
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Sethi, Jatin; Farooq, Muhammad; Österberg, Monika; Illikainen, Mirja; Sirviö, Juho Antti
Stereoselectively water resistant hybrid nanopapers prepared by cellulose nanofibers and water-based polyurethane

Published in:
Carbohydrate Polymers

DOI:
[10.1016/j.carbpol.2018.07.028](https://doi.org/10.1016/j.carbpol.2018.07.028)

Published: 01/11/2018

Document Version
Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

Published under the following license:
CC BY-NC-ND

Please cite the original version:
Sethi, J., Farooq, M., Österberg, M., Illikainen, M., & Sirviö, J. A. (2018). Stereoselectively water resistant hybrid nanopapers prepared by cellulose nanofibers and water-based polyurethane. *Carbohydrate Polymers*, 199, 286-293. <https://doi.org/10.1016/j.carbpol.2018.07.028>

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

1 **Stereoselectively water resistant hybrid nanopapers**
2 **prepared by cellulose nanofibers and water-based**
3 **polyurethane**

4 Jatin Sethi¹, Muhammad Farooq², Monika Österberg², Mirja Illikainen¹,
5 and Juho Antti Sirviö^{1*}

6 1. Fibre and Particle Engineering, University of Oulu, Oulu, Finland.

7 2. Department of Bioproducts and Biosystems, Aalto University, Helsinki, Finland.

8 ***Corresponding Author:** Juho Antti Sirviö, **Email:** juho.sirvio@oulu.fi

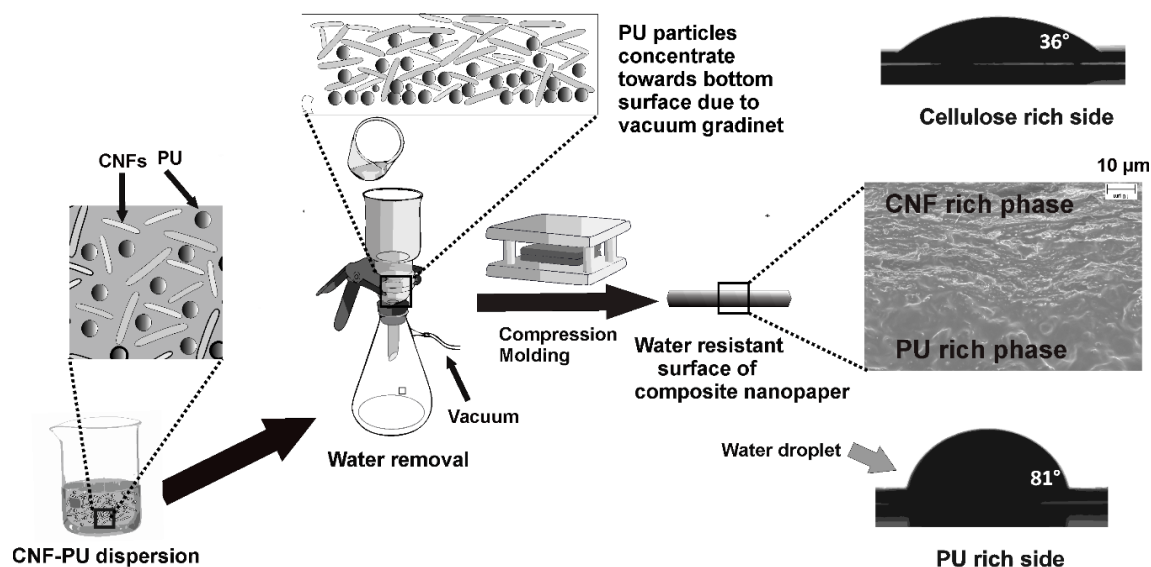
9 **Abstract**

10 Cellulose nanopapers, known for excellent mechanical properties, loses 90% of their
11 stiffness in the wet conditions. In this study, we attempt to improve the wet mechanical
12 properties of cellulose nanopaper by incorporating polyurethane by a novel and
13 ecofriendly method. Water based PU was dispersed along with CNFs in water and
14 hybrid nanopapers were prepared by draining water under vacuum followed by forced
15 drying. These hybrid nanopapers have a gradient interpenetrating structure with PU
16 concentrated towards one side and CNFs towards the other, which was confirmed by
17 scanning electron microscopy, x-ray photoelectron spectroscopy and contact angle
18 measurements. Because of this, the nanopapers are water resistant on one surface (PU
19 rich side) and hydrophilic on the other (cellulose rich side), making them
20 stereoselectively water resistant. When wetted with water on the PU side, the hybrid
21 nanopaper with 10% PU is able to retain 65% modulus; on the other hand, the reference
22 retains only 10% of the modulus. Similar results are seen in the tensile and the yield
23 strength. Additionally, the hybrid nanopapers have higher elongation than the reference
24 indicating their relevance to the reported material in applications such as flexible

25 electronics. Finally, the hybrid nanopapers have an improved thermal stability
 26 according to TGA results. The reported material is relevant to the applications such as
 27 flexible electronics and transparent displays.

28

29 Graphical Abstract



30 Stereoselectively water resistant composite nanopaper

31 **Keywords:** Cellulose nanopapers; Polyurethane; Flexible composites; Hybrid materials;
 32 Gradient interpenetrating network; Water resistance.

