

Nanofibrillated cellulose: properties reinvestigated

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Abstract The scientific publications on nanofibrillated cellulose (NFC) were reviewed in the light of recent developments in the field of characterization of NFC, and the evolving understanding of the material. This led to several insights, which challenged few of the established assumptions with regard to e.g. rheological properties of NFC suspensions, and factors affecting tensile strength and barrier properties of NFC films. The realizations may promote the wider application of nanofibrillated celluloses.

Keywords Nanofibrillated cellulose (NFC) · Rheological properties · Barrier properties · Centrifugation · Tensile strength properties

Introduction

Nanocellulosic materials have generated an immense interest from the research community, governmental bodies and the industry during several decades. This can be related to several exciting properties and the possibility of producing the materials from a multitude of sustainable resources. Nanocelluloses broadly include bacterial nanocellulose (BNC), nanocrystalline cellulose

(NCC) and nanofibrillated cellulose (NFC). Even though BNC and NCC possess several unique properties, the advantage of NFC (to BNC and NCC) is that it can be produced at industrial scales, with a variety of functional groups, and by a multitude of industrially attractive processes. Consequently, NFC is today used in several industrial applications, e.g. as strengthening additive in the production of paper and cardboard products,¹ as rheological modifier in cosmetics² and as an odour-eliminating agent in diapers.³

The production, general characteristics and potential applications of NFC have been the subject of numerous reviews; see e.g. (Klemm et al. 2011; Dufresne 2013; Lindström et al. 2014). There are also several reviews that focus on specific properties and applications of NFC (Berglund 2005; Lavoine et al. 2012; Boufi et al. 2016; Nechyporchuk et al. 2016). However, these contributions often lack a more in-depth reviewing of the findings, which would be valuable to the reader. For example, there is still a lack of knowledge of the importance of the chemical pretreatment process and the amount of mechanical shearing (in the NFC manufacturing process) on

¹ http://www.paperage.com/2011news/05_31_2011stora_ensomatra.html.

² <http://www.pulpapernews.com/2015/09/oji-to-develop-nano-cellulose-for-cosmetic-applications>.

³ <http://www.japantimes.co.jp/news/2015/11/27/business/corporate-business/nippon-paper-invest-nanofibre-head-off-challenges-print/>.

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different NFC properties. There is also no clear understanding of the impact of parameters such as crystallinity index and degree of polymerization on barrier properties and mechanical strength of NFC films. Understandably, the knowledge is necessary for the efficient employment and the broadening of the areas of application of NFC.

This limitation may be related to the still growing understanding of the properties of the NFC, which complicates the reviewing work. However, a major reason is also the lack of universally accepted protocols for sample preparation and characterization of NFC-based systems, which hinders the effective comparison of different findings. It is noted that despite the urgency of the problem, there are very few contributions (Saarinen et al. 2009; Naderi and Lindström 2015; Olié 2016) that come close on the subject of developing characterization methods for NFC-based systems.

In this communication, the existing scientific publications on NFC, obtained through four different characterization methods (rheological measurements and centrifugation studies on NFC suspensions, together with tensile strength and oxygen permeability measurements on NFC films) are reviewed and the findings are re-evaluated by considering current understandings.

Rheological studies

Rheological measurements are highly sensitive to system differences. Hence, the employment of the method requires stringent protocols for sample handling and analysis. For example, Saarinen et al. (2009) reported that rheological studies on highly flocculated NFCs should be conducted with a concentric cylinders geometry and a gap size of at least 1 mm. Naderi and Lindström (2015) showed that pre-shearing of an unstable NFC (with phase-separation tendencies) is a pre-requisite for achieving reliable results. And Nechyporchuk et al. (2014) stressed the importance of using serrated geometries, instead of smooth geometries, in the study of concentrated NFCs as a mean to diminish slip effects.

The recording of the true rheological responses of NFC systems requires knowledge about the motion of the constituents of the systems and behaviour of the entire suspension, which is difficult to obtain.

Nevertheless, an attempt was recently made by Nechyporchuk et al. (2014), by combining rheological measurements and a visualization device. These authors reported of shear banding phenomenon at certain shear rates in the study of enzymatically pre-treated (NFC_{Enz}) and TEMPO-based (NFC_{TEMP}) nanofibrillated celluloses.

A characteristic of NFC systems is the exponential increase of storage modulus (G') of the NFC gels, which occurs beyond the critical network forming concentration of the systems. The theoretical work (on entangled semiflexible polymer systems) proposes an exponential value (α) of about 2.2, for the evolution of G' as a function of concentration (MacKintosh et al. 1995). Tatsumi et al. (2002) reported an exponential value of about 2.2 for a presumably low-charged NFC. And, Naderi et al. (2014b) found $\alpha \approx 2.4$ for a carboxymethylated nanofibrillated cellulose (NFC_{Carb}, 0.6 meq/g). There are, however, numerous contributions that have reported significantly higher α -values; see e.g. (Pääkkö et al. 2007; Agoda-Tandjawa et al. 2010; Shogren et al. 2011). The larger magnitudes of α may be related to different NFC structures, as proposed by e.g. Tatsumi et al. (2008). However, the high α -values could also be due to the incorrect selection of NFC suspensions (in the fitting process); that is the inclusion of NFC-concentrations that reside below or just above the critical network formation concentration.

