Rheology of aqueous dispersions of Laponite and TEMPO-oxidized nanofibrillated cellulose

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Abstract. The viscoelastic and flow properties of aqueous Laponite/TEMPO-oxidized nanofibrillated cellulose (TEMPO-NFC) systems are investigated with the aim to study the effect of content and proportion of both components on the properties. Both Laponite and TEMPO-NFC aqueous dispersions can find numerous applications in different fields (from industrial to biomedical one) due to their structural and rheological properties. The most important effects of blending are observed at low Laponite fractions, also with qualitative changes in the shape of the flow curves and mechanical spectra. Positive synergistic effects are ascribed to the interpenetration and electrostatic interactions between TEMPO-NFC fibrils and Laponite nanodisks. These mechanisms are more effective in Laponite-poor blends when a minority of clay nanoparticles and its aggregated forms are distributed within the nanocellulose matrix, acting as bridging agents between polymer nanofibrils. The synergistic effects are compared to those observed for Laponite blends with a nonionic biopolymer, scleroglucan.

Keywords. TEMPO-oxidized nanofibrillated cellulose, Laponite, blending effects, hydrogels, rheology

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1. INTRODUCTION

Nanocellulose is, due to its highly abundant feedstock, a promising biopolymeric material (Dufresne, 2012; Lin & Dufresne, 2014; Lindström, 2017; Naderi, 2017) for different applications including medical/pharmaceutical products (Hoeng, Denneulin, & Bras, 2016; Jackson et al., 2011; Kim et al., 2015; Leppiniemi et al., 2017). Biocompatible, non-toxic and biodegradable physical hydrogels made of nanocellulose may be quite interesting in the preparation of controlled/sustained drug release systems and other biomedical devices. For example, TEMPO-oxidized nanofibrillated cellulose (TEMPO-NFC) hydrogels have been designed for controlled drug delivery (Paukkonen et al. 2017; Weishaupt et al., 2015) and other advanced applications in biomedical field (Cheng, Park, & Hyun, 2014; Halib et al., 2017; Lin & Dufresne, 2014; Park, Lee, & Hyun, 2015; Rees et al., 2015; Zander, Dong, Steele, & Grant, 2014). Incorporation of non-toxic nanoparticles, such as clay nanodisks, in a biopolymer hydrogel structure can further improve its properties and performance, which derive from weak interchain associations due to chain entanglements, hydrogen bonds, ionic bonds or strong van der Waals interactions between chains, hydrophobic interactions or crystallites bringing together two or more macromolecular chains. In the present work Laponite, a synthetic hectorite belonging to the family of (2:1) phyllosilicates, widely used as a rheology modifier in cosmetics and pharmaceuticals, is added to aqueous TEMPO-NFC matrix. To the best of our knowledge the aqueous Laponite/TEMPO-NFC dispersions have not been studied yet.

Nanofibrillated cellulose (NFC) produced from plants and bacteria by mechanical and chemical methods (Abdul Khalil et al., 2014; Dufresne, 2012; Klemm, Heublein, Hink, & Bohn, 2005; Klemm et al., 2011) consists of fibrils with a diameter of nanometer scale. Highly fibrillated nanocellulose has been obtained by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) mediated oxidation pretreatment (Johnson, Zink-Sharp, & Glasser, 2011; Saito & Isogai, 2004; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006; Saito, Kimura, Nishiyama, & Isogai, 2007; Isogai, Saito, & Fukuzumi, 2011; Sirvio et al., 2014). The TEMPO pretreatment introduces a negative charge to the fibrils' surface by converting the primary -OH groups of cellulose D-glucose units into -COO⁻ groups. At concentrations higher than 0.1 wt.% (Mendoza, Batchelor, Tabor, & Garnier, 2018b), aqueous TEMPO-NFC suspensions exhibit stable physical hydrogel properties (Jowkarderis & van de Ven, 2014; Jowkarderis & van de Ven, 2015; Naderi & Lindström, 2014; Nechyporchuk, Belgacem, & Pignon, 2016). The hydrogel microstructure, which is affected by pH value and ionic strength of the aqueous phase and nanocellulose particle morphology, surface charge and

