Sonication-assisted surface modification method to expedite the water removal from cellulose nanofibers for use in nanopapers and paper making
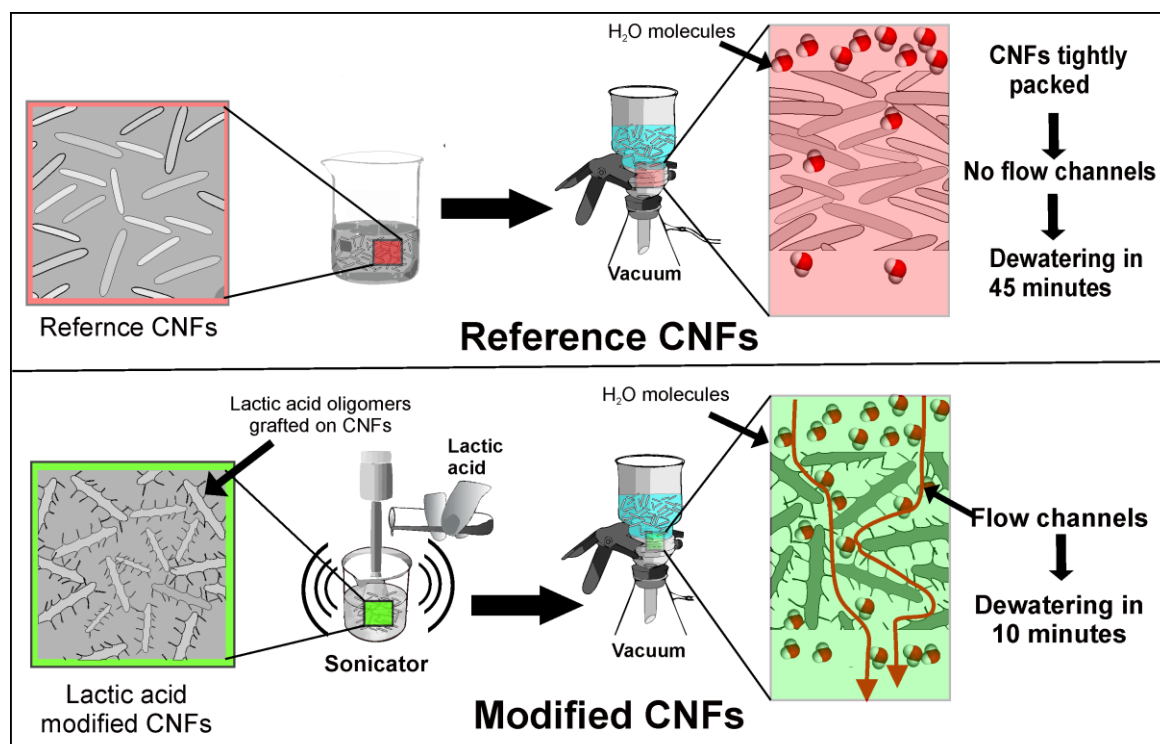
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Graphical abstract

Rapid dewatering in lactic acid modified cellulose nanofibers

Abstract

This paper addresses the issue of high water retention by cellulose nanofibers (CNFs) that lead to exorbitant time consumption in the dewatering of CNF suspensions. This has been a bottleneck, which is restricting the commercialization of CNF derived products such as nanopapers and CNF reinforced paper sheets. As a remedy, we suggest an eco-friendly water-based approach that involves the use of sonication energy and lactic acid (LA) to modify the surface of CNFs. The suggested modification resulted in rapid water drainage, and dewatering was completed in 10 minutes; with unmodified CNFs, it took around 45 minutes. We have also compared the draining characteristics of LA modification of CNF suspensions with a common draining agent (NaCl); LA modification drains water 56 % faster than the use of NaCl, and produced mechanically superior dimensionally stable nanopaper. Additionally, LA modification allows the addition of 10 wt.% CNF in paper sheets, with dewatering done in 2 minutes (while the unmodified CNFs took 23 minutes).

Keywords

Dewatering, Cellulose nanofibers, Lactic acid, Surface modification, Nanopapers, Paper making

1 Introduction

Cellulose, being a naturally occurring and an easily accessible resource, has been used in everyday materials such as paper, textiles and films for the past 150 years (Habibi, 2014). With the advent of nanotechnology, it was discovered that nanoscale cellulose has the potential to be used in advanced functional products. Cellulose nanopaper is one such material that has evolved as a major research area in the field of nanocellulose. It is prepared by draining the water from diluted cellulose nanofiber (CNF) suspension and drying the obtained CNF wet cake to get an ultra-strong nanopaper. It is known to have the elastic modulus of tens of gigapascals and the tensile strength of several hundred megapascals (Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008; Sehaqui et al., 2012). Apart from being ultra-strong, it offers added advantages, such as a lightweight structure, a simple water-based processing route and an endless availability of raw

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material. Due to these advantages, nanopapers are likely to find their application in high-end products such as electronic displays (Sehaqui, Zimmermann, & Tingaut, 2014), packaging (Sehaqui et al., 2014), flexible electronics (Koga et al., 2014) and separators in lithium ion batteries (Chun, Lee, Doh, Lee, & Kim, 2011) in the near future.

Despite of being celebrated for their numerous benefits, nanopaper has a notorious disadvantage in that it takes an inordinate amount of time to drain the water from CNF suspensions, which is a key step to prepare nanopapers. It has been reported that the usual drainage time for nanopapers can be between 1 hour (Sehaqui, Liu, Zhou, & Berglund, 2010) to 3–4 hours (Iwamoto, Nakagaito, Yano, & Nogi, 2005), which is too long for any successful commercial product. The problem of a long drainage time is not only relevant to nanopapers, but is also a bottleneck for the industrial processing of nanocellulose into other finished products. In paper processing, nanocelluloses have been proven to be a strength enhancer (Boufi, González, Delgado-Aguilar, Tarrès, & Mutjé, 2016; Eriksen, Syverud, & Gregersen, 2008) and a rheology modifier (Liu et al., 2017), but the use of nanocelluloses causes draining difficulties in paper processing (González et al., 2012; Taipale, Österberg, Nykänen, Ruokolainen, & Laine, 2010). Drainage, sometimes referred as dewatering, is an important industrial scale process and has a direct impact on production (Afra, Yousefi, Hadilam, & Nishino, 2013). It is an energy demanding process (McGregor & Knight, 1996), which leads to an extended processing time, and consequently a reduction in the production rate. Therefore, this challenging roadblock should be resolved to safeguard the commercial utilization of cellulose fibers with different size scales (Klemm et al., 2011).