33 1 Introduction

34 Non-degradable plastic materials have dominated the world of materials for almost a
 35 century, which until recently, was proudly addressed as the age of plastics. Plastics
 36 evolved as a corrosion free, lightweight, durable material for non-structural applications
 37 (Greene & Tonjes, 2014). Characteristics with such a stark contrast to corroding and
 38 expensive metals skyrocketed their popularity, making them mandatory for everyday
 39 materials. In course of modernization and progress, they became irreplaceable. As the
 40 population grew, so did the demand and supply of the plastics. The perils of plastics

41 were ignored for a long time. However, during last couple of decades, it has been
42 realized that such materials are damaging our environment on a massive scale. Plastics
43 are one of the major pollutants produced by us. Plastic has created (and is still creating)
44 a massive amount of landfill deposits. If not lying dormant under the ground, plastics
45 will be floating in the oceans for a long time (Barnes, Galgani, Thompson, & Barlaz,
46 2009). There is no easy way to get rid of such ultra-stable materials. The hailed
47 durability of plastics is, in fact, a curse in terms of sustainability and environmental
48 protection. Additionally, the crude oil resources are depleting faster than ever (Gamadi,
49 Elldakli, & Sheng, 2014). It has become a matter of paramount interest among the
50 material scientists to find environment- friendly alternatives for the everlasting plastics.
51 A common trend is to combine the synthetic plastic with renewable polymer to obtain a
52 new environment-friendly polymeric material (Kim & Park, 1999; H. J. Lee, Lee, Lim,
53 & Song, 2015).

54 In search of renewable materials, researchers have refocused on the cellulose, which is
55 the most abundant polymer in the world. Cellulose, a biodegradable polymer, was a
56 major source material for a long time much before industrial revolution (in the form of
57 paper and wood). In search of alternative, new eco-friendly materials, it received a head
58 start as its chemistry is well-documented and understood. Additionally, it was found
59 that nanoscale, cellulose offers exciting opportunities for functional materials (Klemm
60 et al., 2011; Shun Li, Qi, & Huang, 2017) Cellulose, present in form of well-arranged
61 crystallites in amorphous matrix of hemi-celluloses and lignin, is the vital structural
62 element of wood. It has been estimated that elastic modulus of cellulose crystal can be
63 as high as 100-160 GPa (Eichhorn et al., 2010; Mittal et al., 2018). Such fascinating
64 properties of a natural material have persuaded researchers to use this ancient material

65 in their modern research. Nanocellulose has started an exciting field of research with
66 promising future, but it is certainly not devoid of challenges.

67 As any new field of research, nanocellulose has brought its own roadblocks, which need
68 to be crossed. The major one was large-scale production in a cost effective way– as
69 grinding pulp to nanosized fibers was a slow and energy consuming process. The
70 problem was solved by using energy-efficient production which involved use of
71 physical, chemical or enzymatic pretreatment of cellulose pulp, followed by
72 homogenization (grinding) (Isogai, 2018; Klemm et al., 2011). Once the feasible
73 production methods were established, the attention was focused on the various aspects
74 of material and its potential uses. One such product is self-standing 100% cellulose film
75 called nanopapers, which are prepared by draining water from cellulose nanofibers
76 (CNFs). They are fascinating as they are known to have an elastic modulus of 10-20
77 GPa and a strength of 200 MPa (Henriksson, Berglund, Isaksson, Lindström, &
78 Nishino, 2008; Sehaqui et al., 2012), which is unheard of in case of a polymeric
79 material. It has been suggested that in the future, nanopaper will find use in high-end
80 applications such as packaging (Sehaqui, Zimmermann, & Tingaut, 2014), electronic
81 displays (Sehaqui et al., 2014), flexible electronics (Koga et al., 2014), lithium ion
82 batteries (Chun, Lee, Doh, Lee, & Kim, 2011), and transformers (Huang, Zhou, Zhang,
83 & Zhou, 2018) .

84 Despite such excellent properties and huge potential, nanopapers are still far away from
85 commercialization. One of the major reasons being their poor performance under water
86 (Benítez, Torres-Rendon, Poutanen, & Walther, 2013). When wetted with water, the
87 nanopaper drastically loses its mechanical properties. It has been reported that the
88 modulus of a soaked nanopaper reduces to 95% of the dry value (Sehaqui et al., 2014).
89 Even in the presence of high humidity, the mechanical properties are heavily mitigated

90 (Benítez et al., 2013). The reason behind this is that the cellulose molecule has pendant
91 hydroxyl groups that make the surface hydrophilic. As a result, water seeps into the
92 interfibrillar region of the nanopaper and causes the nanofibers to slide easily under
93 external load leading to poor mechanical properties (Benítez et al., 2013). We found that
94 this issue, understandably an important one, has rarely been discussed in literature.
95 Sehaqui et al. modified nanofibers by grafting them with alkyl chains through
96 esterification (Sehaqui et al., 2014). The presence of hydrophobic chains instead of
97 hydrophilic hydroxyl group rendered the resulting nanopaper hydrophobic with 20-fold
98 improvement in wet strength as compared to a reference. Recently, we used lactic acid
99 modification to improve the water resistance and dimensional stability of nanopapers
100 (Sethi, Farooq, et al., 2018). In this research, we hypothesized that using nanoscale
101 polymer particles in tandem with cellulose nanofibers would be a possible way of
102 preparing nanopapers with improved water resistance. It was decided to use water-based
103 latexes as they are already stable in an aqueous suspension and have a nanoscale particle
104 size (Product center coatings Covestro, 2018). The idea was to combine a renewable
105 material (cellulose) with a synthetic polymer to prepare a superior hybrid material with
106 minimal environmental impact. The structure was inspired by wood, which is more than
107 50% cellulose and still water resistant, due to the presence of lignin that gives it its
108 extraordinary strength even in rain. Biomimicking is an interesting approach to prepare
109 advanced materials. Nature has found a perfect way to make natural materials to
110 particular standards. The key to commercialization of such materials can be in seeking
111 inspiration from nature.