The viscosity of NFCs also changes exponentially with concentration. Tatsumi et al. (2002) reported an exponential value (β) of about 2 for the evolution of shear stress (at constant shear rate) for a presumably low charged NFC; the value was proposed to be indicative of two-body collisions. Similar β -values have since been reported by Lasseguette et al. (2008) for an NFC_{TEMP} (presumably highly charged) and by Naderi et al. (2014b; 2015c) for an NFC_{Carb} (0.6 meq/g) and a CMC-grafted nanofibrillated cellulose system (NFC_{CMC}, 0.17 meq/g).

Another characteristic behaviour of NFC suspensions is their thixotropic behaviour. Lasseguette et al. (2008) conducted several cycles of shear rate measurements on an NFC_{TEMP} (presumably highly charged), and observed that the apparent viscosity did not change after the second cycle. These authors proposed different kinetics for the breaking and formation of fibril flocs as an explanation for their observation. Iotti et al. (2011) conducted a similar

study as Lasseguette et al. on an NFC (presumably low-charged); however, these authors did not observe a change in the magnitude of viscosity as a function of number of shear rate measurements. The observation of Iotti et al. proposes a very rapid network formation, which may find support in the studies of Naderi and Lindström (2016), who investigated the thixotropic properties of several NFC-grades (NFC_{Carb}, NFC_{CMC}, and NFC_{Enz}) and found a rapid rebuilding of the NFC networks upon the scission of shearing of the systems.

On a related note, Iotti et al. also observed a rheopectic effect in their shear rate measurement studies. The observations were proposed by these authors to occur through the formation of structures due to the “unique characteristics” of NFC. However, a review of the available literature reveals that the observed rheopectic behaviour may not be a general characteristic of NFCs. Rather, the review suggests that the effect is more often observed for lesser fibrillated NFCs; see e.g. (Karppinen et al. 2012; Naderi and Lindström 2016).

The viscosity measurements of Iotti et al. revealed another interesting phenomenon, in which the viscosity curve based on decreasing shear rates remained (in a wide shear rate interval) above the viscosity curve recorded on increasing shear rates. This observation was related (by these authors) to time-dependent reorganization processes.

On a related context, many reported shear viscosity measurements are characterized by a kink in the viscosity curves (Pääkkö et al. 2007; Besbes et al. 2011; Karppinen et al. 2012; Naderi et al. 2014b); the kinks have the character of a plateauing region. Karppinen et al. (2012), who combined rheological measurements and image-analysis of a presumably low-charged NFC, have related the origin of the kinks to the creation of large flocs and voids. However, it is pointed out that the conclusion is based on the study of the macro-sized constituents of the investigated NFC. Further reviewing of the literature may, however, provide an alternative explanation. For example, a closer examination of the contribution of Naderi et al. (2014b), in which the shear viscosity of an NFC_{Carb} (0.6 meq/g) as a function of NFC concentration was investigated, reveals that the plateauing region appears at lower shear rates as a function of NFC concentration. Interestingly, the rheopectic effect in the report of Iotti et al. displayed a similar shift as a function of NFC concentration. Of interest to the discussions is

also the report of Besbes et al. (2011), who investigated the impact of number of passes through a high pressure homogenizer on among others the rheological properties of an NFC_{TEMP} (1 meq/g). From the results of Besbes et al., it can be discerned that the kinks in the curves are shifted to lower shear rate values with increasing number of passes (that is increasing degree of fibrillation). Similar observations can also be discerned from the publications of Naderi et al. (2015a; 2016b), who studied the impact of number of microfluidization passes on the properties of an NFC_{Carb} (0.6 meq/g) and a phosphorylated NFC (NFC_{Phos}, 0.7 meq/g). The apparent correlation between the NFC concentration in shear rate measurements and the degree of fibrillation, and the positioning of the kinks (and the rheopectic effects) suggests that there is a correlation between the kinks and the amount of the nanomaterials in the studied NFC systems. Furthermore, the results also indicate that the shift of the kinks to lower shear rates with the increasing degree of fibrillation is indicative of the formation of larger aggregates, as the characteristic shear rate is proportional to the inverse of the characteristic time of the system—which increases. The creation of larger aggregates may be rationalized by the formation of highly entangled entities, viz. fibril aggregates, when the number of nanofibrils is increased.

The impact of temperature on the viscosity of NFC was first studied by Herrick et al. (1983). These authors found that the viscosity of the studied NFC (presumably low-charged) decreased with increasing temperature. The observation was rationalized by the decreasing viscosity of water, in the NFC suspension, with temperature. Recently, Naderi and Lindström (2016) performed shear rate and oscillatory measurements on several nanofibrillated systems, among others a low charged (0.03 meq/g) NFC_{Enz}. These authors made similar observations as Herrick et al.; however, a decrease in G' and an increase in G'/G'' with increasing temperature were also observed. On the other hand, the impact of temperature was found to be lower for a medium charged (0.16 meq/g) NFC_{CMC} and insignificant for a highly charged (0.6 meq/g) NFC_{Carb}. Naderi and Lindström did not provide any explanation for these observations. However, these authors pointed out that dissolution of cellulose is known to decrease with increasing temperature, which has been proposed to be related to the amphiphilic

nature of the material (Medronho et al. 2012). Hence, the trends in the results may be understood by the extent of the amphiphilicity of the fibrillated material, with the lowest charged systems NFC displaying the highest relative lowering in viscosity, due to a higher release of water.

