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## 1 Water-soluble polysaccharides promoting production of

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- 3

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## 13 Abstract

14 To date, the energy-intensive production and high-water content severely limits 15 nanocellulose applications on a large scale off-site. In this study, adding water-soluble polysaccharides (PS) to achieve an integrated process of water-redispersible 16 17 nanocellulose production was well established. The addition of PS, in particular carboxymethylated-galactoglucomannan (cm-GGM), facilitates fibre fibrillation 18 19 enabling homogenization at a higher solid content at 1.5 wt% compared with around 20 0.4 wt% for neat fibre. More importantly, the addition of cm-GGM saved 73% energy 21 in comparison without PS addition. Good water redispersibility of thus-prepared 22 nanocellulose was validated in viewpoints of size distribution, morphology, viscosity 23 and film properties as compared with neat nanocellulose. The tensile strength and optical transmittance of nanocellulose films increased to 116 MPa and 77% compared 24 25 to those without PS addition of 62 MPa and 74%, respectively. Collectively, this study 26 provides a new avenue for large-volume production of redispersible nanocellulose at a 27 high solid content with less energy-consumption.

Keywords: Nanocellulose; water-soluble polysaccharides; redispersibility; fibre-tofibre interaction, energy consumption decrease

## 30 **1. Introduction**

31 Fibrillated cellulosic materials are obtained by mechanically breaking millimetre-32 scale fibres, yielding micro- and nano- scale fibrils, i.e., microfibrillated cellulose 33 (MFC) and cellulose nanofibrils (CNF). These products possess massive specific 34 surfaces (Yang et al., 2020), huge water-preservation ability (Sim et al., 2015) and 35 outstanding mechanical properties (Du et al., 2019), etc. Most often defibrillation 36 requiring high-intensity mechanical grinding, e.g., high-pressure homogenizers, 37 microfluidizers and grinders is an energy-intensive process (Ämmälä et al., 2021; Ang 38 et al., 2019; Ankerfors, 2012). To decrease energy consumption, chemical and 39 biochemical pre-treatments, such as 2,2,6,6-tetrame-thylpiperidine-1-oxyl (TEMPO) 40 mediated oxidization, acid hydrolysis, alkaline treatment, as well as enzymatic-41 mediated pretreatment (Li et al., 2015; Hu et al., 2018; Lee et al., 2018; Ribeiro et al., 42 2019), are conducted prior to mechanical fibrillation. However, these measures cause 43 other associated issues such as increasing cost and toxicity, and may also cause fibre 44 degradation (Li, B et al., 2015; Isogai et al., 2011; Saito et al., 2006). Meanwhile, the 45 highly exposed free-hydroxyl groups of the fibres, which impart good water-retention 46 is challenging for large-scale industrial applications due to increased storage and 47 transportation weight and space, even with a low solids content (Thomas et al., 2020). 48 The re-dispersion of micro/nano-sized cellulose fibres in aqueous after drying is an 49 enticing yet demanding means to address this issue. However, the irreversible 50 aggregation of cellulose fibres during drying caused by intermolecular hydrogen 51 bonding, *i.e.*, 'hornification' or 'co-crystallization' hamper an effective re-dispersion

process (Butchosa et al., 2014). Methods like the addition of dispersing additives/agents have been suggested to accomplish a good redispersibility, that is, in essence to disrupt 'hornification' and diminish nanofibre aggregation as well as flocculation (Butchosa et al., 2014; Dias et al., 2019; Missoum et al., 2012). However, achieving highly consistent fibrillated cellulosic products that preserves good dispersibility while imbuing them with a good redispersibility after drying is a far more demanding matter to address.

58 Water-soluble polysaccharides (PS) and their derivatives have been proven to 59 intrinsically adsorb onto the fibre surface due to strong hydrogen bonds and other 60 driving factors (Lucenius et al., 2014, 2019), interfering fibre-to-fibre interaction. 61 Carboxymethyl cellulose (CMC) with polyelectrolyte nature has been validated as a 62 dispersant for stabilizing MFC in suspensions by decreasing flocculation between fibres 63 (Lowys et al., 2001), due to its irreversibly adsorption feature onto fibre surface (Laine, 64 J et al., 2000). Moreover, CMC was found to aid the water redispersibility of cellulose 65 nanofibrils (CNF) by introducing CMC into CNF suspension before oven drying 66 (Butchosa et al., 2014). Controversially, several peer studies have also revealed that 67 CMC was not necessarily absorbed onto fibres in a way (Liimatainen et al., 2019; 68 Sorvari et al., 2014), in this case, but rather created a repulsive interaction between 69 fibres that prevent flocculation. Essentially, the presence of PS in proximity to cellulose 70 surface played an imperative role in serving as an inhibitor of fibre aggregation, e.g., 71 interfering interaction among fibres and reducing flocculation corresponding to 72 enhancing water redispersibility of CNF (Albornoz-Palma et al., 2020; Dias et al., 2019; 73 Eronen et al., 2011).