112 This paper presents a water-based method to prepare polyurethane (PU) –CNF hybrid
113 nanopapers from a water based method. A commercially available PU dispersion
114 (Bayhydrol[®] UH 240) and a CNF suspension was combined and water was drained to

115 make nanopapers with PU concentration of around 1 wt.-%, 10 wt.-%, 30wt.-% and
116 60wt.-%. The morphology was analyzed by scanning electron microscopy. X-ray
117 photoelectron spectroscopy (XPS) and contact angle measurements were used to
118 characterize the surface properties. Tensile testing (dry and wet) was used to evaluate
119 the mechanical properties and Thermogravimetric analysis (TGA) was used to evaluate
120 the thermal stability. The papers prepared were significantly more water-resistant than
121 the reference and were also thermally stable. The hybrid nanopaper containing relatively
122 small amount (10 wt.-%) of non-biodegradable polymer exhibited superior properties
123 compared to reference nanopaper from pure CNF.

124 **2 Materials and methods**

125 Bayhydrol[®] UH 240 (henceforth, referred to as UH 240), an anionic surfactant based
126 polyurethane dispersion was kindly provided by Covestro. The characteristics of UH
127 240 are provided in Table S1 (supplementary file). Cellulose nanofibers were prepared
128 from softwood sulfite pulp provided by Stora Enso (Oulu, Finland). For grinding, pulp
129 with a concentration of 1.6 wt.-% was fed to a Masuko grinder. The initial contact mode
130 was 0-point, and the distance was gradually decreased from - 20 (3 passes), - 40 (4
131 passes), - 60 (5 passes) and - 90 (7 passes). The chemical composition of the reference
132 pulp was 95.0 wt.-% cellulose, 4.2 wt.-% hemicellulose, 0.3 wt.-% lignin and 0.5 wt.-%.
133 L-(+)-Lactic acid (80%) was purchased from Sigma-Aldrich.

134 **2.1 Preparation of nanopaper**

135 CNF suspension was diluted to a concentration of 0.2 wt.-% and UH240 was added to
136 obtain a proportion of CNF to PU as 95:5, 80:20, 50:50 and 30:70. The CNF-PU
137 suspension was mixed with a high speed ultraturrax at 10000 rpm. Lactic acid (equal to
138 amount of dry CNF) was used as additive to reduce the draining time. The sample was

139 sonicated till the energy imparted was 300 J/ml. The details of this method is reported
140 elsewhere (Sethi, Oksman, Illikainen, & Sirviö, 2018).

141 The nanopapers were prepared by filtering the suspension of CNFs and UH 240 through
142 a Durapore PVDF membrane filter (Fisher Scientific, Pittsburgh, USA) with a pore size
143 0.65 μm . The vacuum was kept at 70 ± 5 kPa. Before filtration, the suspension was
144 degassed under a vacuum of 70 kPa for half an hour. The wet CNF-PU sheet was peeled
145 off from the PVDF membrane and kept between two steel mesh cloths (mesh size 70
146 μm), along with absorbent papers and carrier boards. The whole assembly was kept in
147 compression molding at a temperature of 100 °C and a pressure of 5 MPa for 30
148 minutes. For composites with PU concentration higher than 50 wt.-%, PU was in a
149 major phase and was infused into the steel mesh under higher temperature and pressure.
150 Therefore, the pressure was reduced to 0.5 MPa to aid the film formation, once the film
151 was dry, the steel mesh was removed and the films were compressed at 5 MPa for 30
152 minutes. The coding of the samples was done according to the amount of PU in the final
153 film. It was observed that some PU was filtering through the PVDF membrane, perhaps
154 due to its spherical morphology and the high vacuum. Therefore, the PU fraction was
155 determined by calculating the increase in weight in comparison to the reference CNF
156 film. The final samples were named as CNF(1)PU, CNF(10)PU, CNF(30)PU and
157 CNF(60)PU, where the number in brackets refer to the actual concentration of PU in the
158 film.

159 **2.2 Characterization**

160 2.2.1 Scanning electron microscopy

161 Zeiss Ultra Plus (Oberkochen, Germany) field emission scanning electron microscope
162 (FE-SEM) was used for studying the morphology of hybrid nanopapers. The in-lens

163 detector was used to collect signals from platinum coated samples after scanning the
164 sample with an electron beam and an acceleration voltage of 5 kV.

165 2.2.2 X-ray photoelectron spectroscopy

166 Thermo Fisher Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS)
167 system was used for conducting chemical surface analysis. XPS spectra were collected
168 using monochromatic Al K α (1486.6 eV) beam. Survey scan pass energy of 150 eV
169 using 1 eV step and High-resolution scan pass energy of 20 eV was with 0.1 eV was
170 used along with charge compensation by ion bombardment. The analysis chamber
171 pressure was about 3×10^{-9} mbar.