Highly charged NFCs are obviously sensitive to changes in the ambient ionic strength. Fukuzumi et al. (2014) investigated the viscosity of a 0.1% (w/w) NFC_{TEMP} (1.5 meq/g) as a function of NaCl concentration. These authors observed an increase in the viscosity of the NFC when the NaCl concentration was increased to 100 mM. At higher NaCl concentrations, the viscosity of the system decreased due to phase-separation. Jowkarderis and van de Ven (2014) used a capillary viscometer to investigate the impact of monovalent inorganic salts on a highly diluted ($\leq 0.02\%$ (w/w)) NFC_{TEMP} (0.7 meq/g). These authors observed that the intrinsic viscosity decreased with increasing ionic strength of the system, if $\kappa d \leq 1$; κ denotes the inverse Debye length of the system and d denotes the diameter of the fibrils. However, at higher salt concentrations ($\kappa d > 1$) the viscosity of the system increased, which was related to the flocculation of the nanofibrils. Naderi and Lindström (2014) investigated the impact of NaCl concentration (0.1–10 mM) on the rheological properties of a 1% (w/w) NFC_{Carb}. These authors observed a noticeable decrease in the viscosity and G'/G'' of the NFC with increasing NaCl concentration. This observation is interesting, as Fall et al. (2011) have shown (by dynamic light scattering studies) that NFC_{Carb} (0.6 meq/g) is stable in $[\text{NaCl}] = 0.1\text{--}100$ mM. The reasons behind the seemingly conflicting results are currently not understood.

The impact of multivalent ions on the rheological properties has also been studied. For example, Jowkarderis and van de Ven (2014) investigated the impact of CaCl₂ on the intrinsic viscosity of an NFC_{TEMP} (0.7 meq/g) and observed a similar trend as when the impact of NaCl was studied (see above). In another contribution Jowkarderis and van de Ven (2015) investigated the impact of CaCl₂ on the creep-recovery of a 0.3% (w/w) NFC_{TEMP} (0.7 meq/g) and observed an initial increase in the net-work deformation by the addition of small amount of salt ($[\text{CaCl}_2] < 0.2$ mM), which was ascribed to the decrease of the double-layer thickness. The network deformation, however, decreased by further increase

of the salt concentration, which these authors rationalized by fibril aggregation or the linking of the nanofibrils with calcium ions. Dong et al. (2013) investigated the impact of several di- and trivalent ions on the gel formation of an NFC_{TEMP} (1.3 meq/g). These authors observed that G' increased in the following order $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+}$, which was proposed to reflect the strength of the metal-carboxylate bonding. However, the trend in the G'/G'' values did not match the G' -trend. These authors explained the observation by the acidity of some of the salt solutions, which led to the protonation of part of the carboxylate groups.

In a related context, the impact of pH on the rheological properties of NFCs has also been the subject of a handful of studies. The more interesting contribution (in the view of this author) is that of Jowkarderis and van de Ven (2014), in which a lowering in the intrinsic viscosity with decreasing pH of a highly charged NFC_{TEMP} (0.7 meq/g) was observed.

Rheological studies on multi-component NFC-based systems are important for the evaluation of NFC in different applications. But, the number of publications in the field is relatively few (Lowys et al. 2001; Karppinen et al. 2011; Quennouz et al. 2016), and the conclusions are often not satisfactorily substantiated due to the inadequate investigation of the modes of interactions of NFC and other system components. The investigations are further complicated by the inadequate knowledge of the proper method of mixing of different components, which has been shown to have a major impact on the recorded rheological properties (Naderi et al. 2015b; de Kort et al. 2016). Rheological studies of multicomponent NFC-based systems should therefore be viewed as an immature field.

Barrier studies on NFC films

One of the more extraordinary properties of NFC is the ability to form highly impregnable layers—which can be designed to repel gas molecules. The capability of NFC to form dense layers can be rationalized by the strong cohesive forces among the nanofibrils, due to the higher surface area of the nano-sized materials as compared to larger entities. It is noted that the high crystalline content of NFC, which renders the material

a denser character thanks to the highly compact structure of the crystalline cellulose ($\approx 1.6 \text{ g/cm}^3$, (Sugiyama et al. 1991; Nishiyama et al. 2002)), has also been proposed as an explanation for the attractive barrier properties of NFC.

Fukuzumi et al. (2013) investigated NFC_{TEMP} with different degrees of crystallinity (crystallinity index = 56–64%). These authors found that at low humidity (RH⁴ = 0%) the NFC with the highest degree of crystallinity displayed the lowest oxygen transmission rate (OTR); however, the barrier property of the different systems became comparable at ambient humidity conditions. Larsson et al. (2013) investigated the oxygen permeability (OP) of NFCs based on unmodified- and periodate oxidized pulps. The investigations revealed that periodate oxidation significantly decreased the crystallinity index (down to 21% from 73% for the unmodified pulp). However, the OP-values of the periodate-oxidized NFCs were about five times lower than the unmodified system at RH = 80%. The observations were rationalized by the ability of the oxidized nanofibrils to crosslink, and thereby hindering the swelling of the NFC film. In this context, it is of interest to also highlight the contribution of Belbekhouche et al. (2011), who found that the highly crystalline NCC has inferior barrier properties to NFC. These authors related their observation to the high porosity of the NCC-film. The reports combined, hence, indicate that barrier properties are more affected by the ability of the NFC to form dense and rigid films, rather than the degree of crystallinity of the nanocellulosic materials (at least in the investigated range).