hydrophilicity, can be described as highly entangled and physically interconnected network with water-trapping properties (Chen, Zhu, & Tong, 2016; Martoia et al., 2015; Martoia, Dumont, Orgeas, Belgacem, & Putaux, 2016; Naderi, Lindström, & Sundström, 2015b). Increased TEMPO-NFC concentration and fibrillation level result in a formation of a more tangled nanocellulose network of higher elastic properties. Therefore, it is not surprising that most of the previous studies dealing with the rheological behavior of TEMPO-NFC suspensions are focused on the dependence of rheological properties on TEMPO-NFC particle properties and concentration (Benhamou, Dufresne, Magnin, Mortha, & Kaddami, 2014; Lasseuguette, Roux, & Nishiyama, 2008; Mendoza et al., 2018b; Naderi et al., 2015b; Nechyporchuk, Belgacem, & Pignon, 2015). The effects of suspension pH value, carboxyl content, and addition of cations have been commonly studied as well (Besbes, Alila, & Boufi, 2011; Benhamou et al., 2014; Dong, Snyder, Williams, & Andzelm, 2013; Jowkarderis & van de Ven, 2014; Jowkarderis, & van de Ven, 2015; Mendoza et al., 2018b; Naderi & Lindström, 2016; Saito, Uematsu, Kimura, Enomae, & Isogai, 2011; Zander et al., 2014). All rheological investigations have shown that TEMPO-NFC hydrogels exhibit shear thinning and thixotropic behavior (Benhamou et al., 2014; Lasseuguette et al., 2008; Mendoza, Gunawardhana, Batchelor, & Garnier, 2018a; Mendoza et al., 2018b; Saito et al., 2007). Despite important reduction of particle swelling ability and suspension viscoelasticity that have been observed when nanocelluloses of different types were dried and re-dispersed in water (Hubbe et al., 2017; Naderi, Lindström, Sundstrom, & Flodberg, 2015a; Okiyama, Motoki, & Yamanaka, 1993; Peng, Gardner, & Han, 2012; Voronova, Zakharov, Kuznetsov, & Surov, 2012; Zepic et al., 2014; Zimmermann et al., 2016), the accessibility of dried nanocellulose offers potentials for novel TEMPO-NFC hydrogel blends and applications. In our previous publication (Šebenik, Krajnc, Alič, & Lapasin, 2018), development of rheological properties of hydrogels prepared from a commercially available freeze-dried TEMPO-NFC powder was investigated. Congruent concentration and ageing effects were observed, i.e. the increase of shear viscosity and viscoelastic parameters with concentration and time was significant. Obtained results are useful for several applications of nanocellulose hydrogels and its blends, such as those with Laponite.

Single layer Laponite nanoparticles are rigid, disk-shaped crystals with an average diameter and thickness around 30 nm and 1 nm, respectively. In the dry state, single layer Laponite particles are stacked and held together electrostatically by sharing sodium ions in the interlayer region, forming tactoids. Upon dispersing Laponite in aqueous media, water enters the inter-disk spaces, tactoids swell, Na⁺ ions dissociate and diffuse out of the stacks

causing a permanent negative charge of faces of Laponite disks. On the other hand, the edge of a particle has small positive charge (typically ~10% of the negative charge of the crystal faces) due to protonation of the hydroxyl groups. Owing to their peculiar features (heterogeneous surface charge distribution, high aspect ratio, extremely high specific surface area and narrow size distribution), Laponite nanodisks can spontaneously self-assemble and give origin to different microstructural arrangements, depending on the relative weight of interparticle attractive (rim–face) and repulsive (face–face, rim–rim) electrostatic interactions, ruled by particle concentration and ionic strength. Marked shear thinning and elastic behavior of aqueous Laponite dispersions is observed when the interactions are so effective that they lead to arrested states. In salt-free aqueous systems (ionic strength $\approx 2 \times 10^{-4}$ M), attractive gel and repulsive glass have been individuated at lower and higher Laponite concentrations, respectively (Ruzicka, Zulian, & Ruocco, 2004). However, various studies have been performed to define the state diagram of aqueous Laponite dispersions (Gabriel, Sanchez, & Davidson, 1996; Jabbari-Farouji, Tanaka, Wegdam, & Bonn, 2008; Levitz, Lécolier, Mouchid, Delville, & Lyonnard, 2000; Mongondry, Tassin, & Nicolai, 2005; Cummins, 2007; Mouchid, Delville, Lambard, Lécolier, & Levitz, 1995; Mouchid, Lécolier, Van Damme, & Levitz, 1998; Ruzicka et al., 2004; Tanaka, Meunier, & Bonn, 2004; Tanaka, Jabbari-Farouji, Meunier, & Bonn, 2005). When interpreting and comparing results of different studies, attention must be paid to protocols of dispersion preparation and Laponite properties (Ruzicka & Zaccarelli, 2011). Sharp transitions in flow properties and linear viscoelastic behavior have been observed with increasing time elapsed after dispersion preparation (Lapasin, Abrami, Grassi, & Šebenik, 2017; Lapasin, Grassi, Abrami, & Šebenik, 2020).

In our previous study aqueous Laponite-scleroglucan mixed systems were prepared by blending Laponite and scleroglucan hydrogels (Lapasin et al., 2017). The hybrid systems displayed rheological properties superior to those anticipated by applying the linear mixing rule to corresponding simple systems, which was especially evident for Laponite rich blends. On the other hand, when Laponite powder was added to previously formed scleroglucan hydrogel, viscous and linear viscoelastic behavior did not change qualitatively and remained similar to those of a typical physical polymer gel. Scleroglucan is a nonionic polysaccharide. Addition of ionic compounds to aqueous Laponite dispersions usually shortens the time required for the transition to arrested state. For example, electrostatic attractions between anionic side groups of a (bio)polymer and positively charged edges of Laponite particles can result in changes in the dynamics of aging and increased stability of the clay dispersion, if

the neutralizing cations (usually sodium) effectively screen the negative charges on Laponite particles' faces (Lapasin et al., 2017). Obviously, interactions of an anionic (bio)polymer with Laponite particles depend on the polymer properties, such as type, density of anionic sites, backbone flexibility and hydrophobicity, branching degree and average molecular weight (Fitch, Jenness, & Rangus, 1991). However, connections between Laponite particles' rims, established by polyelectrolyte chains, make possible the formation of a dense gel network structure, as observed in cases of Laponite/sodium polystyrene sulfonate (Savenko, Bulavin, Rawiso, & Lebovka, 2014), Laponite/carboxymethylcellulose (Fitch et al., 1991), Laponite/xanthan (Lapasin, 2016; Maiutto, 2005) and Laponite/alginate (Davila & d'Ávila, 2017) systems.