Hemicelluloses, a group of water-soluble polysaccharides considered as sidestream products in massive quantities, exhibits an intrinsic affinity to the cellulose surface (Eronen et al., 2011; Lucenius et al., 2019; Xu et al., 2019). Hemicelluloses

were found to play a role of facilitating nano-fibrillation rendering individual fibril
liberation and consequently saving energy during mechanical defibrillation (Dias et al.,
2019). Both Eucalyptus pulp with around 8% hemicellulose content and pine pulp
containing around 10% hemicellulose content after alkaline treatment showed effective
fibrillation during grinding resulting in an energy saving of 38% and 62%, respectively
(Dias et al., 2019).

83 In the present work, an integrated approach was developed to produce water-84 redispersbile nanocellulose via homogenizing the coarsely refined pulp with the 85 addition of polysaccharides. A wide range of water-soluble polysaccharides, *i.e.*, CMC 86 and cationic guar gum (CGG), as well as four hemicellulose derivatives (O-acetyl-87 galactoglucomannan (GGM), cationic-GGM, anionic-GGM and xylan) were 88 scrutinized for obtaining water-redispersible nanocellulose with good performance 89 towards barrier applications. The effect of adding different PS on the degree of 90 fibrillation during homogenization, as well as on water redispersibility in regards to 91 viscosity, the optical and mechanical properties after sample re-dispersion were 92 assessed. Addition of different PS, especially hemicelluloses, interferes fibre-to-fibre 93 interactions during mechanical treatment, improving the defibrillation and fibre 94 redispersibility, yielding a green and sustainable nanocellulose production.



96 Figure 1. Schematic of processing methods to produce nanocellulose with good redispersibility

## 97 2. Experimental section

## 98 2.1. Materials

99 Bleached birch kraft pulp (Chemical composition: cellulose: 76.5%, hemicellulose: 100 21.6% determined by acid hydrolysis and acid methanolysis methods, followed by 101 analysed gas chromatography (Sundberg et al., 1996) was kindly provided by UPM, 102 Finland. Carboxymethyl cellulose (CMC, Mw:160 kDa) was kindly provided by CP 103 Kelco, Finland. Cationic guar gum (CGG) was purchased from Making Cosmetics 104 Company (U.S.A.). O-acetyl-galactoglucomannan (GGM, Mw: 27 kDa), cationic-105 GGM (cat-GGM, Mw: 45 kDa) carboxymethylated-GGM (cm-GGM, Mw: 61 kDa), 106 and xylan (Mw: 51 kDa) were extracted in-house and syntheses were conducted 107 according to previous works (Kisonen et al., 2014; Stevanic et al., 2014; C. Xu et al., 108 2010, 2011) in our group. All the molar mass of used polysaccharides are available in 109 Table S1.

110 **2.2 Methods** 

## 111 2.2.1. Preparation of nanocellulose from refined pulp by high-pressure 112 homogenization

The coarsely refined pulp in terms of microfibrillated cellulose (MFC) was obtained by refining the bleached birch kraft pulp with a customized laboratory refiner, Valmet ProLab<sup>TM</sup> at Åbo Akademi University.(Sjöström, 2018) Prior to refining, the pulp was soaked in water overnight for a sufficient swelling. The swollen pulp was then injected into a pulp mixer for pre-mixing at solid content of 3.5 wt%, followed by a stepwise refining process. MFC was collected when the Schopper-Riegler (°SR) value was higher than 90°.

In order to prepare nanocellulose, MFC was further mechanically treated in a highpressure homogenizer (AH-100D, ATS Engineering Co., Ltd., China) in the absence or

122 presence of PS, as illustrated in Figure 1. Prior to homogenization, a step of rigorously 123 mixing MFC and PS stock solutions was conducted to ensure an effective PS adsorption 124 to the cellulose surface obtaining a homogenous slurry. The obtained slurries were 125 passed through the homogenization chamber (the inner chamber diameter of 100 µm at 126 1000 bar) for 2 cycles under a pressure of approx. 200 bar followed by 10 cycles under 127 a pressure of 1000 bar to achieve nanocellulose production. From here on in this text, 128 we name all the nanocellulose samples as MFC/PS X%, and the mass ratio of MFC to 129 PS is 95:5, 90:10, 85:15 and 80:20 as listed in Table S1, where PS stands for 130 polysaccharide type, and X for polysaccharide concentration, as mass percentage 131 calculated between PS and PS+MFC. The obtained products were stored at 4 °C. 132 Moreover, in order to investigate the effects of PS on the homogenization steps, the 133 energy consumption values were calculated by a previously described pressure drop 134 equation (Ankerfors et al., 2012) as following:  $W = \{(P_2-P_1) * 1/\rho\}/c$ , where W is the 135 estimated energy consumption, in units kWh/tonne, P<sub>1</sub> is the atmospheric pressure, P<sub>2</sub> 136 is the homogenizer pressure at 1000 bar,  $\rho$  is the density of the obtained suspension and 137 c is the suspension solid content in weight percentage (wt%).