Intuitively, NFCs with a higher degree of fibrillation should form denser NFC films, as they have a lower fibre fragment (which is detrimental to the integrity of the film) content. However, as it can be seen in Table 1, the impact of degree of fibrillation is not straightforward. Aulin et al. (2010) investigated the effect of the degree of fibrillation on the barrier property of a highly charged (0.5 meq/g) NFC_{Carb}; these authors found that the property was not affected by the degree of fibrillation. This observation is in agreement with the findings of Siró et al. (2011), who studied an NFC_{Carb} similar to that of Aulin et al., and the finding of Österberg et al. (2013) who studied a highly fibrillated and presumably low-charged NFC.

The cited observations are, however, not supported by the investigations of Naderi et al. (2015c; 2016b), which showed that the barrier properties of NFC_{CMC} (0.17 meq/g) and NFC_{Phos} (0.7–1 meq/g) significantly improved when the degree of fibrillation of the NFCs increased (by increasing the number of microfluidization passes). In another contribution, Naderi et al. (2016a) compared the barrier properties of a low charged (0.03 meq/g) and low fibrillated NFC_{Enz} and a highly charged (0.6 meq/g) and efficiently fibrillated NFC_{Carb}, and observed a lower OP-value ($\approx 0.04 \text{ cm}^3 \mu\text{mm}^{-2} \text{ d}^{-1} \text{ kPa}^{-1}$) for NFC_{Enz} as compared to that of NFC_{Carb} ($\approx 0.2 \text{ cm}^3 \mu\text{mm}^{-2} \text{ d}^{-1} \text{ kPa}^{-1}$) at RH = 50%.

The compilation in Table 1 suggests that a critical, yet low, degree of fibrillation must be reached for producing dense NFC-layers. Beyond this critical point, little improvement is achieved by increasing the degree of fibrillation of NFC.

This realization can be useful for the employment of NFCs in barrier applications. Table 2 contains the tensile strength index (TSI) and the OP of a never-dried and fully dried and then redispersed NFC_{Carb} (0.6 meq/g). As it can be seen, the lower magnitude of the TSI of the redispersed NFC_{Carb} indicates that full redispersion has not been achieved; yet the OP-values of the never-dried and redispersed systems are comparable. In this context, it is noted that low-charged NFCs, viz. NFC_{Enz}, have been shown to be incapable of regaining their never-dried barrier properties (Naderi et al. 2015b), which may be rationalized by that the degrees of fibrillation of the redispersed NFCs are below the critical values of the systems.

It is pointed out that the results (in Table 2) also suggest that a lower degree of fibrillation is required for making effective NFC-based gas barriers than for producing strong NFC films.

The barrier properties of NFCs may be expected to be highly influenced by the chemical pre-treatment process in their manufacturing. The summary of several contributions in Table 1 reveals, however, that the pre-treatment method has little influence on the gas barrier properties of NFCs—when a sufficient degree of fibrillation has been achieved. Furthermore, the results indicate that NFCs with a higher number of charged groups generally sorb more water, which increases the gas permeability.

The deterioration of the barrier properties of NFC films at high humidity conditions is a major

⁴ Relative humidity.

Table 1 The impacts of pre-treatment method, mechanical fibrillation process and amount of shearing (in the fibrillation process) on the barrier properties of NFC films

Pre-treatment	≈Charge density (meq/g)	Fibrillation process	Amount of shearing	RH (%)	OP (cm ³ μmm ⁻² d ⁻¹ kPa ⁻¹)	References
None	–	Microfluidization	6 passes	53	0.2	Österberg et al. (2013)
None	–	Microfluidization	11 passes	50	1	Larsson et al. (2013)
None	–	Microfluidization	11 passes	80	10	Larsson et al. (2013)
None	–	Masuko grinder/microfluidization	4–9 passes	50	1	Bessonoff and Paltakari (2015)
Periodate oxidation without crosslinking	0.01	Microfluidization	4 passes	50	0.4	Larsson et al. (2014)
Periodate oxidation without crosslinking	0.01	Microfluidization	4 passes	80	6	Larsson et al. (2014)
Carboxymethylation	0.5	Microfluidization	10 passes	50	0.2	Aulin et al. (2010)
Carboxymethylation	0.6	Microfluidization	1 pass	50	0.2	Naderi et al. (2016a)
Carboxymethylation	0.6	Microfluidization	1 pass	80	13	Naderi et al. (2016a)
Carboxymethylation	0.6	Microfluidization	5 passes	50	0.5	Siró et al. (2011)
CMC-grafting	0.17	Microfluidization	1 pass	50	Out of range	Naderi et al. (2015c)
CMC-grafting	0.17	Microfluidization	5 passes	50	0.6	Naderi et al. (2015c)
CMC-grafting	0.17	Microfluidization	1 pass	50	67	Naderi et al. (2016a)
CMC-grafting	0.03	Microfluidization	1 pass	80	Out of range	Naderi et al. (2016a)
Enzymatic	0.7	Microfluidization	1 pass	50	0.04	Naderi et al. (2016a)
Enzymatic	0.7	Microfluidization	1 pass	80	13	Naderi et al. (2016a)
Phosphorylation	1	Microfluidization	1 pass	50	Out of range	Naderi et al. (2016b)
Phosphorylation	1	Microfluidization	1 pass	80	–	Naderi et al. (2016b)
Phosphorylation	1	Microfluidization	1 pass	50	0.2	Naderi et al. (2016b)
Phosphorylation	1	Microfluidization	1 pass	80	37	Naderi et al. (2016b)
Phosphorylation	1	Microfluidization	2 passes	50	0.2	Naderi et al. (2016b)
Phosphorylation	1	Microfluidization	2 passes	80	10	Naderi et al. (2016b)
TEMPO oxidation	1.6	Double-cylinder homogenizer	–	45	1	Shimizu et al. (2016)
TEMPO oxidation	1.6	Double-cylinder homogenizer	–	80	100	Shimizu et al. (2016)
TEMPO oxidation	1.1	Masuko grinder	–	50	1	Bessonoff and Paltakari (2015)

