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Drying stresses to tune strength and long range order in nanocellulosic materials

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- 20
- 21 ABSTRACT

22 A vast range of extraction processes, chemistries, and wet processing methods 23 have been explored to improve the opto-mechanical properties of nanocellulosic 24 materials. However, the stresses that arise during drying have been scarcely 25 explored, in particular for their impact on performance. As with papermaking, 26 drying is a critical step that significantly impacts the properties of nanocellulosic 27 materials. The nano- and micro-scaled dimensions of nanocelluloses provide 28 opportunities beyond those achievable in paper science, as the associated drying 29 stresses are several orders of magnitude higher than those at the macroscale. 30 Drying may thereafter be utilized towards the generation of assemblies with 31 functional structures and enhanced properties. Herein, we highlight recent 32 examples where such drying stresses were used to tether the structure of 33 nanocellulosic materials. Using cellulose nanocrystals (CNCs), we then further illustrate how the stresses that develop upon consolidation, and that remain 34 35 thereafter (i.e. residual stresses), correlate with the mechanical performance of 36 the obtained materials. We extend this analysis through results that highlight the 37 impact of the "history" of drying of CNCs on the dynamics of the residual stresses. 38 We also briefly discuss how inhomogeneous concentration gradients in drying 39 suspensions may play an important role in the formation of superstructures across a range of nanocellulosic materials. Overall, we expect that highlighting the 40 41 importance of drying will result in a more closely scrutinized science of drying 42 towards improved nanocellulosic materials.

43 I Introduction

44 In paper science, the formation of large capillary bridges between pulp fibers 45 during drying has long been known to be responsible for the wet web strength 46 prior to drying (Tejado and Van De Ven 2010). During drying, such capillary bridges 47 become smaller and the Laplace pressure of the meniscus increases, allowing the 48 fibers to come in close contact, which leads to supramolecular interactions 49 between lignocellulosic polymers across different fibers. Accordingly, the resulting 50 capillary forces that pull the fibers together are the main drivers behind fiber 51 interactions and eventually behind the actual strength of the formed paper 52 (Persson et al. 2012).

53 The cohesion of the dried macro-fibers network results from mechanical 54 interlocking and from supramolecular interactions between pulp fibers (Hubbe et 55 al. 2007; Schmied et al. 2012). In such a case, supramolecular interactions 56 between the individual fibers can lead to peeling from the pulp fibers upon fracture 57 (Fischer et al. 2014). This is associated with the irreversibility of changes occurring 58 to pulp after drying, known as hornification, which also includes the irreversible 59 closure of pores within each fiber, which significantly affects the water uptake 60 capacity of the network. This highlights the importance of the distinction between 61 "dried" and "never-dried" for cellulosic building blocks. Such interactions, for 62 instance, are known to be one of the main detrimental factors for the strength 63 development of recycled paper. Surprisingly, in the case of pulp fibers in paper, 64 the actual area in molecular contact between fibers, where supramolecular cellulose-cellulose interactions exist, is proportionally small (Hirn et al. 2013). This 65 66 is mostly a result of a multi-scale roughness and that the overlap between fibers 67 in paper is partial to begin with (Figure 1a).

68 For the past decade, cellulose research have been enriched by micro- and nano-69 scaled lignocellulosic fibers, i.e. nanocelluloses (Li et al. 2021). Non-covalent and 70 supramolecular interactions between nanocelluloses form the basis of the high 71 performance materials assembled from these nanocelluloses, where the obtained 72 opto-mechanical performance warrant their use towards new classes of 73 sustainable materials (Tardy et al. 2021). The nanoscaled dimensions of these 74 components also introduce unique considerations regarding water interactions 75 (Ajdary et al. 2020). Particularly, the previously mentioned capillary forces are 76 expected to highly impact the supramolecular interactions between 77 nanocelluloses. The presence of numerous nano-scaled capillary bridges during 78 drying will result in large drying stress. Furthermore, given the uniformity of 79 nanocelluloses in terms of surface chemistry and surface roughness, one can 80 expect the area in molecular contact to become rather large - especially compared 81 to pulp fibers. This is indirectly observed through the fact that both the strength 82 and toughness improve when increasing the degree of nanofibrillation from macro-83 scaled fibers (Zhu et al. 2015).