172 2.2.3 Water contact angle

173 CAM 200 (KSV Instruments Ltd, Finland) was used for contact angle measurements. A
174 6.5 μ L drop of Milli-Q water was placed on both sides of the surface, and 60 images
175 were captured via the CCD camera (1 image/sec). The contact angle was determined by
176 the software provided by the instrument manufacturer. Three measurements at different
177 positions were made and the average values with standard deviation are reported.

178 2.2.4 Mechanical properties

179 Tensile testing of the samples was done using Instron 5544 universal material testing
180 machine (Norwood USA). Strips (50mm x 5 mm) were cut from the hybrid and
181 reference nanopapers and stored in controlled environment chamber for at least 96 hours
182 before testing, which was maintained at a humidity of 50% and a temperature of 23 °C.
183 The tests were conducted using a 100 N load cell, and the crosshead speed was 2
184 mm/minute. The distance (gauge length) between the grips was 3 mm. The elastic
185 modulus was calculated from the slope of the stress-strain curve in the linear region of
186 the curve with the help of Origin software. The results are reported as an average of
187 minimum of 5 samples. The same tensile testing parameters and equipment was used

188 for wet tensile testing, which was planned on the basis of procedure described by
189 Sehaqui et al. (Sehaqui et al., 2014). Briefly, a drop of 50 μl was carefully placed on the
190 middle of the strips (50 mm x 5 mm). Stress-strain curves were recorded after 60
191 seconds of wetting and the results are reported as an average of three samples. The
192 procedure was recorded on both sides to test the water resistance of both the surfaces.
193 Wet by dry stiffness ratio ($E_{\text{wet}}/E_{\text{dry}}$) was used to compare the modulus reduction in
194 different samples.

195 2.2.5 Swelling studies

196 Swelling studies were conducted to measure the water absorption. Samples were dipped
197 in the water overnight and the increase in weight was recorded. Before weighing, the
198 excess water was removed by pressing samples in blotting paper.

199 2.2.6 Thermal stability

200 Thermogravimetric analysis (TGA) of the hybrid nanopapers was conducted with the
201 aid of TA-TGA Q500 (New Castle, USA). 10 mg sample was heated in platinum pan
202 till a temperature of 900 $^{\circ}\text{C}$ was reached under the nitrogen atmosphere, with a heating
203 rate of 10 $^{\circ}\text{C}/\text{min}$.

204 3 Results and discussion

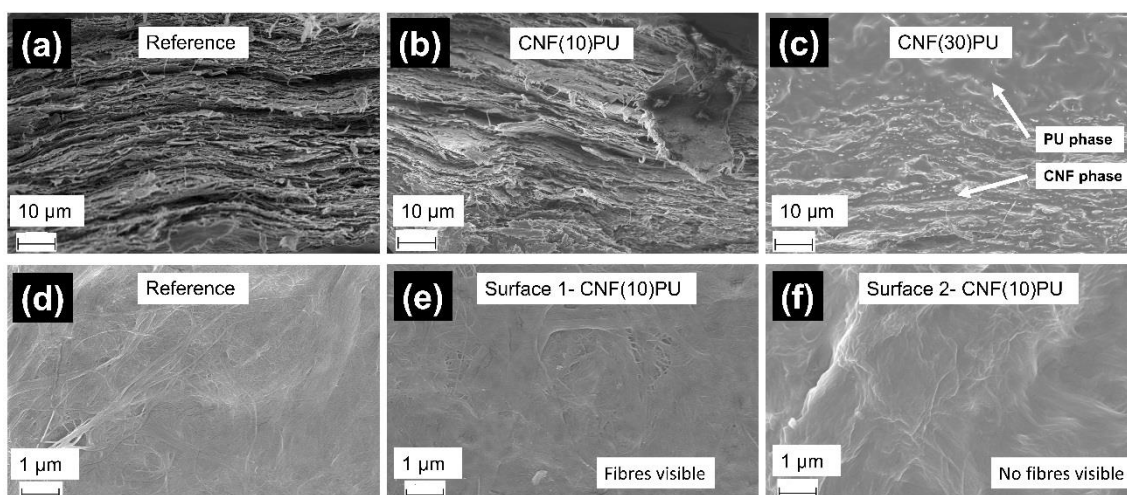
205 3.1 Morphology

206 Introduction of PU in the nanopaper led to significant change in the morphology as
207 observed in Figure 1 (a,b, and c), which shows FESEM images of the cross-section of
208 samples fractured in tensile testing. Both the reference and the hybrid nanopapers have a
209 layered structure, which is characteristic of cellulose nanopapers. However, in the
210 hybrid nanopapers, the contrast due to the presence of PU is obvious, especially, in CNF
211 (30) PU where the CNF layers are seen well-embedded in the PU matrix. Additionally,

212 there is a difference in the phase structure of PU and CNFs across the cross-section.

213 There is a PU rich phase towards the top surface and a CNF rich phase towards the
214 bottom surface (CNF(30)PU). The preferential presence of PU towards one surface is
215 confirmed by FESEM images of the surface (Figure 1(d, e, and f), which presents the
216 surface morphology of the CNF(10)PU hybrid nanopaper (both surface; Figure 1e and
217 f) and reference nanopaper (Figure 1d). Interestingly, CNF fibers are visible on one of
218 the surfaces on hybrid nanopaper, which is much the same as it is in reference
219 nanopaper. However, on the other surface of CNF(10)PU, the characteristic fibrous
220 surfaces of CNF are not observed. The images also indicate that the PU is uniformly
221 distributed among the fibers, and doesn't form a mere coating.