Although the problem of dewatering is highly relevant one to nanopaper preparation and use of CNFs in papermaking, we found out that it has rarely been discussed in the literature with the focus on nanocelluloses. Few notable articles have been published. Precipitate calcium carbonate (PCC) was used by Rantanen *et al.* to decrease the draining time of nanocellulose and pulp mixture (Rantanen, Dimic-Misic, Kuusisto, & Maloney, 2015); on the other hand, NaCl was used by Sim *et al.* to improve the draining properties of nanocellulose suspensions (Sim, Lee, Lee,

& Youn, 2015). Researchers have also used high pressure and filter paper with a larger pore size to decrease the draining time (Varanasi & Batchelor, 2013). Apart from these handfuls of exceptions, this issue has gone widely unnoticed and therefore, lacked the attention it deserves. A detailed study is needed to highlight the issue.

The reason behind the slow drainage is the hydrophilic nature of cellulose, which can be credited to presence of the hydroxyl groups on cellulose, which are capable of retaining large amounts of water. This water bound to the cellulose is termed as "hard to remove" water (Hatakeyama, Inui, Iijima, & Hatakeyama, 2013). Additionally, the finer the size of the cellulose entities, the greater the amount of available hydroxyl groups and the more the amount of water retained (Afra et al., 2013; Chang, Lee, Toba, Nagatani, & Endo, 2012). During the planning of this study, we hypothesized that replacing the hydrophilic hydroxyl group with hydrophobic lactic acid (LA) moiety might be able to reduce the water retention, and consequently can improve drainage. Grafting is a common method to modify the properties of nanocellulose (Peltzer, Pei, Zhou, Berglund, & Jimenez, 2014) or nanocellulose based composites ((Lizundia, Vilas, & León, 2015) (Zhou et al., 2013) (Hua, Chen, Liu, Yang, & Yang, 2016). It is effective in improving the interfacial adhesion of hydrophilic nanocellulose and hydrophobic polymer. However, use of cellulose grafting as draining aid has not been studied yet.

In this study, we address the problem of the high water retention of cellulose nanomaterials and offer a solution in the form of water-based surface modification by ultrasonic energy in the presence of LA. Sonication was used as modification method, as it can provide enough localized energy to cause chemical reactions (Suslick, 2000). The draining time was characterized after surface modification with different sonication energies and with various quantities of LA. We have also compared the effectiveness of the proposed method with an earlier proposed method using sodium chloride (Sim et al., 2015). Apart from draining time measurements, nanopapers were also prepared by both methods (LA modification and NaCl addition) and were characterized for mechanical properties, water absorption and warpage. Finally, 120–140 gram per square meter (GSM) paper sheets, with 10 wt.% CNFs (original and LA-modified CNFs) were made and

92 characterized for draining and tensile properties. It is worth mentioning that this study is a

93 continuation of our earlier published study, which details the findings about mechanically improved

94 water-resistant nanopapers (Sethi et al., 2018). This one particularly focuses on the improvement

95 in the draining time and ease of dewatering resulting from CNF modification.
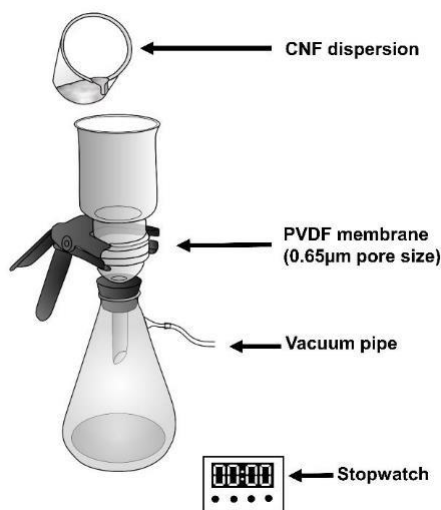
96 2 Materials and Methods

97 CNFs were prepared from bleached soft wood sulfite fibers, kindly supplied by Stora Enso (Oulu,

98 Finland). The pulp, which had a consistency of 1.6 wt.%, was repeatedly grinded in the Masuko

99 grinder. The pulp was repeated fed in the contact mode from 0-point, and the distance was

100 gradually decreased from - 20 (3 passes), - 40 (4 passes), -60 (5 passes) and -90 (7 passes). The

101 chemical composition of the reference pulp was 95.0 wt.% cellulose, 4.2 wt.% hemicellulose, 0.3

102 wt.% lignin and 0.5 wt.% inorganics. L-(+)-Lactic acid (80%) was purchased from Sigma-Aldrich.

103 For modification, the CNF suspensions were diluted to the concentration of 0.35 wt.% and

104 LA was added in various amount according to the CNF dry content (0.5 times, 1 times, 5 times and

105 10 times of CNF dry content in suspension). The detailed formulation of CNF suspensions is given

106 in Table S1 of supplementary data. The coding of samples was done according to ratio of CNF and

107 LA in the suspension. For example, the sample which has an amount of LA equivalent to 10 times

108 the dry weight of CNF is coded as CNF(10)LA. The nanofibers, water and LA were mixed in a high-

109 speed stirrer (ultraturrax) at 1500 rpm for 5 minutes and sonicated with the help of Heilscher UP

110 400s, equipped with titanium tip (22 mm in diameter). This experiment was conducted at various

111 sonication energies with a maximum imparted sonication energy of 600 J/ml, which corresponds to

112 10 minutes of sonication. The amount of sonication was quantified according to the following

113 formula.

$$E = \frac{P \times t}{V}$$

Equation 1

114 Where E is the sonication energy is J/ml, P is the power of sonicator in watts, t is the time

115 of sonication and V is the volume of liquid. For NaCl modification, 0.35 wt.% CNF suspension was

116 prepared in water and 0.1 M NaCl was added and mixed in a high-speed stirrer modification.

5

117
118   For draining time measurements, the water was drained from the modified CNF

119   suspensions under a vacuum (70 ± 10 kPa) through a 0.65 µm Durapore PVDF membrane filter

120   (Fisher Scientific, Pittsburgh, USA). A schematic representation of draining experiments is

121   presented in Figure 1. A standard stop-watch was used to record the draining time. The draining

122   was assumed to be completed when the difference between the consecutive drops falling from the

123   funnel was 30 seconds. Non-treated sulfite pulp paper sheets (120–140 gsm) with 10 wt.% original

124   and LA modified CNFs were also drained under similar conditions. The pulp-CNF concentration of

125   the suspension was 0.2 wt.% solid content.

126

127   *Figure 1 Schematic diagram explaining the details of draining experiments.*

128   The water retention value (WRV) was determined by centrifuging modified and reference

129   CNF suspensions and measuring the amount of water retained by the CNFs. The cellulose

130   suspensions were prepared according to the formulation in Table S1 of supplementary data. All the

131   suspensions were supplied with a sonication energy of 250 J/ml. The reference and modified CNF

132   suspensions were centrifuged at 6500 rpm for 10 minutes at room temperature (3000g force). The

133   supernatant (separated water) was discarded, and wet CNF gel obtained was weighted and dried

134   at 100 °C for 24 hours. The WRV was determined as the fraction of water retained in the wet cake

135   according the following formula:

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$$WRV = \frac{W_w - W_d}{W_d} \qquad \qquad \text{Equation 2}$$

136   Where, W_w is the weight of the wet sample after centrifuging, and W_d is the weight of the

137   dried sample.