The impact of drying stresses on the properties of nanocellulosic materials is hereafter the main topic of this article. We first briefly introduce a range of studies, which have directly or indirectly put forward such impacts. Experimental data showing that drying stresses from cellulose nanocrystal suspensions are correlated with the tensile strength of the equivalent materials are then introduced. The impact of the hysteresis and overall history of drying stresses is then described experimentally and discussed. Finally, we also reflect on the impact of drying stresses in other dimensions, particularly during the formation of
nanopaper and suggest an intriguing impact from instabilities associated with
drying stresses.

94 **2 Materials and Methods**

95 Materials

96 Cellulose nanocrystals (CNCs) were obtained from the Process Development 97 Center in the University of Maine, U.S.A. The CNCs were prepared by sulfuric acid 98 hydrolysis of wood pulp, by the Forest Product Laboratory of the USDA, in Madison, 99 Wisconsin. They were supplied as a 10.4 wt% aqueous slurry (Klockars et al. 2023). 100 100 kDa PEG (PEG_{100k}) was purchased from Sigma Aldrich. 14 kDa PVA (PVA_{14k}) 101 was purchased from BDH Chemicals. The CNC slurry was diluted with Milli-Q water 102 (U.S.A. Millipore, Synergy UV) and/or with the additives that were also dissolved in 103 Milli-Q water.

104

105 Fabrication of nanofibrillated cellulose films

106 The fabrication of tempo-oxidized nanocellulose films is described in details in 107 (Beaumont et al. 2021). Briefly, the produced nanofibrillated cellulose suspension 108 (0.1%) was filtered using a pressurized air system (4 bar, 16 h) through a 109 polyvinylidene fluoride (PVDF) membrane filter (Durapore®, 142 mm diameter, 110 0.22 µm pore size, REF GVWP14250, Merck Millipore©), and a Schleicher & Schüll Rundfilter (150 mm diameter, Whatman[™], Ref. No. 300212). The obtained 111 112 hydrogel were hot-pressed in a Carver Laboratory Press 18200-213 (Freds Carver 113 Inc. Hydraulic equipment, NJ, USA) at 1500 lb and 80 °C for 50 min.

114

115 Measure of drying stresses

116 Drying stresses were measured as previously reported (Klockars et al. 2023). 117 Briefly, a glass cantilever was coated with a 5.5 wt% aqueous CNC suspension and allowed to dry at 22 \pm 1 °C and 20 % RH. The cantilever underwent deflection 118 119 upon drying and was monitored via an optical goniometer (a KSV Instruments CAM 120 200 or a Biolin Scientific Attension Theta Flex). Three glass cantilevers were each 121 coated as above but instead inside either a cold room at ~6 °C or in an 60 °C oven 122 with moderate ventilation. Once dried to equilibrium, they were carefully carried 123 to ambient conditions (23 or 26 % humidity, and ~23 °C) for measuring residual stresses. The stresses were also measured from prior cast cantilever-supported 124 CNC films in different relative humidities (24, 28 and 34 %). The average 125 126 thicknesses of the films were expected to be around 21 μ m. This value is based 127 on previous work (Klockars et al. 2023), which utilized the same areal density as 128 the one used herein.

129 Mechanical properties

130 CNC films were cast for measuring mechanical properties using a different 131 approach than that detailed in (Klockars et al. 2023), but using the same 132 suspensions as introduced in section 2.1. Films were cast using an approach 133 described in earlier work (Tardy et al. 2019), where a paraffin (Parafilm) frame was 134 placed on a nylon substrate to allow evaporation-induced self-assembly of 5 x 1 135 cm large free-standing CNC films cast from 1.2 ml of 5.5 wt% aqueous CNC 136 suspension. Each dried film was then cut into two 2.5 x 1 cm strips. For measuring 137 the tensile stress at a constant 2.5 mm/min strain rate, an MTS 400M tester was 138 used with a 2 kN load cell, and a clamping distance of either 5 or 8 mm. 139 Measurements where slippage or fractures near the clamps occurred were 140 discarded. Thereby, the data reported are averages of 4 (no additives), 5 (PVA), 141 and 3 (PEG) measurements. The thicknesses for these films were calculated based 142 on previous work (Klockars et al. 2023). In short, the thicknesses measured 143 previously were multiplied by 4.03 because of the differences in areal densities 144 used in the present (242 μ l/cm²) or in the previous study (Klockars et al. 2023) (60 145 μ l/cm²).