As mentioned above, TEMPO-NFC is a chemically modified nanocellulose, a biopolymer with fibrils containing carboxylate groups, which in aqueous dispersions shows stable physical gel properties at pH values near to or above the pKa value of the carboxylic acids. On the other hand, recently, a chemical stability phase diagram has been proposed which indicates that aqueous Laponite dispersions having higher concentrations of Laponite and salt are more stable, whereas Laponite particles in dispersion are more prone to degradation with increase in time elapsed since preparation (Mohanty & Joshi, 2016). Conversely, contrary to the usual belief, initial pH value of water over the range 3-10 has practically no effect on chemical degradation (Jatav & Joshi, 2014).

Therefore, aqueous Laponite/TEMPO-NFC blends appear to be worthy of consideration for biomedical applications, in particular for the preparation of hydrogel-based release systems with targeted fast release in acidic conditions and diffusion-controlled release in a wide pH range. Laponite addition to TEMPO-NFC weak gel could contribute to faster developing of final gel properties (aging), better control the kinetics of release as well as to improve the mechanical properties of the matrix. Starting from these practical perspectives, the present work has been addressed to study the rheological properties of aqueous Laponite-TEMPO-NFC mixed systems, in particular, to examine the effect of blend composition on its viscoelastic and flow properties. The synergistic effects created by blending are compared to those observed for Laponite/scleroglucan.

2. EXPERIMENTAL

2.1 Materials

Freeze-dried TEMPO-NFC powder, made from wood pulp, with chemical formula $[(C_6H_{10}O_5)_x(C_6H_9O_4COONa)_y]$ was purchased from The Process Development Centre,

University of Maine (UMaine PDC), USA. According to specifications given by the producer its carboxylate level is 0.2-2 mmol/g solids, NFC structure is branched or forked, with dimensions of 20-50 nm in width and lengths of up to several microns. The determined carboxylate content was 1.4 mmol/g solids. The determined aldehyde content was 0.58 mmol/g solids.

Laponite®XLG (provided by Rockwood Additives Ltd, UK) is a synthetic purified hectorite with high surface area (BET 370 m²/g). Laponite nanoparticles are rigid, disk-shaped crystals with an average diameter of 30 nm and a thickness of 1 nm.

2.2 TEMPO-NFC characterization

The carboxylate content in the purchased material was determined by conductometric titration. TEMPO-NFC powder was suspended in demineralized water (100 mg/100 mL). pH value was adjusted to 3.0 using 0.05 M HCl. The suspension was titrated with 0.011 M NaOH to pH value 11.

NaOH titration after addition of NH₂OH·HCl solution was used to determine the content of aldehyde groups. pH value of the suspension (100 mg of TEMPO-NFC was suspended in 100 mL of demineralized water) was adjusted to 3.5 by adding 0.1 M HCl. 10 mL of 5 wt % NH₂OH·HCl solution (pH value of 3.5) was added, mixture was stirred and titrated back to pH value 3.5 using 0.0973 M standardized NaOH solution.

2.3 Sample preparation

A 2.00 wt% aqueous TEMPO-NFC gel sample was prepared by slowly adding demineralized water with 0.02 wt% of NaN₃ (to prevent eventual microbiological contamination) to TEMPO-NFC freeze-dried powder. The non-homogeneous dispersion was stirred at 500 rpm using a four-blade propeller stirrer. After 2 h, the dispersion was placed in an ultrasonic bath for 1 h. Then the obtained dispersion was stirred over night at 750 rpm at room temperature. The sample pH value was 7.

A 2.00 wt% Laponite dispersion was prepared by gradually adding Laponite powder to distilled water under mechanical stirring. The obtained dispersion with pH value 7 was stirred for additional 2 h at 750 rpm using the propeller stirrer.

TEMPO-NFC and Laponite gel samples of lower concentrations were obtained by diluting the 2.00 wt% samples and stirring (four-blade propeller stirrer, 2 h at 750 rpm, room temperature). Transparent, homogeneous dispersions with pH value 7 without visible NFC or Laponite particles were achieved.

Laponite/TEMPO-NFC aqueous dispersions were prepared by blending Laponite and TEMPO-NFC simple systems. The blends were prepared 1 day after the preparation of the

205 simple systems was completed. For dilution, where necessary, distilled water containing
 206 0.02 wt% of NaN_3 was added. For homogenization the same stirring procedure was
 207 employed (four-blade propeller stirrer, 2 hours at 750 rpm, room temperature).
 208 It has been shown previously (Lapasin et al., 2017; Šebenik et al., 2018) that rheological
 209 parameters of freshly prepared aqueous Laponite and TEMPO-NFC dispersions change
 210 with time until a stable dispersion structure is developed. Therefore, after their preparation,
 211 separate samples of each system were stored in fridge at temperature of 8°C before being
 212 examined at different times.