138   Settling studies were conducted on 250 ml CNF suspensions (modified and reference).

139   Suspensions were diluted to the concentration of 0.05 wt. % in aqueous medium and kept

140   overnight in a measuring cylinder. The results were observed visually and reported in the form of

141   photographic images.

142   The viscosity of reference and LA modified suspensions was measured by Brookfield DV-II

143   + Pro EXTRA viscometer. A vane-shaped spindle (V- 73, spindle diameter 12.7 mm) was used.

144   The shear rate was varied by changing rotational speed of spindle from rest to 10, 20, 50, and 100

145   rpms.

146   Nanopapers were prepared by diluting the modified (CNF(10)LA) and reference suspension

147   to 0.2 wt.% and draining the water under the vacuum, as mentioned in the draining experiments

148   above. The wet CNF sheet obtained after the water draining was kept between two steel mesh

149   cloths with a mesh size of 70 μm and further stacked to the paper carrier board. The whole

150   assembly was compressed and heated at a temperature of 100 ℃ at a pressure of 10 MPa for 30

151   minutes to remove the water. The LA-modified nanopapers were further pressed at 10 MPa and

152   150°C for 30 minutes to increase the yield of esterification based on the results reported earlier

153   (Sethi et al., 2018). For comparison, CNF(0.1M)NaCl nanopaper was prepared by adding 0.1 M

154   NaCl.

155   Tensile testing was conducted on 50 mm long and 5 mm wide strips of CNF(10)LA, CNF-

156   NaCl and reference nanopaper. Samples were conditioned in a controlled condition in a room that

157   was maintained at a temperature of 23°C and relative humidity (RH) of 50 % for 48 h prior to the

158   testing. The testing was done in the same room to nullify the effect of humidity. The crosshead

159   speed of 5 mm/min and gauge length was kept at 20 mm. A load cell of 1 kN was used. The elastic

160   modulus (E) was determined from the slope in the linear region, and the yield strength ($\sigma_{0.2}$) was

determined by the intersection of a 0.2% offset line and stress strain curve. On average, a minimum of five specimens per sample are reported.

The warpage was determined visually by keeping the nanopapers in controlled conditions (23°C and relative humidity (RH) of 50 %) overnight after preparation. The results are reported as photographic images.

Paper sheets (with CNFs and modified CNFs) were prepared. The amount of CNF in papersheet was kept at 10 wt.%. The formulation of suspensions is presented in Table S2 of supplementary data. After mixing with high-speed stirrer (ultraturrax) at 1500 rpm for 5 minutes, the LA-CNF-pulp suspension was sonicated until sonication energy was 200 J/ml. The draining equipment was used as presented in Figure 1 and the draining time was measured. Paper sheets were prepared by drying wet pulp-CNF cake in a semiautomatic sheet former (rapid köthen under the vacuum of 1 bar and temperature of 95 °C for 10 minutes and characterized for tensile testing according to the procedure similar to the nanopaper tensile testing mentioned above.

3 Results

3.1   Draining time

The LA modification has a direct impact on the draining time of CNF suspensions, as shown in the Figure 2, which it shows the evolution of the draining time with the variation in the sonication energy for CNF(1)LA suspension. It can be observed that with an increase in the sonication energy, the draining time is decreased. The reference suspension took approximately 45 minutes for the dewatering, whereas after the LA modification the draining time was reduced to 10 minutes, which is a 75% improvement over the reference. It can also be observed that after a particular amount of sonication time, the draining time approaches a plateau value around 10 minutes in this case. Additionally, it is worth mentioning that even mild sonication (5 J/ml) improved the draining time by 50% (23 minutes). Interestingly, the mere addition of LA to nanocellulose improved the draining time by 35%.
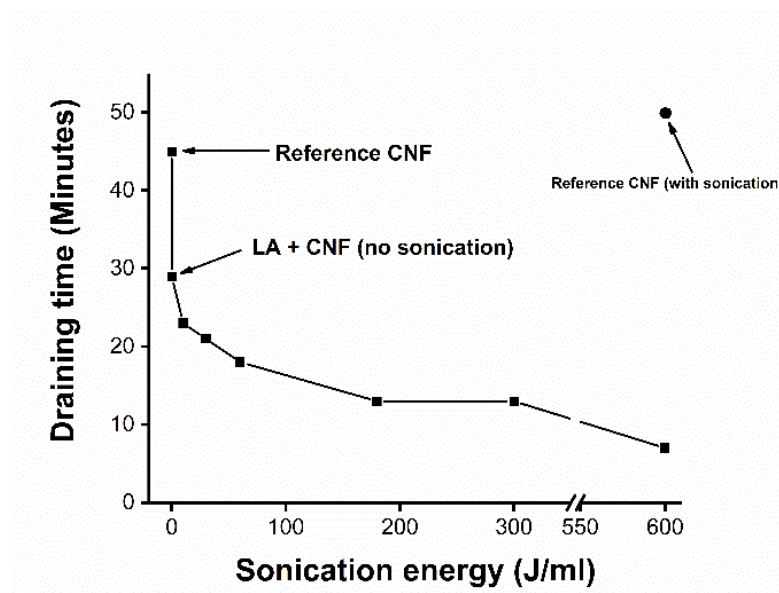
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Figure 2 Sonication energy vs draining time (in minutes) for nanopaper preparation (corresponding to CNF(1)LA sample). 100 J/ml of sonication energy corresponds to 100 seconds of sonication, and so on.

The improvement in the draining time can be explained by the replacement of hydrophilic hydroxyl groups of cellulose by hydrophobic moieties of LA. The hydroxyl groups of cellulose are primarily responsible for high water retention(Hatakeyama et al., 2013). LA has a carboxylic group, and in the presence of sonication, it is capable of participating in the esterification reaction with the hydroxyl groups of cellulose. Sonication is known for making miniscule vacuum cavities in the liquid medium, which on collapsing gives a temperature of 5000 K and pressure of 1000 atms. Such extreme conditions are sufficient to produce chemical reactions (Suslick, 2000), in this case esterification. The FTIR results of LA modification, after repeated washing in dioxane (which was done in order to remove the unreacted LA oligomers that are not attached to the CNFs) is presented in our earlier published study (Sethi et al., 2018). Another premise that can be used to understand the improvement in water drainage is the hydrophobization of CNFs due to the presence of LA moieties. The CNFs absorb water because the surface is hydrophilic, once the hydroxyl groups are replaced by hydrophobic groups, it makes sense that they will lose the capacity to bound water, which can be seen in Figure 4. Our results are in agreement with Hakovirta *et al., who* reported that hydrophobization by modifying the hydroxyl groups renders the CNFs less susceptible to water absorption and improve draining (Hakovirta, Aksoy, Nichols, Farag, & Ashurst, 2014).