146

147 Scanning electron microscopy imaging

Scanning electron microscopy (SEM) was performed with a Zeiss Sigma VP
device with a Schottky field emission source. The film was cryo-fractured and
coated with a 4 nm thick layer of platinum/palladium alloy.

151

152 **3 Results and Discussion**

153 3.1 Overview of drying stresses and their use for structuring 154 nanocellulosic materials

Considering distances below the capillary length of a liquid, the attractive force 155 156 between two objects bound by this wetting liquid (contact angle $< 90^{\circ}$), i.e. the 157 capillary force, is proportional to the radius of curvature of the object, the distance 158 between the objects, and the radius of curvature of the wetting meniscus, which 159 is also proportional to the contact angle (van de Ven 2008; Butt and Kappl 2009). 160 While other aspects may play a role, such as roughness, these variables and 161 particularly the latter two are most critical and will not scale linearly with 162 decreasing dimensions of- and distances between the two objects (Pakarinen et 163 al. 2005; Butt and Kappl 2009; Liu et al. 2011). A qualitative representation of such 164 scaling is shown for nanocellulose in **Figure Ic**. However, the exact scaling 165 relationship remains undefined, as the stresses will bend nanocelluloses. Furthermore, solving the wetting contour is not trivial because of the unique 166 167 morphology of nanocellulose, and the radius of curvature of the meniscus is not 168 negligible compared to that of nanocelluloses.

169 Drying stresses have been shown to have a significant impact on the structure of 170 mechanically fibrillated nanocelluloses after drying (Mattos et al. 2019). Because 171 such nanocelluloses consist of bundles of elementary fibrils within a softer 172 hydrated hemicellulose matrix, the elementary fibrils are re-arranged and the 173 bundle collapses into flattened structures upon drying (Figure IbI). The 174 importance of drying stresses on the interaction between individual crystals has 175 been indirectly demonstrated in the context of crystallite fusion from elementary 176 fibrils, which allows cellulose nanofibers to co-crystallize upon drying (Figure 1b2) (Daicho et al. 2018, 2021). This has thereafter suggested new chemistries to foster 177 this co-crystallization (Beaumont et al. 2021), and aim at transferring the 178 179 outstanding nano-scaled properties of nanocelluloses (e.g. a strength of up to 7 180 GPa) into the macro-scale. To fully control the materials properties reachable with 181 cellulosic compounds, one must therefore optimize the application of drying 182 stresses.

183

anuscript 184 Figure I. Overall impact of drying stresses in different configurations and at different scales. A) In the case of pulp fibers, a high multi-scale roughness and a 185 186 high modulus of the individual fibers prevents strong molecular interactions 187 between fibers while (B_2) in the case of interactions between individual 188 nanocelluloses (elementary fibrils), a high molecular interaction can even lead to crystallite fusion. **BI**) In the case of mechanically fibrillated cellulose, the bundled 189 190 elementary fibrils deform upon drying. C) Qualitative representation of scaling of 191 capillary forces with scaling down of the cellulosic fiber size. Panels A and B 192 reproduced with permission from (Urstöger et al. 2019) and (Mattos et al. 2019), 193 respectively.

194 In addition to enhancing supramolecular interactions, tethering drying stresses 195 also offers the opportunity to control the long-range order of nanocelluloses. In a sessile volume, drying will occur faster at the edge than at the center of the 196 197 volume, and the drying rate gradient further depends on the profile of the drying 198 front. This drying rate gradient results in a so-called capillary flow that drives a 199 concentration gradient in the drying volume (Greca et al. 2021). Therefore, the 200 shape of the sessile volume can be used to tether inhomogeneities in capillary 201 flows within the volume (Figure 2a) (Klockars et al. 2019). This can be further 202 exploited within macroscopic capillaries (circular or rectangular), where drying 203 stresses can improve the homogeneity (long-range order) of the assembly within 204 millimetric or micrometric confinements. For instance, nanoparticle assembly can 205 be tethered by 1D- or 2D- planar capillary confinement of varying geometry or 206 even in packed beds of larger particles (Figure 2b) (Cherpak et al. 2018; Mattos et al. 2020; Tardy et al. 2020; Kim et al. 2021). Finally, substrate or anchoring 207 208 effects can also be applied to direct the drying stresses towards structuring the materials in three dimensions. For example, when a nanocellulose suspension is 209 210 drying onto a macroscopic textile mesh, a curvature will be induced on the fabric 211 from the stresses applied between the filaments (Tardy et al. 2017, 2019). In turn, 212 these anchoring stresses from the filaments will be applied in-plane to the 213 consolidating gel of nanocelluloses and result in the alignment of the nanoparticles