222 The shape of the PU and the CNF particles in suspension might explain the preferential
223 migration of PU towards one of the surfaces. PU is present as spherical particles while
224 CNFs are fibrous entities. When mixed together to form a suspension in water, they will
225 be equally distributed. However, when the water is drained through the PVDF
226 membrane to make nanopaper, CNFs are retained on the membrane to form a fibrous
227 network structure caused by "concentration induced aggregation and floc
228 formation"(Benítez et al., 2013). On the other hand, PU particles are in spherical shape
229 and under the influence of vacuum gradient, they are likely to get sucked through the
230 CNF web as particles through a membrane, thus concentrating towards the membrane
231 and resulting in a PU rich phase. The whole system can be seen as an intricate network
232 of CNFs embedded in a matrix of PU, which forms its own network, with concentration
233 varying along the cross-section. This kind of formation is called a gradient based
234 interpenetrating network, where concentration of individual components varies across
235 the cross-section (Lipatov & Karabanova, 1995).



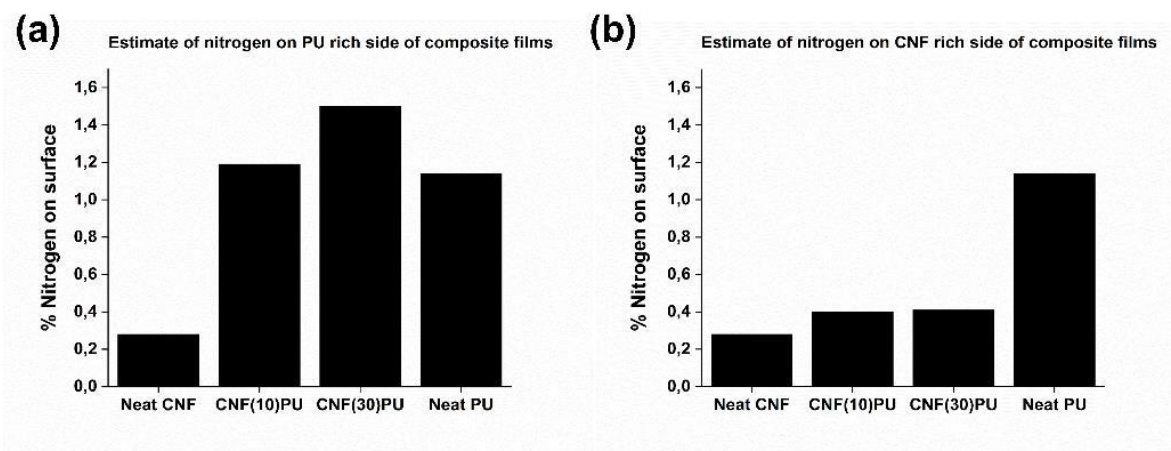
236

237 Figure 1 (a), (b), and (c). The layered structure of the reference and hybrid nanopapers
 238 (CNF(10)PU and CNF(30)PU). Impregnation of the CNF structure by PU is clearly
 239 visible in CNF(30)PU. (d), (e), and (f) FESEM images of surface of reference
 240 nanopaper and both, CNF rich and PU rich, surfaces of CNF(10)PU. The reference and
 241 the surface 1 (CNF rich) of CNF(10)PU have the same surface profile where fibres are
 242 visible, while in the surface 2 (PU rich) of CNF(10)PU, there are no fibers visible
 243 indicating that PU is accumulated towards that surface.

244 3.2 X-ray photoelectron spectroscopy

245 The XPS analysis confirms that PU is preferably concentrated towards one surface. XPS
 246 was used for surface analysis in this study because it is a surface specific method, which
 247 characterizes the 0–10 nm of top section of material (H.-L. Lee & Flynn, 2006). The
 248 relative concentration of nitrogen atoms on the surface of the pure CNF, neat PU and
 249 hybrid nanopapers (CNF(10)PU and CNF(30)PU) are shown in Figure 2. It confirms
 250 that nitrogen atoms are present at a higher concentration towards one surface than on the
 251 other. The complete quantitative results of XPS analysis are presented in Table S2(
 252 supplementary file). The PU rich surface of CNF(10)PU has a nitrogen concentration of
 253 1.19 %, and for the CNF rich side, the concentration is 0.4 %. A similar pattern of
 254 distribution can be seen in the CNF(30)PU. XPS could be used to determine the
 255 presence of PU for it has a peculiar chemical structure as compared to the other
 256 polymers. PU has nitrogen atom in the polymer chain; on the other hand, cellulose has
 257 none. The chemical structures of PU and cellulose and Lactic acid (additive) are

258 presented in Figure S2 (supplementary file). XPS results confirm the differential
 259 distribution of PU across the cross-section as indicated by the SEM pictures (Figure 1).