213 **2.4 Instrument and experimental procedures**

214 The rheological measurements were performed at 25 °C. Properties were investigated on
 215 Anton Paar Physica MCR 301 rheometer equipped with 50 mm diameter crosshatched
 216 plate-plate geometry using 1 mm gap. To prevent water evaporation a glass solvent trap
 217 cover was used.

218 The steady flow behavior of the samples was determined by applying an increasing
 219 sequence of constant stress segments and measuring the corresponding shear rate.
 220 Frequency sweep measurements were performed within the linear viscoelasticity range,
 221 which was defined by oscillatory stress sweep tests at 1 Hz

222 **2.5 Models for data correlation**

223 The experimental viscosity data, when using shear rate as independent variable, were fitted
 224 using the Cross equation (Cross, 1965):

$$225 \quad \eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\lambda \dot{\gamma})^n} \quad [1]$$

226 In Eq. (1), η_0 and η_{∞} are the asymptotic values of the viscosity at zero and infinite shear
 227 rates, respectively, λ is the characteristic time and n measures the shear rate dependence
 228 of viscosity in the power law region. The critical shear stress σ_{cr} is calculated from the critical
 229 shear rate $\dot{\gamma}_{cr}$, i.e. from the reciprocal of the relaxation time λ .

230 When using shear stress as independent variable, the Roberts–Barnes–Carew (RBC) model
 231 was applied (Roberts, Barnes, & Carew, 2001):

$$232 \quad \eta = \eta'_{\infty} + \frac{\eta'_0 - \eta'_{\infty}}{1 + (\sigma/\sigma_c)^m} \quad [2]$$

233 In Eq. (2) σ_c is the critical stress, which positions the transition region between the high-
 234 viscosity Newtonian plateau at low shear stress and low-viscosity Newtonian plateau at high
 235 shear stress. For high m values (m describes the rate of viscosity decrease in the transition
 236 region) σ_c is the apparent yield stress. The RBC model is more flexible than the original Ellis

equation (Ellis, 1927), since it contains η'_0 and η'_∞ functions of the shear stress:

$$\eta'_0 = \frac{\eta_0}{1+(\sigma/\sigma_1)^p} \quad [3]$$

$$\eta'_\infty = \eta_\infty[1 + (\sigma/\sigma_2)^s] \quad [4]$$

σ_1 and σ_2 (critical shear stresses in the composite Ellis model), p (a dimensionless exponent) and s (a dimensionless power-law exponent) are adjustable parameters likewise the η_0 and η_∞ . The RBC model includes three characteristic stresses, $\sigma_1 < \sigma_c < \sigma_2$. The critical stress σ_{cr} marking the transition from the upper Newtonian plateau to the shear thinning region can be assumed to be equal to σ_1 , while σ_c belongs to the intermediate shear thinning region or individuates the viscosity drop in plastic systems, so representing an apparent yield stress. A strict correlation between σ_1 and σ_c is generally found.

The experimental data obtained by frequency sweep tests, were described by the classical generalized Maxwell (GM) model (or Maxwell-Wiechert model). 5 Maxwell elements were enough to fit the data of mechanical spectra. Eq. (5) describes how the elastic modulus depends on frequency. Eq. (6) gives the frequency dependence of the viscous modulus:

$$G' = G_e + \sum_{i=1}^5 \frac{G_i \lambda_i^2 \omega^2}{1 + \lambda_i^2 \omega^2} \quad [5]$$

$$G'' = \sum_{i=1}^5 \frac{G_i \lambda_i \omega}{1 + \lambda_i^2 \omega^2} \quad [6]$$

G_e is the equilibrium modulus ($\omega \rightarrow 0$), while G_i and λ_i are the relaxation modulus and the relaxation time of the i^{th} Maxwell element, respectively. The recurrent constraint for the relaxation times ($\lambda_{i+1} = 10\lambda_i$) was applied in the minimization procedure in order to reduce the correlation degree between the adjustable parameters.

3. RESULTS AND DISCUSSION

3.1 Rheological behavior of simple systems at different concentrations

In the first section the rheological characterization of aqueous dispersions containing only TEMPO-NFC or Laponite (simple systems) at different concentrations (2.0, 1.5, and 1.0 wt%) is shown to draw the necessary background for the investigation of blends. More rheological data on aging of the simple systems can be found elsewhere (Lapasin et al., 2017; Šebenik et al., 2018). Rheological properties of the samples were measured at different times after their preparation. In Fig. 1 the flow curves after 20 and 80 days of storage are shown. To be exact, the 1.0 and 1.5 wt% samples were measured on days 26

267 and 83, while 2.0 wt% samples were measured on days 21 and 85.