214 (Tardy et al. 2017). Additional anchoring stresses can be applied via an underlying 215 substrate that can compensate for such drying-induced distortion of the fabrics. 216 An evaporation-induced chiral-nematic order within the nanocellulose suspension 217 can thereafter be forced to follow a complex contour such as that of a filament, or 218 a spheroid in another example (Figure 2c) (Li et al. 2016; Tardy et al. 2019). By 219 confining cellulose nanocrystal (CNC) dispersions between two plates, i.e. 2D-220 planar confinement, temperature decreases or humidity increases were shown to 221 increase the contact area substantially (Borrero-López et al. 2022). These 222 dimensional changes are caused by an increase in the drying stresses, as the 223 contact angle will be lower in those circumstances, and therefore the capillary 224 forces will increase. An additional anchoring method can be applied by maintaining 225 a pre-formed material under tension (2 points mechanical anchoring) and allow 226 the material to anisotropically contract during drying. This has been applied onto 227 networks of nanocelluloses formed by bacteria (bacterial cellulose) and resulted 228 in a high alignment enabling a high strength or specific anisotropy of thermal 229 conductivity in the material (Figure 2d) (Uetani et al. 2017; Mredha et al. 2018; 230 Wang et al. 2018). Lastly, in an interesting example, it was shown that, in addition 231 to bending, drying can substantially influence the chirality of individual CNCs 232 (Ogawa 2019; Ogawa et al. 2020).

Since drying stresses affect the long-range order of nanocelluloses in the 233 234 consolidated materials, it will also affect the optical properties of the formed 235 materials. For example, when the methodology described in Fig. 2D was applied 236 to films, i.e. drying under tension, an increase in transparency was reported (Wang 237 et al. 2018). Films containing nanocelluloses, which are more tightly packed will 238 also reduce scattering and improve overall transparency. For example, when films 239 of nanocellulose were formed from aqueous suspensions, a highly transparent film 240 was observed (Toivonen et al. 2015, 2018). However, when drying from hexane, 241 opaque films with low transparency were obtained due to the resulting loosely 242 arranged nanocellulose network. This general trend associating an increase in 243 transparency with alignment of, or tightly packed, nanocelluloses can be found 244 across the literature (Kaschuk et al. 2022). Thereafter, drying stresses may be 245 more directly studied for its potential to influence transparency.

246

247 Figure 2. Overall impact of drying stresses in different configurations and at different scales, considering the opto-mechanical properties of nanocellulosic 248 249 materials. A) Inhomogeneous drying rate at the edges when compared with the 250 center of sessile suspensions leads to inhomogeneous depositions of coatings. **B**) 251 In capillary confinement, edge effects are symmetrical (a meniscus is formed) and 252 more intensified, leading to a uniform impact on the long-range order of the 253 nanocellulosic materials obtained. The bottom illustrations highlight that the 254 stresses are not homogeneous due to the formation of a concentration gradient 255 from the outer edge to the inner part (left to right) of the consolidating gel. This 256 result in sequential fractures observed over time C) By tuning the wetting angle 257 between an underlying support and a porous support, the drying stresses can 258 result in templating of nanocellulosic material, which follows the contour of the 259 porous support. D) Under tension, uniaxial drying stresses result in alignment of 260 nanocelluloses within the necking area. Panels A, B, C, and D reproduced with 261 permission from (Klockars et al. 2019), (Tardy et al. 2020), (Tardy et al. 2019), and

262 (Mredha et al. 2018) respectively. The abbreviation CNC in the figure refers to263 cellulose nanocrystals

264 **3.2 Dynamics of drying stresses and correlation with mechanics**

Overall, drying stresses are a major factor behind the ultrastructure as well as the
performance of nanocellulosic materials, as summarized in Figures I and 2.
Considering these stresses in the context of nanocellulose will be key to reaching
the optimal performance from such promising building blocks, which are currently
already reaching commercialization.