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206   The quantitative results of the draining times for CNF suspensions with various amounts of

207   LA are presented Table S3 of the supplementary data. It is surprising that the amount of LA in

208   solution has no significant effect on the draining time. A possible reason might be that only LA that

209   is available/adsorbed on the surface of nanocellulose effectively participates in the modification,

210   which again is a function of hydroxyl content, which remains and might be independent of the

211   amount of total LA in nanocellulose. It is worth mentioning that the sonication of reference CNFs,

212   without the presence of LA, resulted in an increase in the draining time to 50 minutes. The reason

213   behind this could be that sonication leads to the fibrillation of CNFs, which generates a greater

214   surface area that holds more water and takes more time to drain.

215   ## 3.2   Water retention

216   The water retention values (WRVs) of the reference and the modified CNFs are listed in Figure 3. It

217   can be seen that the increase in the amount of LA decreases the amount of water retained by

218   CNFs. The WRV, which is defined by the ratio of water to dry fiber mass after centrifugation (under

219   the force of few thousand g), is a measure of the amount of water held by fibers (Hakovirta et al.,

220   2014). The WRV findings indicate that after LA modification, CNF loses its capacity to bind water.

221   This inability of modified CNFs to bind water can be observed in Figure 4, which are photographic

222   images of CNF suspensions (reference and modified) after centrifugation. It can be observed that

223   the reference gives a soft, gel-like appearance where water has been retained (not drained), even

224   after the high centrifugal force of 3000g. On the other hand, the water has been drained out from

225   the LA-modified sample, which results in a coagulated lumpy appearance, and CNFs are

226   separated, forming a thick layer towards the wall. Clearly, the reference has a higher amount of

227   water that is bound to CNF fibers, while the modified samples are well-drained, which can be

228   explained by hydrophobization of CNF surface due to LA modification. It has been reported that

229   hydrophobization of CNFs leads to reduction of WRVs (Han, Lee, & Kim, 2010)
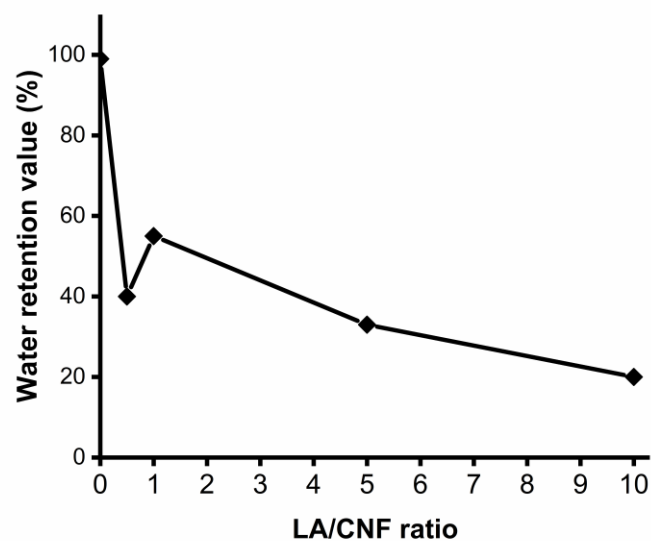
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231   *Figure 3 WRV of CNF after LA modification. The WRV decreases with the increase in amount of LA.*
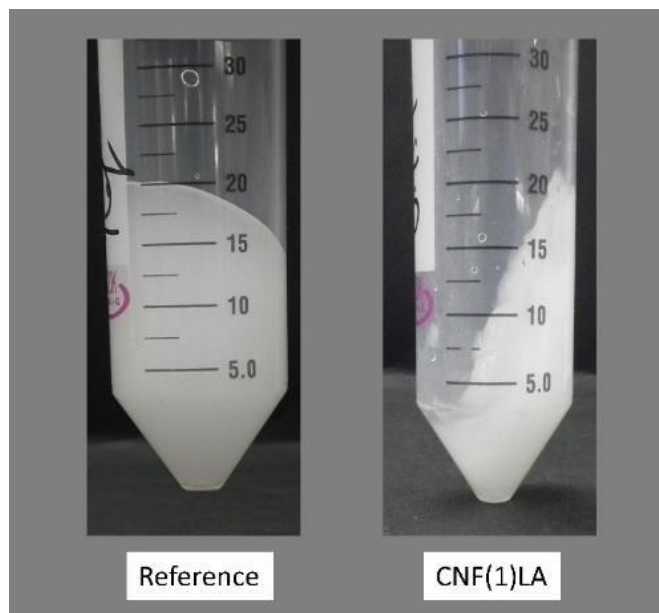

232

233   *Figure 4. Photographic image displaying the reference and LA-modified samples after centrifugation*
234   *and draining the excess water under gravity. The reference clearly has a gel-like appearance, while the*
235   *modified sample has water drained out, indicating the lower water retention. (Both samples have the same*
236   *amount of solid CNF)*

3.3   Settling study

238   Figure 5 presents the image of the settling of the reference and CNF(1)LA suspension at a low

239   concentration (0.05 wt.% in water), which is left undisturbed overnight. Interestingly, the settling

240   volume is higher for modified CNFs. The reference settled into a dense network (based on the

241   observed volume) to the mark of 70 ml, while the modified samples settled to the mark of 90 ml

242 and 100 ml for 5 seconds and 60 seconds sonication, respectively. This provides an insight into the

243 reason for improved dewatering. The relatively less-dense settling of LA-modified CNFs indicates

244 the presence of flow-channels, which allows the water to drain at ease as compared to reference,

245 which is tightly packed. In a simplistic approach, the settling of LA modified CNFs can be pictured

246 as a porous structure with connected voids through which water can flow without being blocked.