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269

270 **Fig. 1: Flow curves for 2.0, 1.5 and 1.0 wt% Laponite (L) and TEMPO-NFC (NFC) dispersions after 20**
 271 **(Fig. 1A) and 80 days (Fig. 1B) of storage. The lines show RBC model predictions.**

272

273 All the Laponite systems exhibit a quite evident plastic behavior (Fig. 1). As expected
 274 (Lapasin et al., 2017), the effects of a prolonged aging of Laponite dispersions, higher
 275 viscosities at low shear and higher yield stress values, become more significant with
 276 decreasing nanoclay concentration. Consequently, the effect of concentration on the flow
 277 behavior progressively diminishes with increasing aging time. As discussed elsewhere
 278 (Lapasin et al., 2017), the time elapsed after dispersion preparation plays an important role
 279 in the Laponite particles' structural reorganizations, which includes clay particles
 280 delamination and rearrangement of discoidal nanoparticles due to edge-face attraction and
 281 edge-edge and face-face repulsion.

282 Less important are the aging effects for TEMPO-NFC systems with respect to the changes
 283 deriving from a concentration increase. In the interval between 1.0 % and 1.5 % the shear
 284 thinning response becomes very pronounced and plastic at 2.0 %, where the apparent yield
 285 stress is around 10 Pa. If compared to the corresponding Laponite system, such a value is
 286 one decade lower as well as the zero-shear viscosity is two decades lower. Moreover, we

287 can remark another difference between the most concentrated systems; the flow curve of
288 2.0% Laponite dispersion shows a dramatic viscosity drop whereas the transition to high
289 shear conditions is smoother for the corresponding TEMPO-NFC system.

290 The slower time evolution of viscosity for TEMPO-NFC systems can be assigned to
291 hydration and swelling of nanocellulose particles, consisted of several fibrils. When particles
292 swell both the effective volume fraction of the disperse phase and the importance of the
293 interparticle physical interactions increase (Šebenik et al., 2018).

294 The lines reported in Fig. 1 show the good agreement between the experimental data and
295 the RBC model predictions. Equivalent quality of data fitting was achieved by the Cross
296 equation. Material properties of the simple systems, the zero-shear viscosity values
297 (obtained by the Cross and RBC models), critical shear stress and viscoelastic moduli
298 (measured at 1 Hz), are given in Appendix A.

299 Mechanical spectra at different aging times are reported in Fig. 2. The lines show the good
300 quality of the GM model predictions. The effects of prolonged aging become more evident
301 with decreasing concentration for both systems (Laponite and TEMPO-NFC). The
302 mechanical spectra of all the Laponite dispersions display the typical feature of gel systems:
303 the storage modulus is nearly independent of frequency, being its values markedly higher
304 (more than one decade) than those of the loss modulus in the whole frequency window
305 between 0.1 and 100 rad/s. The linear viscoelastic behavior of the TEMPO-NFC systems is
306 characterized by lower values of both moduli, being the difference from the corresponding
307 Laponite responses more and more pronounced with decreasing concentration. In the case
308 of TEMPO-NFC 2.0% system both elastic and viscous moduli show a slight frequency
309 dependence, with G' higher than G'' , being the traces slightly convergent at increasing
310 frequency. At lower concentration (1.5 %) a crossover condition is attained (above 10 rad/s)
311 after 26 days of aging, which shifts to higher frequency with increasing aging time, since G'
312 increases more than G'' . Consequently, a more extended plateau region can be individuated
313 at lower frequencies. The linear viscoelastic response of the less concentrated TEMPO-
314 NFC system (not shown in Fig. 2) can be experimentally determined with sufficient accuracy
315 only in a narrow frequency range, owing to the low values of both moduli.

316

Fig. 2: Frequency dependence of viscoelastic moduli for 2.0 (Fig. 2A) and 1.5 wt% (Fig. 2B) Laponite (L) and TEMPO-NFC (NFC) dispersions after 20 and 80 days of storage. Lines show GM model predictions.

Fig. 3 reports a comparison of mechanical spectra of Laponite and TEMPO-NFC systems of different concentrations after prolonged aging. Here, we can observe that the linear viscoelastic response of the less concentrated TEMPO-NFC system is essentially reduced only to the viscous component even after 80 days of storage – the G' curve could not be constructed due to its very low and unreliable values.

Fig. 3: Frequency dependence of viscoelastic moduli for 2.0, 1.5 and 1.0 wt% Laponite (L) and TEMPO-NFC (NFC) dispersions after 80 days of storage. Lines show GM model predictions.

330

331 **3.2 Rheological behavior of blends at different concentrations and Laponite** 332 **fractions**

333 The content and proportion of TEMPO-NFC and Laponite affect the viscoelastic and flow
334 properties of the dispersion. In view of practical applications, such as controlled drug
335 delivery, it is important to quantify the effects and to explain them by appropriate structural
336 properties and rearrangements. A short selection of data is reported in Fig. 4 and 5 to give
337 a synthetic but significant look at the effects of blending, aging and total solids content.

338 The limited effect of prolonged aging for 1.5 wt.% Laponite system and blends can be
339 evinced by comparing Fig. 4A and 4B. A more pronounced effect can be observed for the
340 simple TEMPO-NFC system. Similar considerations can be made for concentrations 1.0 and
341 2.0 % of total solids, which is not illustrated in the figures.