270 We recently explored the quantification of drying stresses as a function the choice 271 of plasticizer and its loading. This included macromolecules of different molecular 272 weight and origin (proteins, poly(ethylene glycol), and poly(vinyl alcohol) (PVA)), 273 as well as small molecules such as glycerol and glucose. These stresses were 274 correlated with fracturing, planar distortions, and long-range order when using 275 liquid crystalline suspensions of CNCs as precursors for coatings (Tardy et al. 2019; 276 Klockars et al. 2023). In this work, we showcase how the drying stresses that 277 remain in the CNC films provide a direct indication of their mechanical properties 278 (Figure 3). For this, we selected a subset of previously explored films in our work 279 to reflect on the vast range of studies that indirectly correlate drying stresses with 280 the functionalities and performance of nanocellulosic films. The set includes CNC 281 films without additive, or with PVA (molecular weight 14 kDa) or polyethylene glycol (molecular weight 100 kDa, PEG_{100k}) (Figure 3). These polymers and their 282 283 associated molecular weights were chosen for their impact on the residual stress; 284 either intermediate (PVA) or high (PEG) stress reductions.

285 The strong supramolecular interactions that develop during drying, and that remain in the material after complete drying, make the CNC films strong but 286 287 brittle. This is evidenced by the high ultimate strength (69 ± 11 MPa) and elastic 288 modulus (7 \pm 1.7 GPa). By adding the macromolecular additives, the 289 supramolecular interactions between CNCs do not fully develop upon drying, resulting in ca. 20 and 70 % lower ultimate strength for PVA and PEG, respectively. 290 291 This coincides with similar reductions of the residual stresses (Figure 3). The 292 strain at break, on the other hand, is inversely proportional to these three 293 parameters.

Importantly, these results show that residual stresses provide a direct indication of the effect of additives on the film mechanical properties. It is noteworthy that this technique benefits from being non-destructive. From a practical standpoint, the measure of residual stresses can also provide real-time information on the mechanical response of biocolloidal gels, films and coatings dried under different conditions or exposed to weathering, aging, and post-treatments (Beck et al. 2013; Natarajan et al. 2017; Bast et al. 2021). 301

Figure 3. a) Summary of the mechanical properties of pristine CNC films, and films were cast from CNC suspensions containing additives (PVA and PEG) to obtain a dry weight ratio of 10:3 (w:w) of CNC to additive. Corresponding residual stress data from previous work (Figure 2C₁ of Klockars et al. 2023) is shown for comparison. The error bars indicate standard deviations. b) Representative stress strain curve of each condition.

308

The relationship between residual (drying) stresses and relative ambient humidity 309 310 is shown in **Figure 4a**, and is caused by humidity-responsive absorption and 311 desorption of water in the nanocellulose coating (Wang et al. 2015). As previously 312 reported with humidity-sensitive mechanical responses of nanocellulosic materials 313 (Wang et al. 2015), a substantial decrease in residual stress is herein observed when increasing the humidity (16.5% decrease in stress for 16.7% increase in 314 315 relative humidity). Figure 4b follows the stress evolution caused by adsorption 316 (black line) and desorption (red line) of moisture in CNC films immediately after 317 removing them from their drying condition at either 60°C (oven) or 6°C (fridge), 318 respectively. Interestingly, when allowed to equilibrate in the same humidity and 319 temperature, the films did not converge to the same stress. Instead, the film that 320 dried faster and assumed an initially higher stress state in the oven, had a lower 321 equilibrium stress (~2.7 mm) than the one with an initially lower stress and slower 322 drying (~3.7 mm). This could have been caused by a larger extent of 323 microfractures forming when water evaporates faster or to a larger extent, which 324 reduce part of the total formed residual stress. Furthermore, at lower 325 temperatures, the higher water surface tension at 6° C (ca. 75 mN m⁻¹) versus that 326 at 60°C (ca. 66 mN m⁻¹) generates higher work of adhesion between the receding 327 water front and nanocrystals (Goldberg et al. 2007). The equilibrium stress 328 obtained from films dried at 6°C is very similar to that of films dried at ambient 329 conditions (Figure 4c). This could stem from the absence of microfractures in both 330 the ambient- and fridge-dried samples, and from the similar water surface tension at such temperatures (ca. 73 mN m⁻¹ at 20°C). Note that there is a small difference 331 332 in relative humidity between panel B (28%) and C (26%), although this difference 333 only results in a negligible effect in a common sample measured at both conditions 334 (oven dried sample). Potentially these differences in stresses could also be the 335 result of individual polymer chain peeling off from nanocelluloses as associated 336 with the high drying stresses.