247 Functionalized cellulose is known for making such flow channels as reported by (Hakovirta et al.,

248 2014). According to them, the functionalized cellulose fibers loosely align themselves in an

249 aqueous medium, which increases their volume (also observed in our study). They suggested that

250 volume not occupied by the fibers acts as a void and aids fluid drainage, which is an important

251 require of water draining. It is also likely that LA moieties on the CNF surface form brush-like

252 structures, which prevents the formation of dense networks. Another reason could be that modified

253 CNFs less stable in water, and they flocculate. This was confirmed by UV visible transmittance.

254 Reference and modified CNFs were diluted to concentration of 10^{-2}, 10^{-3}, and 10^{-4} wt.% before

255 measuring the transmittance in the range of 400 nm to 800 nm. The modified CNFs had lower

256 transmittance, indicating that the modified CNFs have flocculated. The results are presented in

257 Figure S1 (supplementary data). It can be observed in Figure 5 that supernatant after settling is

258 turbid, indicating the presence of fines. However, in modified samples the suspension is

259 transparent. This visible flocculation is supported by decrease in viscosity discussed in detail in the
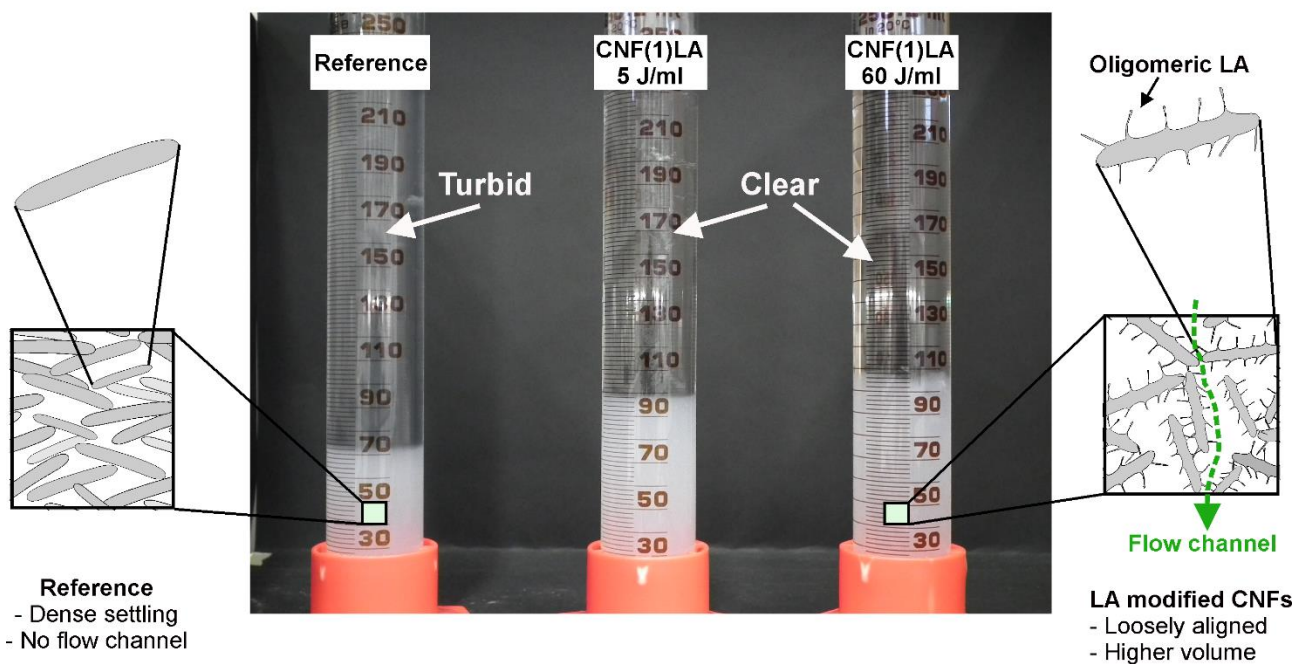
260 next section.

261

Figure 5. Graphical representation of overnight settling in reference CNF suspension (0.05 wt.%) and CNF(1) LA suspensions (0.05 wt.%) in aqueous medium. For CNF(1)LA, 5 J/ml represent the sonication time of 6 seconds and 60 J/ml with sonication time of 75 seconds. The settling volume of modified CNFs is higher, indicating the presence of voids caused by loose alignment of CNFs due to hydrophobic surface

3.4 Viscosity

The viscosity of LA modified CNF dispersions is less than that of the reference dispersion (Figure 6 (a)). However, no particular pattern is observed in the variation of the viscosity with the variation of the concentration of LA. The viscosity of CNF(0.5)LA is higher than CNF(1)LA at all the rpms (10,20,50, and 100). However, viscosity of CNF(10)LA is irregular. At low rpms (10, 20 and 50), the viscosity of CNF(10)LA is lower than that of CNF(0.5)LA and higher than CNF(1)LA. Unexpectedly, at 100 rpm, the viscosity of CNF(10)LA drops to a value which is less than both CNF(0.5)LA and CNF(1)LA. The draining time of all these dispersions (CNF(0.5)LA, CNF(1)LA and CNF(10)LA) is similar (Table S3 in supplementary data); therefore, it can be concluded that although the viscosity of suspensions is changing, it is not a parameter that affects the draining. Additionally, it was observed during experimental work that temperature have no significant effect on the draining time. After sonication, the temperature of modified CNFs would go as higher as 65 °C. The draining time of heated suspensions were the same as the suspensions at room temperature. Since the viscosity is highly sensitive property and dependent on temperature, same draining time indicates that

13

280   viscosity of suspension has no significant effect on draining time. The co-relational analysis of

281   viscosity with draining time is presented in Figure S2 (supplementary data). It can be observed that

282   CNF(0.5) LA, CNF(1)LA and CNF(10)LA are draining in same amount of time (9-10 minutes) but

283   there viscosity is different.

284   The decrease in the viscosity suggests that the CNFs are flocculating. Weakening of

285   hydrogen bonding is understandably the reason for flocculation (Nussinovitch, 1997). Hydroxyl

286   groups are replaced by LA moieties and the surface is becoming hydrophobic, as a result CNFs

287   lose their stability in water and flocculate. The tendency of LA modified CNFs can be observed in

288   the images from settling study (Figure 5). The supernatant of reference CNF dispersion is slightly

289   turbid indicating the presence of fines. On the other hand, the supernatant of LA modified CNFs is

290   clear indicating the absence of fine, which must have flocculated during modification. It has been

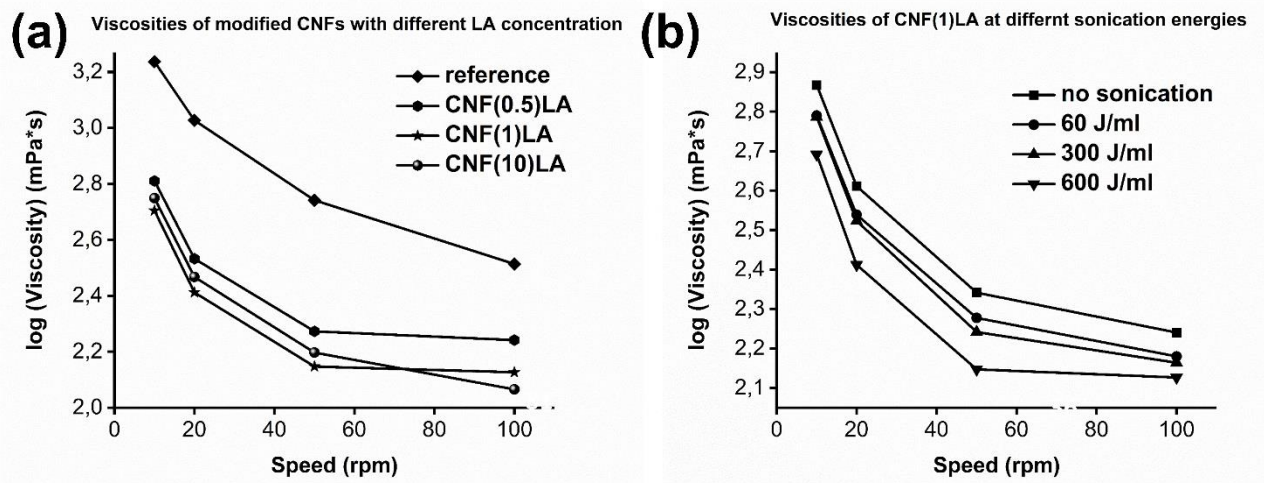291   reported that flocculation (or aggregation) decreases the viscosity (Missoum, Bras, & Belgacem,

292   2012).