342 The most important effects of blending are observed at low values of the Laponite fraction
343 Φ_L (i.e. the Laponite weight fraction in the solids content of the system). Qualitative changes
344 in the shape of the flow curve and larger viscosity differences occur in the range from 0 to
345 0.25 of Laponite fraction, more evident at lower total concentration, which may be observed
346 by comparison of curves shown in Fig. 4B, 4C and 4D.

347 Similar considerations can be deduced from the analysis of the corresponding mechanical
348 spectra. A more prolonged aging leads to an increase of both moduli, which is almost
349 uniformly distributed along the frequency axis. In the case of TEMPO-NFC system, the
350 curves of both moduli shift not only vertically but also toward higher frequencies so that a
351 more extended plateau region can be observed within the experimental frequency window.

352 The generalized Maxwell model gives a satisfactory data fitting, so that all the mentioned
353 effects can be quantitatively examined through the variations of the equilibrium modulus G_e
354 and the relaxation time spectrum $g_i-\lambda_i$. The example given in Fig. 6A and 6B illustrates the
355 effect of blending for systems with 1.5 % of solids content on day 26.

356

357

Fig. 4: Flow curves of blends with different Laponite fractions: 1.5 wt% of total solids after 20 (Fig. 4A) and 80 (Fig. 4B) days; 2.0 wt% of total solids after 80 days (Fig. 4C); and 1.0 wt% of total solids after 80 days (Fig. 4D). The lines show RBC model predictions.

Fig. 5: Frequency dependence of viscoelastic moduli for blends with different Laponite fractions: 1.5 wt% of total solids after 20 (Fig. 5A) and 80 (Fig. 5B) days; 2.0 wt% of total solids after 80 days (Fig. 5C). Lines show GM model predictions.

Fig. 6: Viscoelastic parameters (G_e and g_i) obtained by fitting using GM model for 1.5 wt% solid contents on day 20: G_e on Laponite fraction dependence (Fig. 6A); The relaxation time spectra g_i - λ_i for blends with different Laponite fractions (Fig. 6B). The lines are drawn for easier reading of the results.

Particularly evident are the synergistic effects produced by blending the TEMPO-NFC dispersion with Laponite system, especially at low Laponite fractions. The equilibrium modulus increases for approximately two decades, while the relaxation time spectrum shifts to higher g_i values, more significantly for higher λ_i values. The spectrum acquires a shape typical of gel systems - similar to that of simple Laponite spectrum. The slower relaxation mechanism on longer length scales might be ascribed to the attractive interactions between carboxylic groups of TEMPO-NFC fibrils and positively charged rims of Laponite nanodiscs, which hence play the role of bridging agents.

The analysis of the linear viscoelastic behavior can be alternatively performed in a more convenient way by using the values of both moduli at a given frequency (e.g. 1 Hz) as a reference guide. So doing, two diagrams are sufficient to illustrate the effects blending and total concentration. The Fig. 7D confirms the moderate effects of aging, previously deduced from Fig. 5A and 5B. The effects of blending and total concentration are similar for G' and G'' at different aging times, with similar increases with increasing total concentration. The G' increase with increasing Laponite fraction is more pronounced than G'' increase, particularly at low Laponite fractions. The increasing elastic character of the systems with increasing Laponite fraction is clearly observable in Fig. 7C.

Fig. 7: Viscoelastic moduli (G' -filled symbols, G'' - corresponding empty symbols) measured at 1 Hz vs Laponite fraction after 20 days (Fig. 7A) and 80 days (Fig. 7B). Loss factor ($\tan \delta$) measured at 1 Hz vs Laponite fraction after 80 days (Fig. 7C). The lines are drawn for easier reading of the results. Viscoelastic moduli vs aging time for 2.0 wt% solid content and different Laponite fractions (Fig. 7D).

Passing from viscoelastic quantities to viscosity data, similar trends are obtained for the dependence of the zero-shear viscosity on Laponite fraction and similar considerations can be derived from them about the effects of aging, blending and total concentration. Fig. 8A and 8B report the value of the zero-shear viscosity obtained from data correlation with the Cross equation. The curves in Figs. 8A and 8B are calculated with the blending model, illustrated hereafter. Fig 8C proves the moderate effect of aging on eta-zero values.

Fig. 8: Zero-shear viscosity (η_0) obtained by Cross model vs Laponite fraction after 20 days (Fig. 8A) and 80 days (Fig. 8B). Zero-shear viscosity (η_0) obtained by Cross model vs aging time for 2.0 wt% solid content and different Laponite fractions (Fig. 8C).

If we refer to data fitting with the RBC model, a quite similar graphical representation is obtained, with the only difference of systematically higher values. Indeed, $\eta_{0,RBC}$ and $\eta_{0,Cross}$ are strictly related to each other ($\eta_{0,RBC} = 1.32 \eta_{0,Cross}^{0.98}$, $R^2 = 0.993$). A good correlation is found also between the zero-shear viscosity and the critical stress σ_{cr} , marking the transition from the lower Newtonian plateau to shear thinning region or plastic flow (yield stress) ($\sigma_{cr} = 0.0063 \eta_{0,RBC}^{0.69}$, $R^2 = 0.993$).