OP denotes oxygen permeability, and RH the relative humidity in the studies

Table 2 Tensile strength index (TSI) and oxygen permeability (OP) of a never-dried and dried and redispersed NFC_{Carb} (0.6 meq/g, produced by microfluidization at 2% (w/w))

	TSI (kNm/kg)	OP _{RH = 50%} (cm ³ μmm ⁻² d ⁻¹ kPa ⁻¹)	OP _{RH = 80%} (cm ³ μmm ⁻² d ⁻¹ kPa ⁻¹)
Never-dried	166 ± 16	0.4 ± 0.06	9.8 ± 1.6
Redispersed	128 ± 14	0.4 ± 0.05	11.8 ± 1.9

The OP-values were measured at RH = 50 and 80% (23 °C). Reproduction from (Naderi et al. 2017)

impediment to the employment of NFCs in barrier applications. This inadequacy has led to the investigation of the feasibility of several approaches, which can be broadly divided into: (a) Alteration of the chemistry of the nanofibrils prior to film formation. (b) Combination of NFC with different materials. (c) Post-modification of NFC films by the attachment of amphiphilic/hydrophobic moieties. (d) Crosslinking of the nanofibrils in the NFC film. Generally, (a–c) do not lead to significantly improved properties as introduction of “alien” groups through chemical modification onto the nanofibrils only changes a fraction of the surface of the nanofibrils. Furthermore, the creation of nanocomposites by the mixture of NFC and other nano-sized materials requires high amounts of the latter and the employment of complicated mixing processes for the efficient dispersion of the different system components (Liu et al. 2011). And finally, the surface modification of the NFC films by e.g. attachment of amphiphilic moieties onto the NFC films does at the best change the surface properties of parts of the outermost NFC-layer (Lozhechnikova et al. 2014).

Today, crosslinking of the nanofibrils seems as the most viable route for producing effective barriers at high humidity conditions. It is noted that OTR-values in the order of 10–20 cm³ m⁻² d⁻¹ have been suggested (Parry 1993) to fulfil the requirement for atmospheric packaging. Hence, contributions viz. that of Shimizu et al. (2016), showing that OP-values in the order of 0.1 cm³ μmm⁻² d⁻¹ kPa⁻¹ at RH = 80% can be obtained through the crosslinking of NFC_{TEMP} films by multivalent ions, are of particular interest—as the calculated⁵ OTR-values (≈ 1 cm³ m⁻² d⁻¹) are an order of magnitude lower than the above-mentioned threshold.

⁵ OTR can be estimated by knowing the OP and film thickness (that was given by the authors): OTR ~ OP/film-thickness.

Tensile strength measurements on NFC films

Nanofibrillated cellulose films are probably the strongest fabricated cellulosic materials, which makes them potentially interesting for several applications. Tensile strength measurements are an integral part in the quality control of paper and cardboard products, and can therefore potentially be used for the evaluation of NFC-based materials. As it can be expected, the measured mechanical properties of NFC films are highly affected by the sample preparation and measuring protocols. However, contributions in the field are scarce (Olié 2016). The problem is further amplified by the inadequate documentation of the experimental set-ups in the available literature. Nevertheless, the following may be discerned.

An example of the importance of the sample preparation protocol may be distinguished by the comparison of the significantly different TSI values on NFC_{Enz}-based films reported by Henriksson et al. (2008) and Naderi et al. (2016a); see Table 3. It is noted that Henriksson et al. employed microfluidization (which is a high shearing process) for dilution of the investigated NFC_{Enz} (0.03 meq/g), prior to film formation, while Naderi et al. employed gentle magnetic stirring to dilute their system. The importance of the dilution process, may find support in Fig. 1, which shows that the magnitude of pulp concentration (in the mechanical fibrillation step) that leads to the maximum fibrillation of a carboxymethylated pulp is shifted to higher values when microfluidization is employed in the dilution process. Hence, if unnoticed, the employment of high shear dilution protocols leads to erroneous conclusions.