## 138

## 2.2.2. Redispersibility of MFC and MFC/PS dispersion and self-standing films

139 In order to assess the redispersibility of nanocellulose products, the homogenized 140 MFC and MFC/PS samples were freeze-dried and subsequently disintegrated using a 141 mixer (Model: PT 3000, Brinkmann Kinematica Polytron) at 20 000 rpm for 10 min. 142 The redispersibility of the products was assessed in the forms of both dispersions and 143 films as shown in Figure 1. The MFC and MFC/PS samples (5 wt%) were soaked with 144 distilled water overnight to a final solid content of 0.4 wt% and underwent the 145 disintegration step. In terms of MFC/cm-GGM (1-20 wt%) samples, the redispersibility 146 studies were carried out at a solid content of 1.3 wt%. The redispersed samples were

147 termed as RD-MFC or RD-MFC/PS. All the redispersed samples were stored in cold 148 room (4 °C) prior to further use. MFC and MFC/PS samples were diluted to 0.4 wt%, 149 followed by overnight stirring at 300 rpm to achieve a homogenous dispersion for water 150 penetration. Suspensions with a 180 mg dry content were slowly poured into a petri 151 dish. Subsequently, the suspensions were dried in a conditioned room (at 23 °C and 50% 152 relative humidity) until reaching a constant weight. Similarly, the films preparation of 153 redispersed samples were done using the same casting methods described above. The 154 films were peeled off from the petri dish after drying and were stored in conditioned 155 room prior to mechanical and optical properties tests.

156

### 2.3 Characterizations

157 The prepared MFC/PS dispersions and redispersibility were thoroughly 158 characterized in the viewpoints of rheological profiles in relation to fibre-to-fibre 159 interaction, fibre distribution via light scattering and fibre imaging analyser, nanofibre 160 morphology change through AFM, TEM as well as SEM. The self-standing films were 161 also cast to assess the redispersibility via film properties of their mechanical and optical 162 properties. More characterization methodologies including sample preparation, 163 instrument setup, and data analyses in detail are referred to Supplementary 164 Information.

165

## 3. Results and discussion

#### 166 3.1 One-step preparation of mechanically defibrillated nanocellulose

#### 3.1.1 Adsorption of PS onto fibre surface achieving energy-consumption reduction 167

168 In this study, addition of hemicelluloses and their derivatives as well as other 169 polysaccharides were established to achieve an integrated process for producing water 170 redispersible nanocellulose with saving process energy. Firstly, when a coarsely refined

171 MFC-grade cellulosic material was used for producing nanocellulose through the 172 homogenization chamber, it was observed that severe clogging issue limiting an 173 effective production to achieve high solid content (max. 0.4 wt% prepared from Prolab<sup>TM</sup> refiner). This is likely due to the high viscosity feature of MFC in course of 174 175 flexible fibres and high aspect ratio (Joachim et al., 2019; Osong et al., 2016). In general, 176 MFC suspension typically is also technically tough and energy-intensive to be homogenized when its solid content is above 2 wt% (Siró et al., 2011). Prior to 177 178 homogenization step, PS was added to the coarsely refined MFC for obtaining a surface 179 absorption to cellulose surface. It was found that the addition of hemicellulose serving 180 as rheology modifier decreased the suspension viscosity prior to homogenization 181 (Figure S1a, b), which could ease the clogging issue and facilitate the production at 182 high solid content (higher than 1 wt%, Table S1) while passed through homogenizer 183 chamber. Nevertheless, the addition amount of less than 5% is insufficient to reduce the 184 viscosity (Figure S1d) to obtain an easy flow through homogenization chamber 185 compared to MFC/PS 5 wt% (Figure S1b). Microscopically, sufficient adsorption of 186 PS onto cellulose fibre surface could impart a friction reduction and strong lubrication 187 effect among fibres (Lucenius et al., 2019). This facilitated the flowability during the 188 homogenization steps, allowing MFC/PS to be homogenized at a higher solid content 189 compared to the neat MFC. The benefits of the adsorbed PS on fibre surface were due 190 to the increased repulsion force between fibres from both the charges and steric (non-191 ionic) stabilizing forces (Sorvari et al., 2014), consequently reducing the flocculation 192 of cellulose micro- and nano-fibres.