337 Water remains in all cellulosic materials post-drying unless they are oven treated 338 at temperatures near or above 100 °C at low humidity (ideally under vacuum). 339 Upon introducing a film dried in ambient conditions into a vacuum oven, the drying 340 stresses rise sharply (visibly increased by at least two fold, Supplementary 341 **video SI**) due to the remaining water evaporating from very small capillaries 342 between the nanoparticles and thus leading to very high capillary forces and 343 associated drying stresses. This high increase in drying stresses highlight the 344 potential mismatch between the obtained materials and their maximum potential 345 strength. The vast majority of the nanocellulosic materials tested for their strength 346 have not been dried in such conditions, even the ones showing outstanding 347 performance, thus showing that they may not yet have reached their maximum 348 potential. It would then be intriguing to evaluate their performance as a function 349 of post-processing drying, especially considering the positive correlation between 350 strength and residual stress.

351

Figure 4. Measurements of residual stresses in CNC films, based on deflections 352 of cantilevers used as their substrates. a) The effect of ambient relative humidity 353 354 on equilibrium residual stress (at 23°C). b) Cantilever-supported CNC films were 355 cast inside a 60°C oven (black line) and a 6°C fridge (red line) and kept there until 356 reaching equilibrium humidity. The residual stress was measured as a function of 357 time after removing the films from the oven into 23 % humidity (black line) or from 358 the fridge into 26 % humidity (red line). The values to the right of the dashed line 359 correspond to an equilibrium residual stress measured at 28 % humidity for both 360 cases. c) The black solid line shows the same data as the solid line in b), but here 361 compared (at 23 % humidity) to the equilibrium residual stress measured for a film 362 dried in ambient conditions. The equilibrium residual stress was further compared 363 for the prior cases in another humidity (26 %) five days later. The ambient 364 temperature was around 23°C in a)-c).

365

366 **3.3 Self-confinement induced nanolayers formation**

367 Lastly we report on an interesting observation, which can be found across the 368 literature, although it has not yet been correlated with drying dynamics. Typically, 369 thin (micrometric) films of nano- or microfibrillated nanocelluloses display periodic 370 structures consisting of rather thin (nanometric) sheets of nanocellulose fibers 371 across their cross-sections. The periodicity varies as a function of drying stresses, 372 e.g. when drying from water (high stresses) or hexane (low stresses) (Toivonen et 373 al. 2015). Another example is shown in **Figure 5**, with a speculative scheme 374 highlighting a possible drying-stress associated mechanism. This is herein 375 speculated to arise from conflicting drying stresses that are a result of 376 concentration gradients of bio-colloids across the consolidating front. A skin layer 377 forms and associated drying stresses arise accordingly. Thereafter, at a critical 378 localized concentration, the film stress will result in detachment of the single layer 379 and the subsequent consolidation of the nano-layer. This process is subsequently 380 repeated until multi-layers are formed. The in-plane residual stresses coupled to 381 dynamic capillary forces will result in periodic structures. This type of "self"-382 confinement is observed across multiple scales (e.g. by closely analyzing previous data), although it has never been explored in the adequate framework and left 383 unnoticed thus far in the context of "nanopaper" and other nanocellulose-based 384 materials. However, previously, in the context of mm-scaled confinement, as 385 386 observed between two plates, such a phenomenon was observed and resulted in

microstructure formation (Cherpak et al. 2018; Tardy et al. 2020; Greca et al.
2021; Kim et al. 2021; Borrero-López et al. 2022). The engineering of drying
stresses could thereafter be used to exploit self-confinement, as hypothesized
herein, to improve barrier properties, tear resistance, or even to introduce other
property gradients across thin films.