260

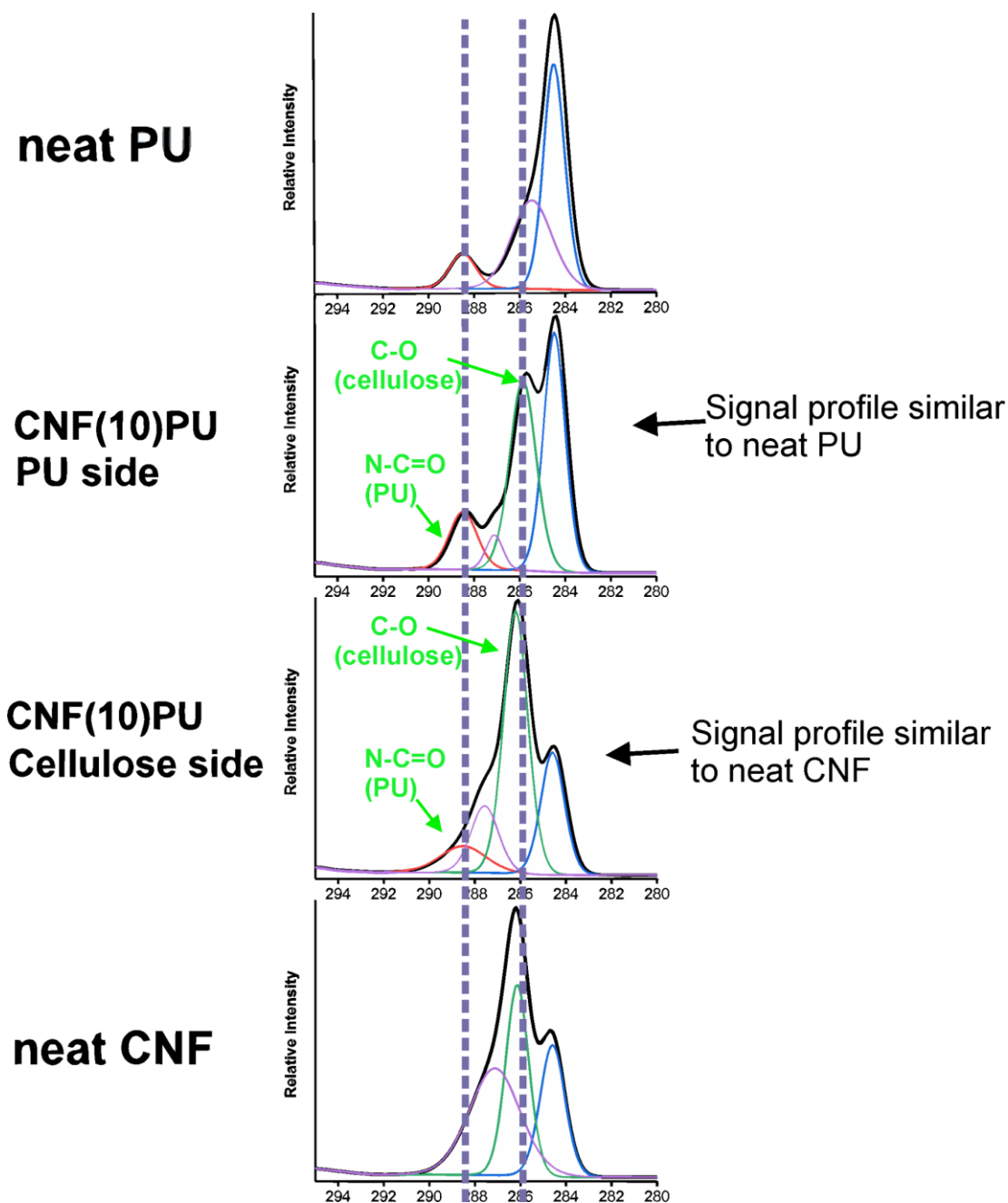
261 Figure 2 Distribution of nitrogen atoms in neat CNF, neat PU, CNF(10)PU (both sides),
 262 and CNF(30)PU (both sides).

263 The detailed XPS spectra of neat CNF, neat PU, CNF(10)PU (PU and cellulose side) is
 264 provided in the Figure 3. The peak PU representing the chemical group $-N-C=O$ is
 265 known to appear at 289 eV (Yang et al., 2001), which can be clearly seen in the PU side
 266 of CNF(10)PU (marked by red color). On the other hand, the intensity of same peak is
 267 significantly less on cellulose side, indicating that PU is present but in less quantity.

268 Similar results were observed for (C-O) peak of CNF which is usually observed at 286
 269 eV (Liao et al., 2016), indicating the presence of CNF on both sides; more towards CNF
 270 side and less towards PU side. Another prominent observation from that figure is that
 271 that NCO bonds are more dominating in PU side and CO bonds on CNF side; yet both
 272 have elements corresponding to presence of both CNF and PU.

273 It is worth mentioning that the neat CNF (reference) sample also gave a nitrogen signal
 274 in XPS, though the concentration was merely 0.28%. The peak from nitrogen in
 275 reference was at 399.8 eV while in PU was 399.2 eV, indicating that the bonding

276 structure of nitrogen in CNF is different in the samples. Therefore, it is not the result of
 277 PU contamination. Perhaps, some additive or impurity was present in the supplied pulp.
 278