193 The adsorption of PS onto MFC surface could also render the defibrillation along 194 the refined fibres (Dias et al., 2019) for nanocellulose production, in particular with 195 addition of CMC, cm-GGM, GGM, and cat-GGM (**Figure 2**). It is intriguing to observe 196 that the MFC/cm-GGM 5% (Figure 2d) exhibited more fibrillation locations along 197 fibres compared to MFC/CMC 5% (Figure 2b). Fibre defibrillation could appear in the 198 middle of a fibre bundle with the addition of cm-GGM (as indicated by green arrow of 199 Figure 2d), in comparison with appearing only at the end of fibre bundle with the 200 addition of other types of PS. This can be probably related to the adsorption of PS to 201 cellulose followed by formation of mono-electric layer interfering fibre-to-fibre 202 interaction with hindering fibre aggregation (C. Xu et al., 2011). For example, the 203 charge density, *i.e.*, degree of substitution of the charged groups, in cm-GGM (DS of 204 carboxymethyl group, 1.5 (C. Xu et al., 2011)) is higher comparing to that of CMC (DS 205 of carboxymethyl group, 0.87). cm-GGM could offer greater repulsion among 206 nanofibers for better fibrillation compared with CMC. The addition of different PS to 207 the above-mentioned effect was backed up from the viewpoints of fibre-to-fibre 208 interaction through the yield stress of the produced nanocellulose suspension, where 209 the gels started flow overcoming the interaction among fibres (Magnin & Piau, 1987). 210 The relation between yield stress and shear rate of the produced nanocellulose was registered in Figure 2i. The yield points were fitted according to Casson equation as 211 212 listed in Table 1. The adsorption of cm-GGM decreased the friction among fibres in 213 MFC with decreasing the yield stress from 0.56 Pa to 0.16 Pa, where the addition of CMC showed a yield point of 0.31 Pa. This might be associated with a higher adsorption 214 215 amount to fibre surface of GGM (1.5 mg/m<sup>2</sup>) than that of CMC (0.1 mg/m<sup>2</sup>) (Eronen et 216 al., 2011; Sorvari et al., 2014).

Given that the benefits of enhancing defibrillation and introducing surface charge interfering fibre-to-fibre interaction *via* addition of cm-GGM, different addition amount of cm-GGM (1–20 wt%) was further tested to achieve successful homogenization at a higher solid content at 1.5 wt%. According to Ankerfors et al (Ankerfors, 2012), the 221 energy consumption is inversely proportional to the feasibly homogenized solid content 222 under the same homogenization pressure with a similar suspension density. Firstly, the 223 feasibility of homogenizing 1.5 wt% MFC/PS was indicated by the decrease of apparent 224 viscosity with increasing addition of cm-GGM imparting an easier flow of MFC/cm-225 GGM through the homogenization chamber (Figure S1c). This phenomenon can be 226 speculated to the reduction of the contact friction among fibres by attaching larger 227 amount of cm-GGM along increasing addition of cm-GGM into the system (Lucenius 228 et al., 2014; Naidjonoka et al., 2020). As a result, the addition of cm-GGM renders a 229 homogenization at a high solid content of 1.5 wt%. More important, the addition of 5 230 wt% of cm-GGM greatly decreased the energy consumption to approx. 2000 231 kWh/tonnes compared to homogenizing neat MFC dispersion with 0.4 wt% PS with 232 energy-consumption of approx. 7500 kWh/tonnes (Table S1) – a reduction of nearly 233 73%.



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Figure 2. AFM height images of MFC and MFC/PS 5% samples: (a) MFC, (b) MFC/CMC 5%, (c)
MFC/CGG 5%, (d) MFC/cm-GGM 5%, (e) MFC/GGM 5%, (f) MFC/ cat-GGM 5%, (g) MFC/xylan
5%, (h) height scale bar for all the images and (i) shear stress-shear rate profiles of MFC and
MFC/PS 5% samples.

## **3.1.2. Size distribution and morphology of thus-prepared nanocellulose**

## 240 *Nanocellulose fibre size distribution in micro- and nano-scale*

The effect of PS addition on fibre dimensions before and after homogenization was investigated at both micro- and nano-scale. Focusing at fibre size distribution in the range of micrometres, the addition of PS led to effective homogenization as shown by an increase of fine ratio, a decrease of length, and an increase of fibre fibrillation ratio. Most importantly, the addition of cm-GGM exhibited an outstanding properties 246 of presenting shortest length, and highest fine ratios of fibrillation comparing with addition of other PS (Figure 3b). Moreover, the addition of cm-GGM reaching the 247 248 highest degree of fibrillation value of 10.56 % is also in line with the observation from 249 AFM image (Figure 1d). It is further observed that the fibrillation degree was increased 250 with the increasing addition of cm-GGM in the MFC systems (Figure S2b). This is 251 possibly associated with the easy separation of fibres and repulsion of the produced 252 nanofibers as a result of absorption of negatively charged cm-GGM onto the surface of 253 the cellulose fibres(C. Xu et al., 2011). It is also worthwhile to stress that the effect of 254 different additive amounts of cm-GGM on the fibre change in nanoscale by DLS 255 (Figure S3) was minor from 5 to 20 wt%. Albeit that the average length of fibres was 256 decreased with increasing addition of cm-GGM, the size of nanocellulose presenting in 257 microscale was not further reduced when the addition of cm-GGM was above 5 wt% (Figure S2b). 258

259 To follow the size distribution of the produced nanocellulose in nanoscale range, 260 DLS results mainly focus on the charge of fibre size at nanoscale (Cebreiros et al., 2021; 261 Prakobna et al., 2015; Suopajärvi et al., 2015). It was found that the change of average 262 size of cellulose fibrils was subtle among MFC and MFC/PS 5% blends when the 263 suspensions were homogenized at the same low solid content of 0.4 wt%. However, 264 introducing cm-GGM 5% to the nanocellulose suspensions resulted in the smallest 265 average size among all PS addition (Figure 3a), probably due to the effective 266 homogenization process benefited by an easier flow in the chamber and the introduced 267 surface charge (Figure S2a).