294   *Figure 6 Viscosity of modified CNFs (a). Different lactic acid concentrations and reference, (b). at*
295   *various sonication enertgies for CNF(1)LA samples.*

296   Sonication energy also contributes to a decrease in viscosity (Figure 6 (b)). The viscosity of

297   600 J/ml was the lowest, followed by 300 J/ml and 60 J/ml. Viscosity of modified CNF suspension

298   is inversely proportional to the sonication energy. However, more insights are needed in order to

299   fully understand the structure property relationship of modified CNFs and effect of sonication on

300 the viscosity. Further work is planned in understanding the behavior of LA modified CNFs in

301 aqueous medium.

3.5   LA modification vs. NaCl addition: a comparison of dewatering

analysis and its effect on properties of nanopapers

304 Once it was established that LA modification leads to improvement in water draining, our next step

305 was to test LA modification method against a proven benchmark currently used for decreasing the

306 draining time of CNF suspensions. NaCl addition was selected because of its popularity, simplistic

307 approach, and convincing results (Sim et al., 2015). It is worth mentioning that we have selected a

308 0.1 M concentration to represent the draining induced by NaCl, as it has been reported that higher

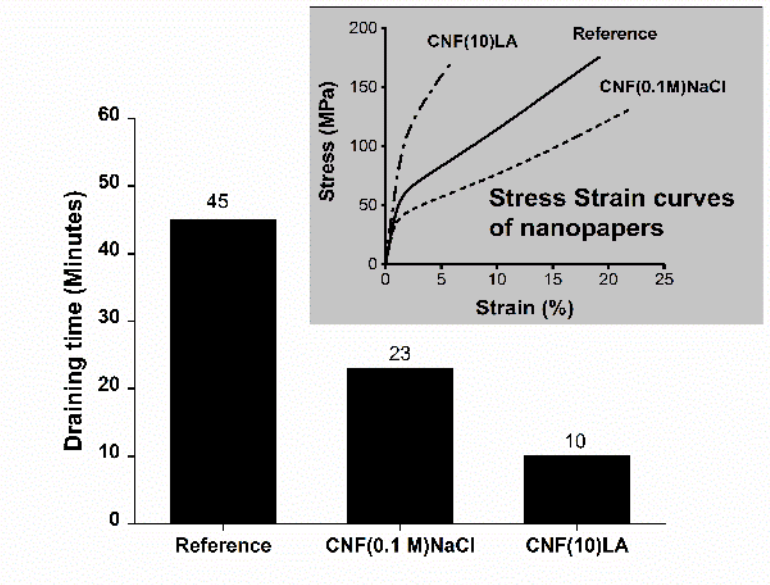309 concentrations resulted in a marginal improvement(Sim et al., 2015).

310 The time taken for draining of CNF suspensions after LA modification and NaCl addition and

311 mechanical properties of resulting nanopapers are presented in Figure 7: both LA modification and

312 NaCl addition reduce the draining time, but LA modification provides noticeably superior results.

313 CNF(0.1M)NaCl has a draining time of 23 minutes, which is a 50% improvement from the

314 reference. However, it is still considerably higher than CNF(1)LA, which drained water in 10

315 minutes. The comparison indicates that LA modification provides superior draining results

316 compared to the addition of NaCl. Not only LA modified CNFs were draining faster – the prepared

317 nanopaper from LA modified CNFs had significantly enhanced mechanical properties when

318 compared to both: reference and CNF(0.1M)NaCl drained nanopapers. On the other hand, the

319 nanopaper prepared by NaCl addition had poorer properties to the reference and CNF(10)LA. The

320 stress-strain curves of all the three nanopapers are presented in Figure 7(inset). Quantitatively, LA

321 modified nanopaper had 41% increase in the elastic modulus and 60 % increase in the yield

322 strength from the modulus and yield strength of reference nanopaper. On the other hand, the

323 elastic modulus of nanopaper after the NaCl addition is 11% less than the reference, and the yield

324 strength is decreased by 31%. The tensile strength of LA modified CNF nanopaper and reference

325 were equivalent, but that of CNF(0.1M)NaCl drained one was 22% less than both. The quantitative

326 results of stress-strain analysis of LA-CNF, NaCl-CNF and reference is provided in Table S4

327 (supplementary data). The use of LA as performance improvement additive is discussed in a study

328 previously published by us (Sethi et al., 2018).

329

330 The reason for increase in mechanical properties of LA modified nanopaper can be briefly explained

331 by condensation polymerization (oligomerization) of LA and hydroxyl group of CNF under high

332 temperature and pressure (Sethi et al., 2018). The entire system of polymerized modified nanopaper

333 acts as a heavily crosslinked system that resists the slipping of chains as the load is increased

334 resulting in improved elastic modulus and yield strength. On the other hand, the effect of NaCl on

335 mechanical properties of nanopaper has yet to be studied in detail. It can be speculated that the

336 presence of sodium and chloride ions interferes with the hydrogen bonding, which is primary reason

337 for stiffness of cellulose nanopapers. Additionally, NaCl, being hygroscopic in nature, absorbs a large

338 amount of moisture, which consequently decreases the mechanical properties. The moisture content

339 of NaCl-CNF nanopaper at 23°C and 50% RH was 8.3 wt.%. The moisture content for LA-CNF was

340 7 wt.%, and for reference nanopaper it was 8.1 wt.%.

341 The tensile testing results provide insight into the advantage of LA modification for draining over

342 reference nanopaper and the addition of NaCl.