The gathered knowledge, from the paper industry (Borch 2002), proposes that the mode of drying may affect the mechanical properties of NFC films; however, the available literature on the subject with relation to NFCs is contradictory. Sehaqui et al. (2010)

Table 3 Tensile strength index (TSI) values of films based on different NFCs

Pre-treatment process	Fibrillation process	Amount of shearing	≈ Charge density (meq/g)	TSI (kNm/kg)	References
None	Microfluidization	–	–	90	Bessonoff and Paltakari (2015)
Periodate oxidation	Microfluidization	4 passes of diluted NFC	0.017	113 ^a	Larsson et al. (2014)
Carboxymethylation	Microfluidization	6 passes	0.6	170	Aulin et al. (2012)
Carboxymethylation	Microfluidization	1 pass	0.6	166	Naderi et al. (2015a)
CMC-grafting	Microfluidization	1–5 passes	0.17	114–164	Naderi et al. (2015c)
Phosphorylation	Microfluidization	1–3 passes	0.6	54–105	Naderi et al. (2016b)
Phosphorylation	Microfluidization	1–3 passes	0.9	106–143	Naderi et al. (2016b)
Phosphorylation	Microfluidization	7	1.4–1.8	130–150	Ghanadpour et al. (2015)
Enzymatic	Microfluidization	1–5 passes	0.03	113–126	Naderi et al. (2016a)
Enzymatic	Microfluidization	Microfluid. of diluted NFC	0.03	100–150	Henriksson et al. (2008)
TEMPO-oxidation	Homogenizer	?	1.5	150–190 ^a	Fukuzumi et al. (2013)
TEMPO-oxidation	Blender-Ultra sonication	?	? (ζ -potential ≈ –80 mV)	150–210 ^a	Saito et al. (2009)

The table contains information about the mode of fibrillation (machinery and amount of shearing) of the chemically pre-treated NFCs

^a Estimated values obtained by dividing the reported tensile stresses with the assumed density (1.5 g/cm³) of the NFC films

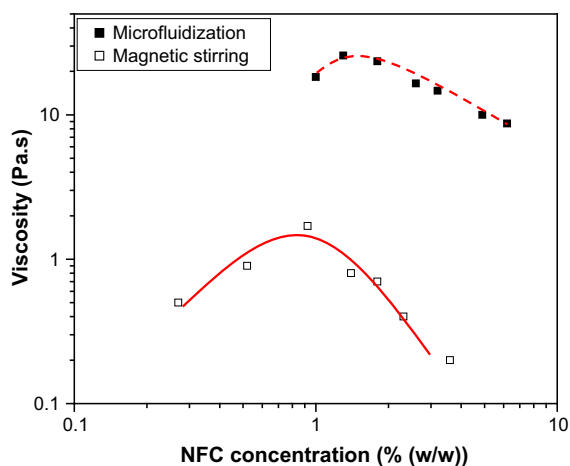


Fig. 1 Shear viscosities of NFC_{carb} systems that have been produced by microfluidization (1 pass) of different concentrations of a carboxymethylated pulp (0.6 meq/g). In each series, the rheological measurements have been conducted at the same NFC concentration, by diluting concentrated NFCs by either microfluidization (to 1% (w/w), Naderi et al. 2014b) or magnetic stirring (to 0.1% (w/w), Naderi et al. 2016a). The aim of the studies was to find the pulp concentration that leads to maximum fibrillation. The lines are to guide the eye

reported that free-standing films (based on an NFC_{enz}) that were prepared by solvent evaporation, had inferior strength compared to films that were prepared by

filtration and drying under restrained conditions. These results are, however, contradicted by the comparison of the mechanical properties of films based on an NFC_{carb} (ca 0.6 meq/g) that have been produced by solvent evaporation (Aulin et al. 2012) or filtration and drying (Naderi et al. 2016a).

Another important parameter (based on the accumulated knowledge in the paper industry; see e.g. Brännvall 2007) in the analysis of the strength of NFC films is the grammage of the films. It is well-known that below a critical grammage the strength of the NFC films rapidly decreases, which may be understood by the increasing impact of film defects. Bessonoff and Paltakari (2015) investigated the impact of grammage of NFC films on the tensile properties of different NFCs. The studies showed that the strength of the NFC films rapidly decreased below a grammage-value of about 40 g/m². Similar findings were recently reported by Olié (2016), who investigated the impact of grammage on TSI of films based on an NFC_{enz} (0.03 meq/g) and an NFC_{carb} (0.6 meq/g). In passing, it is noted that this author also investigated the impact of several other measuring parameters in tensile strength studies. It is interesting to note that NFC films that have been prepared by solvent evaporation have reported grammage values that are considerably

lower than 40 g/m^2 . Hence, these notions may provide an explanation for the contradictory results of Sehaqui et al. (2010) and those of Aulin et al. (2012) and Naderi et al. (2016a).