268 Morphology of the nanocellulose with effect of polysaccharide addition

The morphological difference of nanocellulose fibres prepared by homogenization
steps at the presence and absence of PS was studied with TEM. Prior to homogenization,

271	a number of microfibril bundles were still present in the coarsely refined MFC sample
272	(Figure 3c). After homogenization, the microfibril bundles were as-expected liberated
273	into individual nanofibrils at the absence of PS, as observed in Figure 3d. With the
274	addition of PS, the liberation of fibres tended to in the form of nanofibrils in large
275	quantity (Figure 3(e, f) and Figure S4 (a-c)). This was attributed to the presence of
276	hemicelluloses on the fibre surface hindering the fibril coalescence along with
277	facilitating subsequent homogenization steps (Dias et al., 2019). Moreover, the
278	microfibrils bundles were readily liberated to individual microfibrils and even
279	elementary fibrils, as the amount of cm-GGM increased, as shown in Figure 4 (g-j). It
280	also indicated that the presence of more cm-GGM possibly resulted in a higher surface
281	coverage and larger electrostatic repulsion among cellulose fibres.
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Figure 3. (a) Size average of MFC and MFC/PS 5% samples before and after redispersion; and (b)
3D plots of fibres dimension: fibre length (x axis), fine ratio (y axis) and fibrillation degree (z axis)
of samples. MFC-BH: MFC prepared before homogenization. TEM images of MFC and MFC/PS
5% samples: (c) MFC before homogenization, (d-j) MFC and MFC/PS 5% after homogenization:
(d) MFC, (e) MFC/CMC 5%, (f) MFC/GGM 5%, (g) MFC/cm-GGM 1%, (h) MFC/cm-GGM 5%,
(i) MFC/cm-GGM 10%, (j) MFC/cm-GGM 20%.

297 **3.2** Improving nanocellulose redispersibility through polysaccharide addition

Redispersibility is a crucial factor in nanocellulose applications with a massive quantity considering its high expense in transportation at the presence of excess water. The strong intermolecular hydrogen bonding interaction and the high surface energy of nanocellulose make it tend to aggregate during and after drying. Interfering fibre-tofibre interaction avoiding nanofibril aggregation through approaches such as surface physical adsorption and chemical modification has been attempted to produce 304 redispersible nanocellulose in water or other organic solvents (Chu et al., 2020). 305 Physical adsorption of dispersants onto nanocellulose surface is a high-efficacy approach to reduce intermolecular hydrogen bonding. Dispersants like glucose, 306 307 xyloglucan, chitosan, CMC, maltodextrin, and tert-butanol have been attempted to 308 reach nanocellulose redispersibility, as summarized in Table 1 (Butchosa & Zhou, 2014; 309 Hanif et al., 2018; Velásquez-Cock et al., 2018; Zhang et al., 2021). However, all the 310 above-mentioned processes have been established after nanocellulose production where 311 the energy consumption was initially intensive and adding process complexity.

In the following parts, the nanocellulose produced *via* addition of hemicellulose and its derivatives will be scrutinized from diverse viewpoints. Particularly, viscosity, size and morphology distribution, as well as mechanical and optical properties of the cast films of thus-prepared nanocellulose before and after redispersion were thoroughly compared.

Substrates	Drying methods	Redispersing agents	Process description	Amount	Property changes	Ref.
CNF, TEMPO- CNF, CNC	Oven drying/fr eeze drying	Tert-butanol(t- BuOH)	a t- BuOH/water mixture remained on the cellulose surface	Water/ter t-butanol (1:9, 5:5 and 9:1)	Similar in particle size, light transmittance, and sedimentation	(Hanif et al., 2018)
CNF	Oven drying	maltodextrin (MDX)	MDX/CNF mixture prevent the hornification of CNF	1-2.5- fold of nanocell ulose	Similar rheological and morphological behaviour	(Velásquez -Cock et al., 2018)
CNF	Oven drying	CMC, cationic and anionic xyloglucan derivatives, chitosan (50% acetylation), hydroxyethyl cellulose	Form an interfacial film around nanocellulos e and preventing aggregation	30% CMC	Lower mechanical properties	(Butchosa & Zhou, 2014)
CNC	Oven drying	Glucose	Glucose adsorption onto CNC via alcohol precipitation	20% glucose	similar particle size distribution and zeta potential	(Zhang et al., 2021)

317 Table 1. Comparison of among different approaches for nanocellulose redispersibility improvement318

# 319 3.2.1 Redispersibility: comparison of viscosity profile before and after 320 redispersion

Viscosity profile is associated to fibre-to-fibre interaction and fibre-water interaction in a microscopic manner (Lowys et al., 2001). Viscosity is meanwhile an essential reflection of nanocellulose redispersibility whether reaching its initial state before drying or not.