3.3 Analysis of synergistic effects

All the previous findings clearly indicate that positive synergistic effects arise from blending

TEMPO-NFC with Laponite systems, particularly important for low Laponite fractions. All the rheological quantities characterizing the viscous and linear viscoelastic behaviors undergo a significant increment and this can be reasonably ascribed to the interpenetration and electrostatic interactions between TEMPO-NFC fibrils and Laponite nanodisks. These mechanisms are more effective in Laponite-poor blends where a minority of clay nanoparticles and its aggregated forms are distributed within the nanocellulose matrix, acting as bridging agents between polymer nanofibrils. In Laponite-rich systems the structural organization is mainly governed by nanodisk edge-face interactions, sufficiently numerous to give origin to a gel network, and then the contribution of nanocellulose fibrils becomes less important.

The synergistic effects can be better highlighted by adopting a reference model, i.e. an ideal mixing rule for blends without interactions. To this purpose, the logarithms of $G'_{1\text{Hz}}$, $G''_{1\text{Hz}}$ and η_0 are assumed as the reference quantities. In absence of TEMPO-NFC interactions with Laponite and synergistic effects a linear additivity of the reference quantities, according to Eqs. (7) and (8), is assumed. In Eq. (8), the values of reference quantities for the simple TEMPO-NFC and Laponite systems (Y_{NFC} and Y_L) are pondered by the Laponite fraction ϕ_L to calculate the reference value for the blend predicted by the ideal mixing rule. Deviations from the linear mixing rule predictions are measured by the excess functions ΔY , which may be positive or negative for positive or negative synergistic effects, respectively (Grunberg & Nissan, 1949; McAllister, 1960):

$$\Delta Y = Y_{exp} - Y_{id} \quad (Y = \log \eta_0, \log G', \log G'') \quad [7]$$

$$Y_{id} = Y_{NFC} + \phi_L(Y_L - Y_{NFC}) \quad [8]$$

In Eqs. (7) and (8), the suffixes *exp* and *id* stand for measured value and value predicted by the linear mixing rule, respectively. The dependence of the excess function ΔY on Laponite fraction can be described by:

$$\Delta Y = B(1 - \phi_L)^a \phi_L^c \quad [9]$$

Eq. (9) is a modified version of the Grunberg-Nissan equation and is similar to that used to describe the mixing effects in pigment concentrate blends (Lapasin, Desobgo Nguépi, & Costa 2002). B , a and c are fitting parameters used for data fitting in Fig. 9.

It can be observed in Fig. 9 that blending effects on viscosity and moduli are similar, $\log \eta_0$, $\log G'$ and $\log G''$ deviations from the linear mixing rule show comparable profiles in dependence of blend composition. For TEMPO-NFC/Laponite blends the effect of blending is maximal when blends are poor in Laponite and diminishes with increasing nanoparticles

455 content. More specifically, if the excess functions of viscoelastic properties are compared
 456 (Fig. 9B), the elastic component is affected at most. At sufficiently low Laponite amount and
 457 total solids concentration, the attraction between cellulose nanofibrils containing COO^-
 458 groups and positively charged rims of Laponite discs contributes significantly to the elastic
 459 behavior. With increasing Laponite amount the contribution of edge-face attraction and
 460 edge-edge and face-face repulsion for Laponite nanodiscs becomes more and more
 461 important for the viscoelastic response. At 95 % Laponite amount negative values of moduli
 462 excess functions were found, especially at higher total solids amounts, which can be
 463 attributed to disruption of highly coordinated Laponite structure in the presence TEMPO-
 464 NFC. On the other hand, by keeping the fraction of Laponite low and increasing the total
 465 solids amount the contribution of nanocellulose fibers interactions (entanglements,
 466 noncovalent and covalent interactions) prevails. As possible physical interactions not only
 467 hydrogen bonding and van der Waals interactions but also electrostatic repulsion should be
 468 identified in this case. On the other hand, covalent crosslinking of nanofibrils may occur via
 469 hemiacetal formation from aldehyde groups, which are introduced on the nanofibril surface
 470 during TEMPO modification.

472 **Fig. 9. Excess functions for zero-shear viscosity (Fig. 9A) and viscoelastic moduli (Fig. 9B) of TEMPO-**
 473 **NFC/Laponite blends with different Laponite fraction (Φ_L) after 20 days of aging. The curves are**
 474 **calculated with the blending model.**
 475

476

477 An opposite trend in the positive synergistic effects was observed when
 478 scleroglucan/Laponite blends were investigated (Lapasin et al., 2017). Excess functions for
 479 zero-shear viscosity and viscoelastic moduli for 2 % scleroglucan/Laponite blends with
 480 different Laponite fraction after 20 days of aging are compared in Fig. 10.