343

344 *Figure 7. Comparison of LA modification method with NaCl addition as a draining aid and its final*
345 *impact on mechanical properties of nanopaper (inset). LA modification which drains water quickly than a*

16

346 *NaCl addition. And addition of NaCl leads to poorer mechanical properties of nanopapers (stress strain*
347 *curves in the inset).*

348   The results from the water absorption test are provided in Figure 8. It can be observed that, apart

349   from being mechanically superior, the CNF(10)LA nanopaper absorbs 80 % less water than the

350   reference and 100% less water than CNF(0.1M)NaCl. After LA modification, the amount of

351   hydrophilic moieties on cellulose is decreased, and hence the water absorption is decreased.

352   CNF(0.1M)NaCl absorbs more water compared to the reference and CNF(10)LA, as NaCl is

353   hygroscopic in nature. Additionally, NaCl is likely to leach out during swelling, leaving micropores

354   that are filled with water. Water resistance is another roadblock that nanopapers face, as they

355   drastically lose mechanical properties in even in slight increase of humidity. Details on the water

356   resistance of LA-modified nanopapers have been discussed previously (Sethi et al., 2018). We

357   would like to emphasize that the primary focus of this paper is the advantages of LA modification in

358   dewatering of CNF suspensions. The results of mechanical testing are briefly discussed here to

359   compare the validity of method with NaCl assisted method. For complete analysis of LA modified

360   nanopapers and structure property relationship, previously published paper should be consulted

361   (Sethi et al., 2018). We would also like to report a small modification in the method in this study

362   from the method that was used in the previous paper. While studying the dewatering, it was found

363   that use catalyst has no apparent effect on the results. Therefore, in this study, the LA modified

364   nanopapers were produced without the aid of $SnCl_2$ catalyst which is a huge improvement from the

365   previous one as heavy metal catalysts are a source of pollution, and getting rid of them makes our

366   method and material eco-friendly in a true sense.

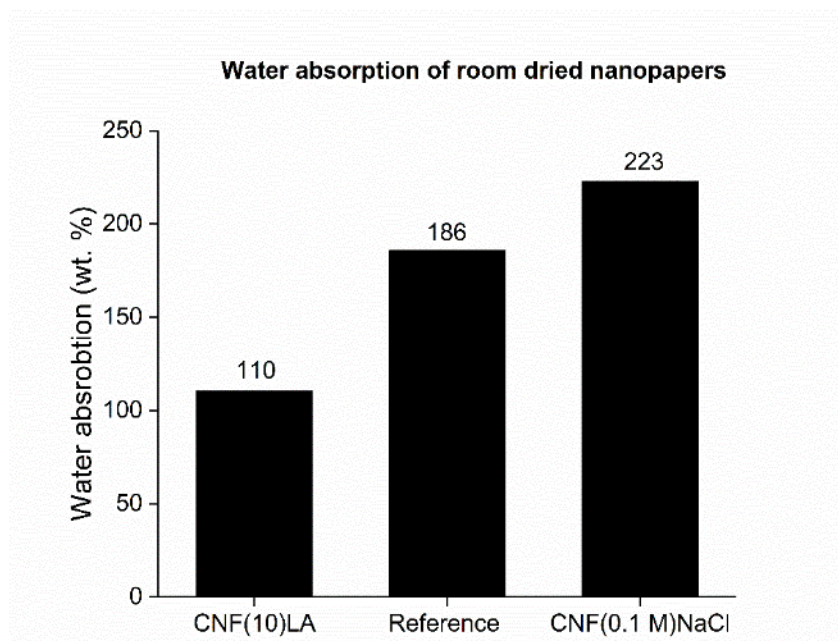**Water absorption of room dried nanopapers**

367

Figure 8 Water absorption of room-dried nanopapers (no oligomerization of LA). CNF(10)LA has significantly less absorption than the reference and CNF(0.1 M)NaCl. On the other hand, CNF(0.1 M)NaCl has more absorption of water than the reference, which can be attributed to the hygroscopic nature of NaCl.

Photographic images of overnight stored nanopapers in 50% humidity and 23 °C are presented in Figure 9. The reference nanopaper and CNF(0.1 M)NaCl have deformed into an irregular shape, indicating heavy warpage, while CNF(10)LA was able to maintain its integrity. Warpage is a rarely discussed phenomenon in cellulose nanopapers, but an important one, as it definitely affects an important desirable quality of commercial materials: dimensional stability. Moisture absorption is known to decrease the dimensional stability of cellulosic materials (Deka & Saikia, 2000). The moisture-resistant nature and rigid structure of CNF(10)LA can be attributed to its dimensional stability. The presence of LA chains on the interface does not allow slipping (as seen in Figure 7(inset)) and prevents nanopaper warpage. At 95% RH, the nanopaper can absorb up to 30 wt.% of moisture, which considerably swells up the nanopaper and have a significant effect on interfibrillar connections. (Benítez, Torres-Rendon, Poutanen, & Walther, 2013). With this change in dimensions along with mitigation of interfibrilar bonding, the fibers result in fiber slipping causing nanopaper deformation. However, in LA modified nanopaper, grafted oligomeric LA acts as glue that binds the fibers together. Even in the presence of moisture, the fibers resist slipping and maintain the integrity.
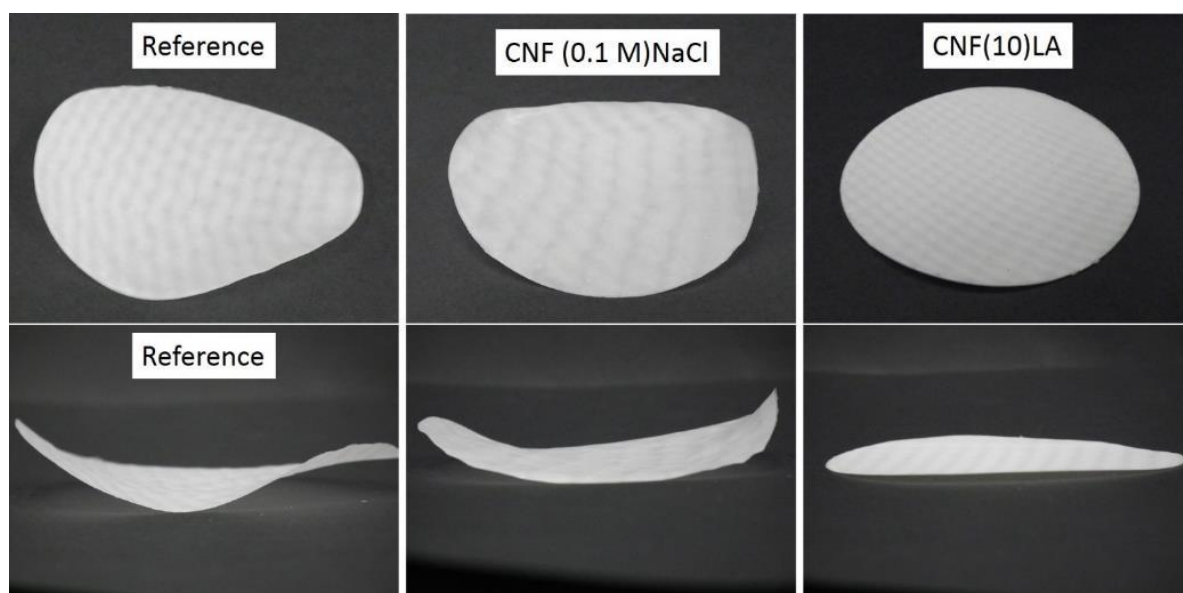
386