325 Firstly, all the prepared nanocellulose suspensions with and without addition of PS, 326 showed a pseudoplastic behaviour (Figure 4a and Figure S5a) while subjected to an 327 increasing shear rate (Mazhari Mousavi et al., 2017; Nazari et al., 2016), featuring the 328 related applications, e.g., in coating and extrusion, etc. The MFC/PS exhibited a lower 329 viscosity profile as compared with that of homogenized MFC alone after 330 homogenization (Figure 4a). It is noteworthy that the viscosity of nanocellulose (*i.e.*, 331 MFC/cm-GGM) decreased with increasing addition amounts of cm-GGM (Figure 4b). 332 This could be attributed to the introduction of surface charge onto the fibre surfaces by 333 the PS adsorption, increasing fibre repusion. Moreover, the viscosity plateau presented at a shear rate of approximately 10 s<sup>-1</sup> revealing the typical feature of thus-produced 334 335 fibres in nanocellulose state, as illustrated in Figure 4a and 4b (Jaiswal et al., 2021; 336 Lowys et al., 2001; Talantikite et al., 2019). The shear flow curve exhibited the different 337 shear rate regimes before and after the viscosity plateau due to that an addition of PS 338 affected the inter-fibrillary structure. This is in line with the fact of PS addition interfering fibre-to-fibre interaction (Figure 2i). It is also worth mentioning the 339 340 apparent dip in the flow curves of all of the MFC/PS 5% suspensions at high shear rates (appearing at around 1000 s<sup>-1</sup>) was outstanding as compared to the neat MFC 341 342 suspension, implying a gel network structure of the produced nanocellulose with PS 343 addition.

344 All the nanocellulose samples were freeze-dried and redispersed at a solid content 345 of 0.4 wt%. Figure 4c and Figure S5b illustrated the shear-thinning behaviours of all 346 redispersed samples under the solid content of 0.4 wt%. The viscosity of redispersed 347 MFC was lower than the homogenized MFC suspension before redispersion in the full shear rate range. In contrast, in the presence of PS, the viscosity of redispersed MFC/PS 348 349 suspension behaved similarly to the initial samples before drying possibly due to the 350 increased ionic strength via the presence of surface charged groups, enhancing the fibre-351 to-fibre interactions (Agoda-Tandjawa et al., 2010). It is notable that the apparent dip 352 at high shear rate exited in the flow curves for redispersed samples, indicating preserved 353 gel-like network after dispersion (Figure 4c). In particular, both the RD-MFC/cm-354 GGM 5% and RD-MFC/GGM 5% enabled the recovery of nanodispersion state after 355 drying. In addition, as the efforts to prepare water-redispersible nanocellulose in a high 356 solid content, the drying of nanocellulose was also tested at a high solid content of 1.3 357 wt%. Figure 4d showed redispersible samples with the addition of cm-GGM(1-20%)358 under the solids content 1.3 wt% subjected to viscosity measurement. All samples in 359 this case had lower viscosity (Figure 4d) than that prior to drying (Figure 4b), 360 indicating more flocculation because of more aggregation among fibres caused by high 361 solid content during drying.



Figure 4. (a) Viscosity profile of MFC, MFC/CMC 5%, MFC.cm-GGM 5% and MFC/GGM 5% at
0.4 wt% solid content, (b) MFC/cm-GGM (1%, 5%, 10% and 20%) at 1.3 wt% solid content, (c)
RD-MFC, RD-MFC/CMC 5%, RD-MFC/cm-GGM 5% and RD-MFC/GGM 5% at 0.4 wt% solid
content, and (d) RD-MFC/cm-GGM (1%, 5%, 10% and 20%) at 1.3 wt% solid content.

## 368 **3.2.2 Redispersibility: change of size and morphology after redispersion**

369 The average size of the fibres in nanoscale after redispersion was examined by 370 DLS as shown in **Figure 3a**. In comparison with the redispersed MFC, the addition of 371 PS preserved the size distribution. This is likely due to those water-soluble 372 hemicelluloses adsorbed on fibre surfaces facilitating fibre reorganization in water during the redispersion process (Yang et al., 2020). The addition of cm-GGM imparts 373 374 the smallest fibres dimension, *i.e.*, short length, high fine ratio and large fibrillation 375 degree, as it is comparable with that of prior to drying (Figure S2a). However, RD-MFC/cm-GGM (1-20%) presented a larger average size and lower fibrillation degree 376

377 at solids contents below 1.3 wt%, compared to prior to drying, particularly with 20% 378 of cm-GGM (Figure S3). Furthermore, the fibres dimension of RD-MFC/cm-GGM 379 exhibited a lower fibrillation compared to MFC/cm-GGM (Figure S2c and 2b). It is 380 notable that the average size of RD-MFC/cm-GGM 5% at a solids content of 1.3 wt% 381 was higher than those samples at the solids content of 0.4 wt% under the same treatment 382 condition. It could be speculated that the solids content (< 0.5 wt%) of nanocellulose 383 suspension prior to freeze drying nanocellulose aerogel played a more dominant role 384 than merely as redispersing aids (Huang et al., 2020; Žepič et al., 2014).