481 For scleroglucan/Laponite blends the positive effect of blending was maximal when blends
 482 were rich in Laponite. The excess function of the viscous component of the viscoelastic
 483 behavior was more affected than the elastic one. Scleroglucan is a nonionic polysaccharide,
 484 which primary structure consists of a linear backbone of (1,3)- β -linked D-glucopyranosyl
 485 residues bearing a single (1,6)- β -linked D-glucopyranosyl unit every three sugar residues of
 486 the main chain (Rinaudo & Vincendon, 1982). In aqueous solution (and also in the solid
 487 state), scleroglucan adopts a highly ordered, rigid, triple helical tertiary structure (triplex).
 488 Therefore, the presence of scleroglucan in Laponite rich systems significantly reduces,
 489 through the steric hindrance, the effect of the face-face and rim-rim repulsion on the
 490 viscoelastic properties. In other words, the nonionic polysaccharide cannot contribute to
 491 elastic behavior through ionic interactions with Laponite.

492

493 **Fig. 10. Comparison of excess functions for 2% TEMPO-NFC/Laponite blends (A) with**
 494 **Scleroglucan/Laponite blends (B) of the same concentration with different Laponite fraction (Φ_L) after**
 495 **20 days of aging. The curves are calculated with the blending model.**

496

497 **4. CONCLUSIONS**

498 Different types and grades of TEMPO-NFC/Laponite hydrogel structures were obtained by
499 blending Laponite and TEMPO-NFC dispersions, by varying their ratio and total solids
500 content. Up to 95 wt% of Laponite content in the total solids, the rheological properties of
501 hydrogels were superior to those given by the linear mixing rule predictions. By introducing
502 Laponite particles in TEMPO-NFC entangled network the equilibrium modulus increased by
503 almost two orders of magnitude and the relaxation time spectrum shifted to higher values,
504 more significantly for longer relaxation times, so that its shape changed and became typical
505 for gel systems - similar to that of simple Laponite spectrum. The upgraded elastic behavior
506 accompanied by slower relaxation mechanism on longer length scales was ascribed to the
507 attractive interactions between carboxylic groups of TEMPO-NFC fibrils and positively
508 charged rims of Laponite nanodiscs, which, thus, play the role of bridging agents. Similar
509 deviations from the linear mixing rule for zero-shear viscosity and viscoelastic moduli of the
510 blends were observed. Then, with increasing Laponite fraction the elastic contribution due
511 to the attraction between cellulose carboxylic groups and positively charged Laponite rims
512 diminishes, since the edge-face attraction and edge-edge and face-face repulsion between
513 Laponite nanodiscs becomes more and more important for the viscoelastic response of the
514 blends. At very high Laponite fraction the negative values of moduli excess functions,
515 especially at higher total solids amounts, were attributed to disruption of highly coordinated
516 Laponite structure in the presence of TEMPO-NFC. However, all the excess function values
517 decreased with increased total solids amount in the whole blend composition range. This
518 means that in more concentrated systems, the effect of the component present in lower
519 fraction on the viscoelastic properties is diminished.

520 To conclude, when scleroglucan/Laponite blends were investigated (Lapasin et al., 2017),
521 the positive effect of blending was maximal when blends were rich in Laponite. At the same
522 time, the excess functions for loss modulus and zero-shear viscosity were more affected
523 than that of the corresponding storage modulus. The difference may be explained by the
524 nonionic nature of scleroglucan, whose presence in Laponite poor system does not
525 contribute to bridging and thus to formation of an associative ionic network. The presence
526 of scleroglucan only reduces the effect of the edge-face, edge-edge, and face-face
527 interactions between Laponite particles on the viscoelastic properties, through the steric
528 hindrance.

529

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533

534 **Appendix A. Supplementary data**

535 Supplementary material related to this article can be found, in the online version.

536

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Supporting Information for:

Rheology of aqueous dispersions of Laponite and TEMPO-oxidized nanofibrillated cellulose

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788 Appendix A. Supplementary data

789

790 Table S1: Rheological parameters (zero-shear viscosity values obtained by the Cross
 791 ($\eta_{0,Cross}$) and RBC ($\eta_{0,RBC}$) equations, critical shear stress ($\tau_{0,RBC}$) obtained by the RBC
 792 equation, and elastic (G'_{1Hz}) and viscous (G''_{1Hz}) moduli measured at 1 Hz) for 2.0, 1.5 and
 793 1.0 wt% simple TEMPO-NFC and Laponite systems. ND: not determined values (from
 794 experimental tests or data correlation).

795

	%	NFC 20d	NFC 80d	L 20d	L 80d
$\eta_{0,Cross}$ (Pa s)	2	9760	10360	670480	797710
	1.5	3290	8490	336580	584320
	1	ND	ND	122440	597920
$\eta_{0,RBC}$ (Pa s)	2	10490	12170	689350	798600
	1.5	2300	5170	370130	579060
	1	ND	ND	113980	548780
$\tau_{cr,RBC}$ (Pa)	2	4.54	8.85	57.3	63.6
	1.5	0.18	0.22	28.8	43.5
	1	ND	ND	13.0	44.0
G'_{1Hz} (Pa)	2	15.1	23.2	417	579
	1.5	1.19	2.94	228	387
	1	0.07	ND	82.4	104
G''_{1Hz} (Pa)	2	5.24	6.76	29.7	41.3
	1.5	0.76	1.19	17.6	30.3
	1	0.15	0.06	6.98	8.31

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