Figure 9. Photographic image depicting the warpage in nanopapers. CNF(10)LA has significantly less warpage than the reference and CNF(0.1M)NaCl.
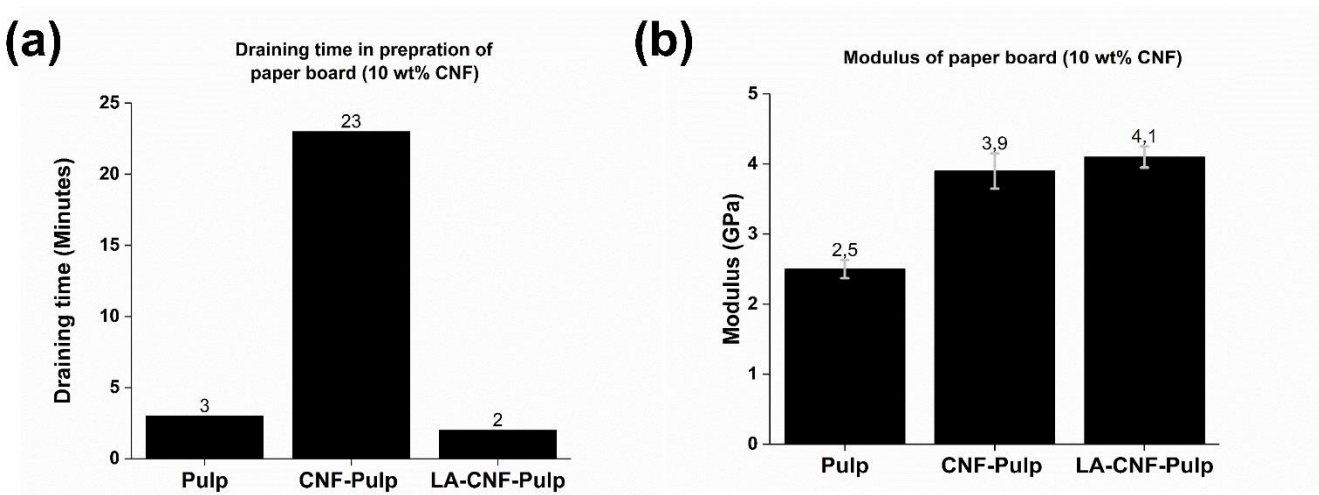
389   The morphology of nanopapers (reference, CNF(0.1 M) NaCl and CNF(10)LA) was also

390   studied. There was no apparent difference in surface characteristics of all the nanopapers.

391   However, cross-section analysis CNF(10)LA has a different morphology, with CNFs glued within

392   the layers. The results are presented in Figure S3 of the supplementary data.

393   As a conclusion to this section, which entails the comparison of LA modification and NaCl addition,

394   LA modification provides multiple advantages such as quicker draining time of CNF suspensions

395   and higher mechanical properties, water resistance and dimensional stability of the nanopapers.

396   Although, adding NaCl provides a simplistic approach to improving the water draining, it diminishes

397   the mechanical performance and makes nanopaper susceptible to water.

398   3.6   Relevance of LA modification in paper making

399   The draining time for the CNF-pulp suspension without LA modification was 23 minutes (Figure

400   10(a)), which was 20 minutes higher than the reference pulp (3 minutes). On the other hand, the

401   draining time of LA-modified CNF-pulp suspension was approximately 2 minutes, which is even

402   less than the reference pulp. This indicate that LA modification of CNFs hugely beneficial in the

403   papermaking. We also tested the tensile properties of the reference, CNF-pulp paper and LA

404   modified CNF paper. The modulus of the CNF-pulp paper and LA modified CNF-pulp paper was

19

405   higher than the reference, 56% and 64%, respectively, indicating the advantage of adding the

406   CNFs to the paper (Figure 10(b)). Additionally, the tensile strength and yield strength for both CNF-

407   reinforced papers (modified and unmodified) were improved approximately 120% and 90%. The

408   stress-strain curves of pulp paper and CNF reinforced paper (LA-CNF and reference CNFs) are

409   provided in Figure S4 (supplementary data), and the quantitative results are provided in Table S5

410   (supplementary data). Therefore, it can be concluded that our method could be used to incorporate

411   modified CNFs in paper-like materials providing a similar reinforcing effect as unmodified CNFs

412   with notable lower retention time. These findings have relevance directly to paper technology

413   where a slight improvement in papermaking results in an exponential decrease in manufacturing

414   costs. CNFs are desired for long-term use in improving the properties of paper (Eriksen et al.,

415   2008; Liu et al., 2017; Rantanen et al., 2015), but draining difficulties are restricted to a great

416   extent. The suggested method can provide a simple yet effective approach to achieve the aim.

417   Additionally, it is industrially compatible, as effective sonicators for large-volume processing are

418   now available, which are capable of completing tasks, such as the dispersion of pigments in paints,

419   the manufacturing of biodiesel and the pasteurization of food (Hielscher ultrasonics gmbh, 2017).

420

421   *Figure 10 (a). Time required to drain water from 120–140 gsm paperboards with and without CNF*
422 *(10 wt. %) before and after modification. (b). Elastic modulus of paperboards. CNF-reinforced paperboards*
423 *have higher mechanical properties than the reference, and the use of LA modification gives papers with*
424 *equivalent mechanical properties of one tenth of draining time than unmodified CNF paper*

4 Conclusions

We suggest a method to improve the draining time of CNFs by 75%. The invented method is simple; it can be assumed to improve the draining time of untreated cellulose fibers with different size scales (CNF, CMF, MFC and NFC), and it produces quick results. It can be used at moderate vacuum levels. Additionally, the method presented here utilized bio-based LA, and the use of harmful catalysts is excluded. Furthermore, the quantity of LA proposed is very small (less than 0.5 wt.% in water), which can be recovered and reused, adding another aspect to its environmental friendliness. Apart from the improvement in draining, the suggested method produces mechanically enhanced nanopapers with a superior modulus (1.4 times) and yield strength (1.6 times) compared to reference nanopaper. The tensile strength remains the same. Furthermore, the method reported has better results than using NaCl as the draining agent. Finally, this method can be advantageous in traditional papermaking, which will particularly benefit from using nanocellulose as a performance-enhancement additive. The detailed interaction of LA with the CNF surface under sonication is a complicated phenomenon and is currently being pursued.

5 Acknowledgements

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