385 Moreover, the investigation of the morphology of fibres from the redispersed 386 samples revealed that severe agglomeration happened in RD-MFC after freeze drying 387 in comparison to the raw MFC suspension as a result of the strong fibre aggregation 388 (Figure S6a). Intriguingly, cm-GGM with a mass fraction of 5-20 wt% resulted in a 389 similar fibre morphology as shown in Figure S7(f-h), although the fibre dimension of 390 cm-GGM 20% observed from FS5 was comparably lower than those of cm-GGM 5% 391 and 10%. It is assumed that nanocellulose agglomeration caused by intermolecular 392 hydrogen bonding of cellulose fibres during drying was minimized, as the negative 393 charges were introduced onto the surface of nanocellulose by absorbed CMC (Butchosa 394 et al., 2014). Collectively, it was conclusive that the addition of cm-GGM for 395 production of nanocellulose plays an imperative role on the aids of the re-defibrillation 396 and improving redispersibility.

# 397 3.2.3 Redispersibility: film mechanical and optical properties of MFC and 398 MFC/PS before and after redispersion

The physical properties such as density and mechanical property of the cast film are good indicators of packing nanofiber network with individual fibres or existence of flocs after redispersion (Nordenström et al., 2021). Prior to redispersion, the density of

all samples was approximately 1.3±0.1 g/cm<sup>3</sup> (Table S2). This is in the density range 402 403 of nanocellulose film, 1.3-1.6 g/cm<sup>3</sup>(Kumar et al., 2014; Nishiyama et al., 2002) 404 confirming a very close packed structure. The tensile strength of cast films using the 405 homogenized MFC (approx. 62 MPa), was much lower than those of MFC/PS (approx. 406 117 MPa), except for MFC/CMC 5% as shown in Figure 5a. This is possibly due to 407 CMC acting as a plasticizer and thus enhancing the strain at break (Table S2) (Ninan 408 et al., 2013). The PS derived from hemicelluloses, *i.e.*, cm-GGM, GGM, cat-GGM and 409 xylan, significantly enhanced the tensile strength (Table S2) as compared to that of 410 commercial PS. This is consistent with other reports of improving the tensile strength 411 of CNF composites by adding hemicelluloses (Jaiswal et al., 2021; Lucenius et al., 412 2014). Moreover, as reported by Larsson et al. (Larsson et al., 2019), the increased 413 defibrillation degree had a positive effect on mechanical properties via exposing more 414 surface groups and binding sites of the fibres. The introduced PS can also act as physical 415 crosslinkers (Oinonen et al., 2016; Lucenius et al., 2014, Prakobna et al., 2015) between 416 the cellulose fibrils, which improves their mechanical properties. The effect of the 417 additive amount of cm-GGM on the mechanical properties was further investigated 418 (Table S3). It was observed that the tensile strength reached a plateau at 5 wt% addition 419 of cm-GGM. Nevertheless, the film tensile strength of MFC/cm-GGM 5% prepared 420 from homogenization at a solids content of 1.5 wt% was comparatively lower than at a 421 solids content of 1 wt% (Table S3 and S2). It is speculated that the slippage of 422 nanofibrils caused by strong interfacial adhesion of cm-GGM under relatively high 423 solids content was restricted, leading to slightly brittle films with weaker toughness, as 424 shown in an earlier peer study (Prakobna et al., 2015). Nevertheless, the produced 425 nanocellulose via the present method offers a mechanically robust film as compared 426 with others where PS was blended with nanocellulose(Jonoobi et al., 2014; Lucenius et 427 al., 2019; Mikkonen et al., 2012; Nakagaito et al., 2018; Oinonen et al., 2016), as shown
428 in Figure 5b.

429 After drying, the cast film of RD-MFC were uneven with a failure of tensile 430 strength (Figure 5a and Table S2), as observed by SEM cross-section image (Figure 431 S8c). This is due to that it failed to achieve a homogeneous dispersion while it was 432 redispersed in water. In contrast, the addition of cm-GGM supplying a high degree of 433 fibrillation and great redispersible state allows the recovery of tensile strength for film 434 of RD-MFC/cm-GGM. This is possibly associated to the presence of PS on the 435 nanocellulose surface, which serves as physical link among cellulose fibrils. Those 436 physical links could interfere the fibre-to-fibre interaction, hampering the formation of 437 intermolecular hydrogen bonding during drying, as illustrated in Figure 6. Meanwhile, 438 the presence of amorphous PS on the surface can facilitate water penetration into dried 439 nanocellulose and thus promote fibre swelling. Moreover, the presence of surface 440 charged PS serves as a dispersant with imparting physically adsorbed charge groups 441 aiding the redispersion. This is also reflected by the fact that the strain at the break of 442 films from the RD-MFC/cm-GGM 5% was slightly higher than that of RD-MFC, as 443 agreed with the studies using TEMPO-CNFs (Sehaqui et al., 2012). In addition, it is 444 notable that the density of all samples from RD-MFC/cm-GGM (1-20%) was decreased 445 compared to that prior to drying (Table S3). This can be explained such that serious 446 agglomeration occurred when the samples were redispersed in water, as supported by 447 large average size (Figure S3), low fibre defibrillation (Figure S2c) and low viscosity 448 (Figure 4d) compared to what was observed for the samples prior to drying. The tensile 449 strength of MFC/cm-GGM (1-20%) did not change excessively before and after 450 redispersion.