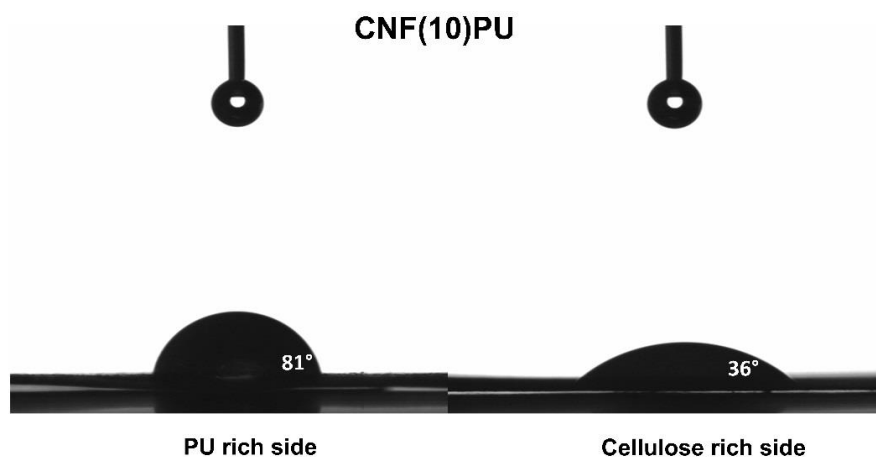


279

280 Figure 3 Detailed XPS spectra of neat PU, CNF(10)PU (PU side and cellulose side),
 281 and neat CNF. Clearly, the PU side of hybrid nanopaper have more concentration of PU
 282 than cellulose side. Additionally, the PU side is similar to neat PU and cellulose side is
 283 similar to neat CNF.

284 3.3 Contact angle

285 The PU rich surface of hybrid nanopapers had significantly different contact angle than
 286 the other surface (Figure 4). For the CNF(10)PU nanopaper, the contact angle with
 287 water is 81° on PU rich side; however, on the CNF rich side it is merely 36° , indicating
 288 the water resistance of the PU rich surface. CNF(30)PU sample, showed a similar
 289 pattern with a difference of almost 25 degrees in contact angle on both sides (63° on PU
 290 rich side and 36° on CNF rich side). The contact angle of neat CNF was 46° and of neat
 291 PU was 81° . The values of contact angles (with standard deviation) of hybrid
 292 nanopapers along with neat CNF and neat PU is provided in Table S3 (supplementary
 293 file).



294

295 Figure 4 Photographic images of the contact angle measurements. The PU rich side has
 296 a considerably higher angle than the CNF rich side.

297 It is worth mentioning that achieving a high contact angle on cellulose nanopaper is a
 298 demanding task. (Sehaqui et al., 2014) grafted different length carbon moieties through
 299 esterification in acetone medium. They achieved a contact angle of 79° when the chain
 300 length was 6 carbons long. For 4 carbon moiety, it was 57° and for 2 carbon, it was 32° .
 301 Only 16 carbon molecule gave the angle of 118° . Additionally, (Peresin et al., 2017)
 302 aminated and silylated the CNF film to achieve a contact angle of 60° and 70° . We were

303 able to achieve a contact angle of 81° without using complicated process and hazardous
304 reagents. This is an added advantage.

305 **3.4 Mechanical Properties**

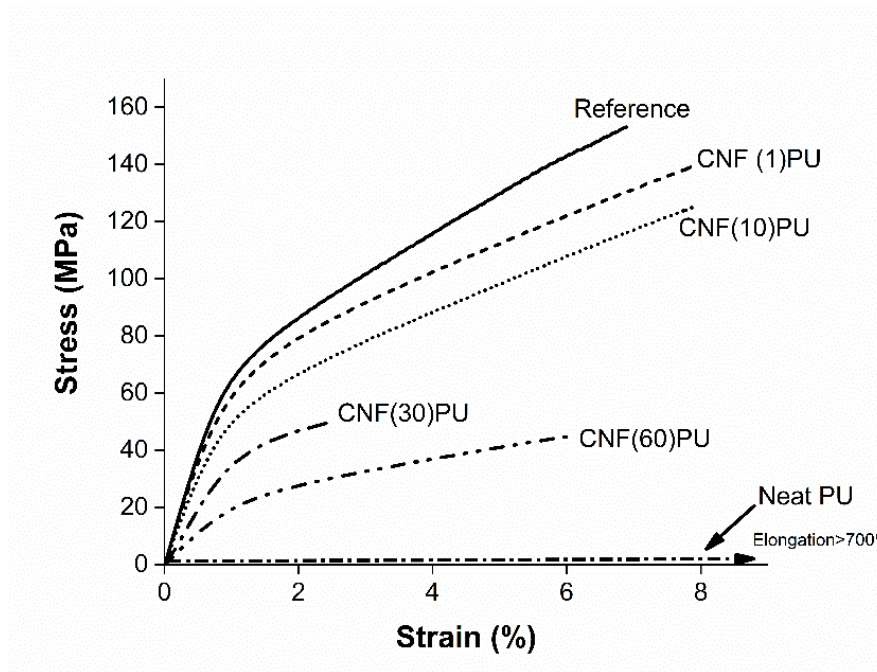
306 The introduction of PU in the CNF network is causing a decrease in the elastic modulus
307 (E), which is shown in Figure 5 (quantitative results in Table 1). The decrease in the
308 elastic modulus of hybrid nanopapers with a PU content of 1 wt.-%, 10wt.-%, 30 wt.-%
309 and 60 wt.-% was 9%, 20 %, 50%, and 70% respectively in comparison to reference.
310 This can be explained by the properties of the neat PU, which is highly elastomeric in
311 nature (more than 700% elongation) and has a modulus of 0.003 GPa, which is vastly
312 lower than that of the reference nanopaper. Introducing such an elastomeric polymer in
313 a stiff CNF network is likely to result in the loss of modulus.