392 These nanolayers can regularly be observed in the literature when closely 393 observing the cross-sectional scanning electron microscopy image of 394 nanocellulosic films. Beyond the omnipresence of these nanolayers in the 395 literature, the hypothesis represented in **Figure 5** can be further supported by 396 previous attempts to draw a "theory" of drying for colloidal and polymeric 397 materials (Scherer 1990; Peng et al. 2012). Previous considerations in the theory 398 of drying highlighted "the constant rate" and "falling rate" drying periods, where 399 the constant rate described the shrinkage and consolidation of the nanocellulose 400 gel. The falling rate period involved a nearly dried outer edge of the gel where 401 capillary pressure between closely-located nanocellulose would be rather high and 402 the diffusion of water vapor from the inner gel to the outer gel would occur by 403 diffusion. We herein hypothesize that the differential drying stresses along the 404 gradient of concentration would lead to separation of layers during drying. To 405 support the hypothesis put forward, it is important to highlight that under planar 406 confinement (i.e. drying in between plates) a nanocellulose gel will fracture 407 internally, leading to the formation of the lamellar structures shown in Figure 2B 408 (Tardy et al. 2020) (see supporting Figure S12). This suggests that the drying 409 stress differential, from highly concentrated nanocellulose regions (at the initial 410 drying) to diluted regions (in the center of the gel), will generate a pressure 411 differential that can result in a vapor phase in the emerging internal fracture from 412 the continuous gel phase. This observation is critical in asserting the impact of the 413 concentration gradient of nanocellulose.

414

415 Figure 5. Top – Schematic illustration of the potential mechanism leading to 416 nanolayers formation. A concentration gradient starts forming (t₀) and 417 subsequently the stresses increase as a nanocellulose "skin" layer starts to form 418 (t_i) . The skin layer has higher internal drying stresses than the bulk suspension 419 due to increased capillary stresses, and a local stress maximum occurs at t_i as the 420 skin layer dries. As the material continues drying, further skin layers form with 421 corresponding similar stress responses (t_i+1). **Bottom –** On the left a scanning 422 electron image highlighting the multi-nanolayers formed from tempo-oxidized 423 nanofibrillated cellulose films (Beaumont et al. 2021) and on the right a schematic 424 hypothesizing on drying stresses at the corresponding times is put forward.

425

426 **4 Conclusions**

427 Comprehensive discussions around cellulose-water interactions have been 428 constantly present in the cellulose community. Commonly overlooked, however, 429 are the stresses arising during the drying of nanocellulose suspensions, which 430 have been exploited directly or indirectly to form materials with a unique set of 431 morphologies and properties.

432 In this work, we put this topic into perspective by showing that:

- 433 Residual drying stresses are proportional to the mechanical performance of 434 the obtained nanocellulosic materials.
- 435 Small remaining water contents in nanocellulosic materials post-formation
 436 may considerably impact their properties as its removal leads to a
 437 significantly increased residual stress.
- The multi-layered structure, characteristic of single-component
 nanopapers, may be profoundly impacted by the stresses arising during
 drying.

In spite of a wide range of past and recent outcomes highlighting the importance of drying, the science of drying nanocellulosic suspensions and materials remain to be fully explored and engineered. With this manuscript, we hope to raise awareness to the importance of the drying dynamics and resulting stresses in the efforts to produce advanced nanocellulosic materials.

446

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450 Ethics approval and consent to participate

451 Not applicable. There are no ethical concerns associated with the manuscript

452 **Consent for publication**

453 Not applicable. All authors consent to the publication of the manuscript.

454 Availability of data and materials

455 Supporting video S1 available describing behavior of CNC-coated cantilever456 post-drying in vacuum.

457 **Competing interests**

458 The authors declare no competing interests

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464 **Authors' contributions**

465 L.G.G. and K.W.K.: Methodology, Experimental work, Formal analysis, Writing
466 - review & editing Orlando J. Rojas: Funding acquisition Blaise L. Tardy:
467 Conceptualization, Funding acquisition, Supervision, Writing - original draft,
468 Writing - review & editing.

469

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C – Qualitative scaling of capillary forces and associated drying stresses



crystallite fusion

Capillary length

Pulp fiber