451 The optical properties of MFC films with the presence of polysaccharides were 452 investigated as another factor revealing nanocellulose redispersibility due to that the 453 transparency is a function of light scattering elements against nanofiber size and 454 homogeneity(Kumar et al., 2014), as shown in Figure 5 c, d and Table S2, 3. Prior to 455 redispersion, the transmittance rate at 550 nm of MFC films was 74%. The addition of 456 PS, in particular cm-GGM, exhibited a slightly enhanced transparency (around 77%) 457 with a reduction of the haze value from 83 % (haze of MFC films) to 68 %, indicating 458 addition of cm-GGM decreasing fibre dimension(Zhao et al., 2017) after mechanical 459 defibrillation. While mechanical defibrillation was carried out at a high solid content of 460 1.5 wt%, the transparency of the cast film is intriguingly increased possibly due to the 461 feature of a less porous film associated with higher density (Table S3). Furthermore, 462 after redispersion, it was observed that the transmittance rate (Table S2) of RD-463 MFC/CMC 5% and RD-MFC/cm-GGM 5% exhibited a similar transparency as those 464 of before redispersion, supporting that fibre dimension can regain its nano-dimension. 465 Moreover, as both the transmittance and haze rate were high, it could also be a 466 promising coating layer in solar cells (Zhu et al., 2013). In conclusion, cm-GGM works 467 as the best candidate among other polysaccharides achieving good water 468 redispersibility upon assessing the redispersibility of nanocellulose in combination with 469 the mechanical property and optical properties.



471 Figure 5. (a) Tensile strength of MFC, MFC/PS 5%, RD-MFC and RD/PS 5%, (b) comparison of 472 tensile strength and Young's modulus in among peer studies and present work, (c) Optical 473 transmittance rate of MFC, MFC/PS 5%, RD-MFC and RD-MFC/PS 5%, (d) Optical transmittance 474 rate of MFC/cm-GGM (1%, 5%, 10%, and 20%) and RD/cm-GGM (1%, 5%, 10%, and 20%).





477 Figure 6. The proposed mechanism of interfering fibre to fibre interaction in presence of

478 hemicellulose addition.

## 479 **4. Conclusion**

480 In the present study, an addition of six polysaccharides, *i.e.*, carboxymethyl 481 cellulose (CMC), cationic guar gum (CGG), O-acetyl-galactoglucomannan (GGM), cationic-GGM, anionic-GGM, and xylan, to the coarsely refined MFC by Prolab<sup>TM</sup> 482 483 refiner was attempted and scrutinized to provide an integrated avenue for water-484 redispersible nanocellulose production. Adding PS was validated for easing the 485 clogging issues during homogenization for nanocellulose production with significantly 486 less energy consumption. Intriguingly, the addition of cm-GGM 5% facilitated 487 nanocellulose production at a high solids content of 1.5 wt%, compared with a 488 maximum of 0.4 wt% obtainable with neat MFC. Moreover, the energy consumption 489 during nanocellulose production was considerably decreased with the addition of cm-490 GGM 5% prior to the homogenization steps. The addition of cm-GGM facilitated 491 defibrillation and reduced fibre size, achieving nanocellulose production. Furthermore, 492 the addition of cm-GGM significantly influenced the transparency and haze of 493 nanocellulose-based films and improved their tensile strength.

494 In this study, it was also confirmed that an addition of PS could facilitate 495 nanocellulose redispersibility. This can ease the transportation of nanocellulose with 496 high solid content, reducing the transportable mass. When assessing the redispersibility, 497 MFC/cm-GGM 5% at the solid content of 0.4 wt% exhibited a noteworthy good 498 recovery to nano-redispersion state as was indicated in courses of viscosity, size 499 distribution on the nano-/microscale, and tensile strength as well as film transparency. 500 This suggests that the addition of hemicelluloses, especially cm-GGM, can improve the 501 redispersibility of nanocellulose at low solid content. However, further studies would 502 be required to get fully redispersible nanocellulose products at high solid content, for

instance looking into how adsorbed PS functions in the vicinity of cellulose fibresurfaces during homogenization.

505

## 506 Author contribution

Liqiu Hu: Methodology, Validation, Formal analysis, Writing-original draft,
Visualization. Wenyang Xu: Methodology, Validation, Writing-review & editing,
Supervision. Jan Gustafsson, Anna Sundberg, Martti Toivakka and Stefan Willför:
Resource, Review & Editing and Supervision. Rajesh Koppolu and Qingbo Wang:
Measurement and review. Emil Rosqvist and Jouko Peltonen: Resource, Review &
Editing. Chunlin Xu: Conceptualization, Methodology, Resource, Review & Editing
and Supervision.

### 514 Notes

515 The authors declare no competing financial interest.

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