polymer science and technology, John Wiley & Sons Inc., Hoboken, pp 1–34. doi:10.1002/0471440264.pst614

Lucian LA, Rojas OJ (2009) The nanoscience and technology of renewable biomaterials. Wiley-Blackwell, Oxford

Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 40:3941–3994. doi:10.1039/c0cs00108b

Pääkkö M, Ankerfors M, Kosonen H, Nykänen A, Ahola S, Österberg M, Ruokolainen J, Laine J, Larsson PT, Ikkala O, Lindström T (2007) Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. Biomacromolecules 8(6):1934–1941. doi:10.1021/bm061215p

Rezayati Charani P, Dehghani-Firouzabadi M, Afra E, Shakeri A (2013) Rheological characterization of high concentrated MFC gel from kenaf unbleached pulp. Cellulose 20(2):727–740. doi:10.1007/s10570-013-9862-1

Saarikoski E, Saarinen T, Salmela J, Seppälä J (2012) Flocculated flow of microfibrillated cellulose water suspensions: an imaging approach for characterisation of rheological behaviour. Cellulose 19(3):647–659. doi:10.1007/s10570-012-9661-0

Saito T, Uematsu T, Kimura S, Enomae T, Isogai A (2011) Self-aligned integration of native cellulose nanofibrils towards producing diverse bulk materials. Soft Matter 7(19): 8804–8809. doi:10.1039/c1sm06050c

Sandquist D (2013) New horizons for microfibrillated cellulose. Appita J 66:156–162

Siquiera G, Bras J, Dufresne A (2010) Cellulosic bionanocomposites: a review of preparation, properties and applications. Polymer 2(4):728–765

Siro I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose 17:459–494. doi:10.1007/s10570-010-9405-y

Tatsumi D, Ishioka S, Matsumoto T (2002) Effect of fiber concentration and axial ratio on the rheological properties of cellulose fiber suspensions. J Soc Rheol Jpn 30:27–32

Tatsumi D, Inaba D, Matsumoto T (2008) Layered structure and viscoelastic properties of wet pulp fiber networks. J Soc Rheol Jpn 36:235–239. doi:10.1678/rheology.36.235

Turbak AF, Snyder FW, Sandberg KR (1983) Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. J Appl Polym Sci Symp 37:815–827

Wågberg L, Winter L, Ödberg L, Lindström T (1987) On the charge stoichiometry upon adsorption of a cationic polyelectrolyte on cellulosic materials. Colloids Surf 27: 163–173

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

Walls HJ, Caines SB, Sanchez AM, Khan SA (2003) Yield stress and wall slip phenomena in colloidal silica gels. J Rheol 47(4):847–868. doi:10.1122/1.1574023

Yoshimura AS, Prud homme RK, Princen HM, Kiss AD (1987) A comparison of techniques for measuring yield stresses. J Rheol 31(8):699–710. doi:10.1122/1.549956