It may be perceived that the tensile strength of NFC films is defined by the chemical pre-treatment method in the NFC manufacturing process. For example, Naderi et al. (2016a) found that films based on NFC_{Carb} (0.6 meq/g) displayed a high tensile strength index ($\text{TSI} \approx 170 \text{ kNm/kg}$), while films based on NFC_{Enz} (0.03 meq/g) and NFC_{CMC} (0.17 meq/g) displayed significantly lower TSI-values ($\approx 110 \text{ kNm/kg}$, when evaluated at the same amount of shearing). However, the summarized contributions in Table 3 reveal that sufficiently fibrillated NFCs display about the same tensile strength ($\text{TSI} \approx 170 \text{ kNm/kg}$), which incidentally has been proposed by Lindström (2016) to be the highest theoretical value for the strength of NFC films. The exception to this observation is perhaps periodate oxidation (Table 3), which is known to significantly reduce e.g. the degree of polymerization (D.P.) of cellulosic materials (Hou et al. 2007). The importance of D.P. on TSI will be elaborated in the following section.

The ease of fibrillation of the cellulosic materials is, however, highly affected by the pre-treatment process. For example, the low-charged NFC_{Enz} (0.03 meq/g) is very difficult to fibrillate (Naderi et al. 2016a), but highly charged NFCs viz. NFC_{TEMP} , NFC_{Carb} and NFC_{Phos} are more easily fibrillated (Fukuzumi et al. 2013; Naderi et al. 2015a, 2016b). The more interesting revelation from the survey in Table 3 is that introduction of charges in the fibrous system (irrespective of their mode of addition) is beneficial for the fibrillation process. For example, Naderi et al. (2015c) found that the degree of fibrillation of NFC_{CMC} could be significantly improved by increasing the energy consumption in the mechanical fibrillation process. It is noted that NFC_{CMC} is produced by physical grafting of CMC chains onto the outer layers of the cellulosic materials (Laine et al. 2000) prior to fibrillation. On the other hand, the pre-treatment processes of NFC_{Carb} , NFC_{TEMP} and NFC_{Phos} are based on the chemical grafting of charged groups onto the nanofibrils.

Saito et al. (2009) studied the impact of D.P. on the tensile properties of NFC_{TEMP} ($\leq 0.8 \text{ meq/g}$), and found that decreasing the D.P. of the NFC lowered the strength of the corresponding film (Fig. 2). Fukuzumi et al. (2013) investigated the impact of D.P. of NFC_{TEMP} (1.5 meq/g) on the tensile properties of the

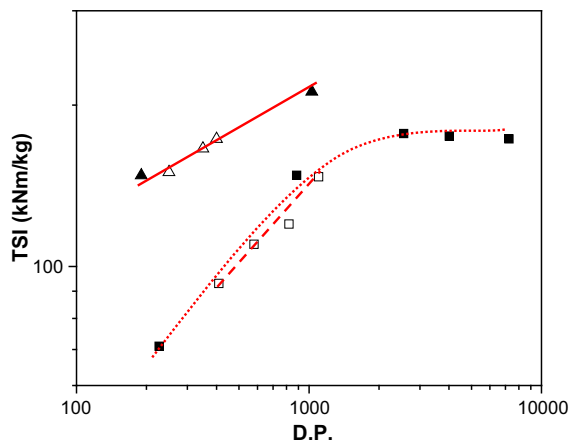


Fig. 2 The impact of D.P. on TSI of NFC films. (*filled square*) NFC_{Carb} (ca 0.6 meq/g), reproduction from (Landmér 2015). (*open square*) NFC_{Enz} (0.03 meq/g), reproduction from Henriksson et al. (2008). (*filled rectangle*) NFC_{TEMP} ($\leq 0.8 \text{ meq/g}$), reproduction from Saito et al. (2009). (*open triangle*) NFC_{TEMP} (1.5 meq/g), reproduction from Fukuzumi et al. (2013). The results of Henriksson et al., Saito et al., and Fukuzumi et al. have been estimated by dividing the reported stress values by the assumed density (1.5 g/cm^3) of the NFC films. The lines are to guide the eye

corresponding films and observed that the tensile strength of the NFC films decreased with the lowering of the D.P. (Fig. 2). On a similar note, Henriksson et al. (2008) observed that the strength of films based on an NFC_{Enz} (presumably low charged) decreased when the D.P. of the pulp decreased (Fig. 2). Interestingly, Landmér (2015) observed that the TSI-values of films based on an NFC_{Carb} (0.6 meq/g) remained unaffected when D.P. of the pulp exceeded a value of about 1000. However, a significant lowering of the tensile strength of films was observed when D.P. decreased below 1000 (Fig. 2). It is interesting to note that a similar critical⁶ D.P. value has been proposed for the strength of cellulose fibres (Gurnagul et al. 1992), which affects the strength of fibrous structures viz. paper sheets.

Centrifugation of NFC suspensions

The ability to estimate the NFC content is highly desirable for quality control purposes, and for process

⁶ The critical value applies for systems in which the degradation process of D.P. is homogeneous and random.

development. However, the highly-entangled state of most NFCs makes the estimation of the nano-fraction of NFCs a virtually insurmountable task. Hence, in the waiting for the development of efficient analytical methodologies the research community has resorted to engineering tools viz. centrifugation. This method assumes that the nanofibril content (NC) in the supernatant (after centrifugation of the highly-diluted sample) increases with the increasing efficiency of the fibrillation process. It is noted that higher charged entities can more effectively resist the centrifugal force than lower charged entities. Hence, care should be taken when comparing NFCs with different charge densities, by centrifugation. In these instances, centrifugation studies must be combined with other analytical methods (viz. tensile strength measurements on NFC films). This point has been raised by Naderi et al. (2016a), who compared the degrees of fibrillation of NFC_{Enz} (0.03 meq/g), NFC_{CMC} (0.17 meq/g) and NFC_{Carb} (0.6 meq/g), by combining several methodologies.

Fall et al. (2011) applied centrifugation on NFC_{Carb} with different charge densities and observed the highest NC for the highest charged system. A similar trend was also observed by Tanaka et al. (2012) who investigated NFC_{TEMP} . Fall et al. (2014) investigated NFC systems based on different wood species and observed a higher NC (by centrifugation of 0.2% (w/w) suspensions) for the species that had a higher hemicellulose content.

The high NFC concentration (0.2% (w/w)) in the centrifugation process of Fall et al. (2014) is noteworthy, as it resides beyond the critical network forming concentration of several NFC systems (Pääkkö et al. 2007; Tanaka et al. 2014). Implications of this notion can be observed in the report of Naderi et al. (2014a), who showed that the suspension concentration should be well below the critical network forming concentration of the system, for the effective separation of the nanofibrils from lesser fibrillated system constituents (Fig. 3).

Naderi et al. (2015a) studied an NFC_{Carb} (0.6 meq/g) that was produced by different amount of shearing, and observed a correlation between NC and shear viscosity (Fig. 4). A correlation between TSI and the nanofibril content was also observed (Fig. 4) for NC up to about 50% (w/w), beyond which TSI plateaued at about 170 kNm/kg. This observation indicates that a very high degree of fibrillation is not required for achieving

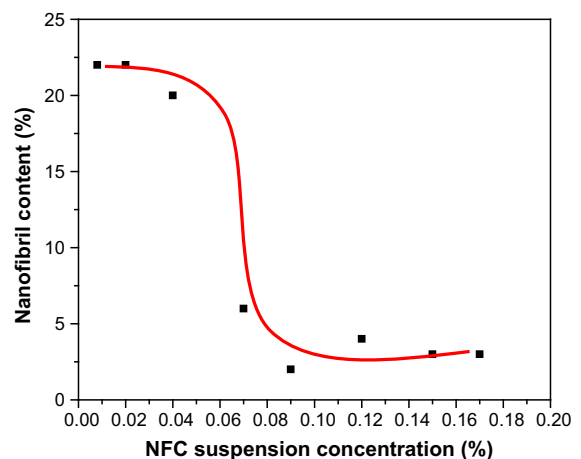


Fig. 3 The impact of NFC_{Carb} (0.6 meq/g) suspension concentration on the apparent nanofibril content as obtained by centrifugation; reproduction from (Naderi et al. 2014a). The line is to guide the eye

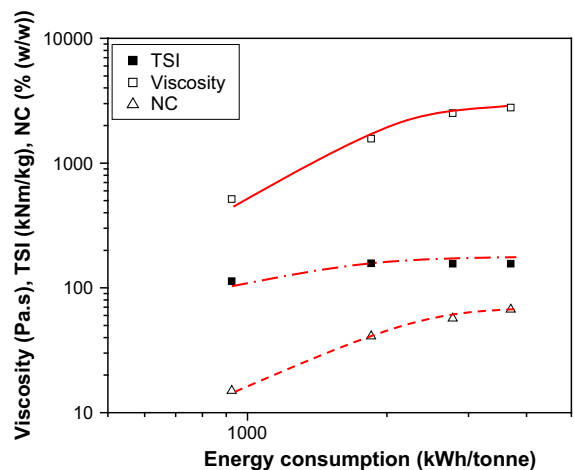


Fig. 4 The impact of amount of shearing (expressed as energy consumption) on the properties of NFC_{Carb} (0.6 meq/g). The shearing was achieved by the repeated microfluidization of a 1.2% (w/w) carboxymethylated system at 400 bar. Reproduction from (Naderi et al. 2015a). The lines are to guide the eye

optimum NFC properties, at least with respect to TSI (and OP, Table 1). It is postulated that a similar conclusion can also be drawn for the rheological properties of NFCs, by e.g. considering the studies of Naderi et al. (2016a). These authors showed that a continued shearing of NFCs beyond their optimum degree of fibrillation results in the deterioration of the rheological properties (due to the proposed shortening of the nanofibrils).

Concluding remarks

In this report, the literature on the properties of NFC was reinvestigated in the light of recent developments in the field of characterization of NFC, and current understandings. The following findings are highlighted:

The success of rheological investigations is dependent on the employment of proper sample handling and measuring protocols. The shear viscosity curves of NFC networks display often a more complex behaviour than highly fibrillated equivalents.

Barrier properties of NFC film, at ambient conditions, are less affected by the crystallinity of the nanofibrils than the ability of the nanofibrils to form dense and rigid structures. Furthermore, the nature of the pre-treatment process has little impact on the property. Interestingly, attractive barrier properties can be obtained by low-fibrillated NFCs, if the degree of fibrillation of the system is above a critical value.

Incorporation of charges in fibrous systems enhances the fibrillation process. Nanofibrillated celluloses based on different pre-treatment processes (except for possibly periodate oxidation) display about the same optimum strength, if the degrees of fibrillation of the NFCs are sufficiently high.

The literature survey proposes the existence of a critical D.P., below which the tensile strengths of NFC films are highly dependent on the magnitude of the D.P. of the fibrillated system.

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