314 Another aspect of the hybrid nanopapers that can be observed in Figure 5 is the higher
315 elongation when comparing to the reference nanopaper. It increased approximately by
316 1% in the CNF(1) PU and the CNF(10) PU samples. It can again be explained by the
317 high elongation of neat PU. This is quite interesting. Usually, introduction of a polymer
318 in a nanopaper leads to reduction in elongation, Although it leads to a higher modulus
319 (Sethi, Farooq, et al., 2018) (Henriksson & Berglund, 2007), the high elongation in the
320 reference nanopaper is due to the sliding of nanofibrils. If a polymer is introduced, it
321 strengthens the structure by embedding the fibers in a matrix and reducing the porosity.
322 However, introduced polymer leads to decrease in the elongation polymers, thus
323 restricting sliding of CNFs, which is a known reason for the inelastic extension of the
324 nanopaper (Henriksson et al., 2008). In our results, the polyurethane, being highly
325 elastomeric in nature, is acting in tandem with the CNFs, as result the elongation is not
326 lost. It can be speculated that when the fibrils slide, the PU matrix keeps the CNF

327 network together even at high elongation. This is an added advantage of the reported
 328 material as flexibility is required in applications such as flexible electronics (Shaohui Li
 329 & Lee, 2017). The results are promising as the nanopapers have combination of
 330 properties from both the constituent materials. The cellulose rich side can be used for
 331 the growth of conductive films and polymer rich surface could protect the conductive
 332 nanopaper against water as shown in the next section.

333 Table 1 Quantitative results of stress-strain analysis of the reference and hybrid
 334 nanopapers.

| | modulus (Gpa) | tensile strength | Elongation |
|-----------|------------------|---------------------|---------------|
| Reference | 7.8 ± 0.6 | 155 ± 12 | 6.9 ± 1.3 |
| CNF(1)PU | 7.1 ± 0.1 | 143 ± 11 | 8.2 ± 1.2 |
| CNF(10)PU | 6.2 ± 0.4 | 126 ± 9 | 7.9 ± 0.7 |
| CNF(30)PU | 4.1 ± 0.2 | 46 ± 7 | 2.5 ± 1.1 |
| CNF(60)PU | 2.3 ± 0.2 | 44 ± 1 | 6.3 ± 0.5 |
| Neat PU | 0.003 | 1.4 ± 0.3 | > 700% |



335

336 Figure 5. The stress-strain curves of the hybrid and reference nanopapers. PU is
 337 extremely elastomeric, due to which the hybrid nanopaper are losing their moduli.

338

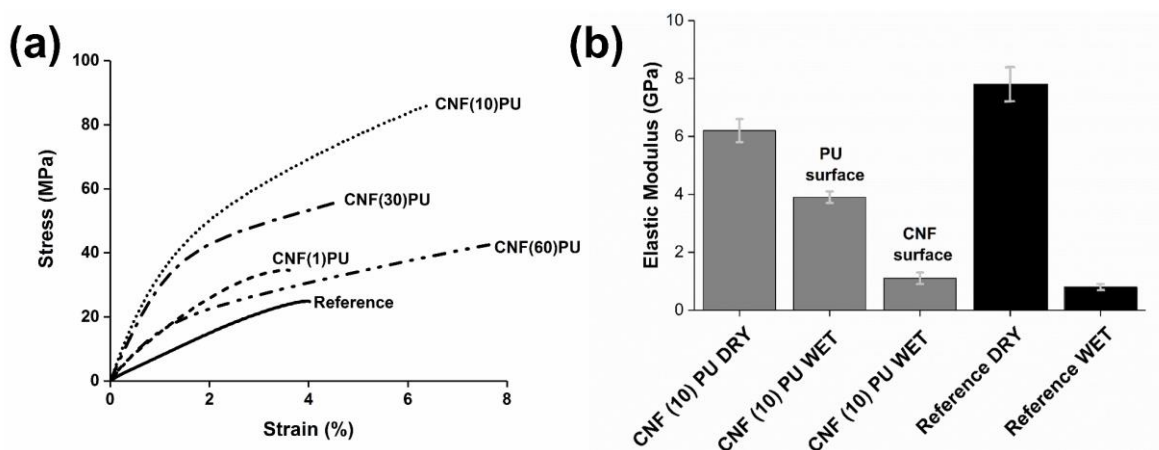
339 Water based polyurethane dispersions are quite versatile and find use in commercial
340 applications such as adhesives and coatings. They are prepared by reacting dihydroxy
341 alcohol with diisocyanate to form a prepolymer, which is further reacted with chain
342 extender to increase the molecular weight. This is later transferred to water medium to
343 form a water dispersion(Tennebroek et al., 2018) (Yoon Jang, Kuk Jhon, Woo Cheong,
344 & Hyun Kim, 2002)(Subramani, Cheong, & Kim, 2004)(Chang et al., 2017). The
345 schematic depiction of water based polyurethane is provided in Figure S1
346 (supplementary file).

347 **3.5 Wet tensile testing**

348 The hybrid nanopapers were water resistant on the PU rich side. Stress-strain curves of
349 wetted samples on the PU side are shown in Figure 6a (quantitative results in Table 2).
350 CNF(10)PU sample outperformed all the other samples in the elastic modulus,
351 elongation, tensile strength and yield strength values, while the reference nanopaper had
352 the poorest mechanical properties in wet conditions. 90 % of its modulus was lost (from
353 7.8 GPa to a 0.8 GPa) in wet state. On the other hand, the CNF(10)PU sample lost only
354 35% of its modulus (down from 6.9 GPa to 3.9 after wetting). The modulus of
355 CNF(10)PU was 400% higher than reference nanopaper (in wet state). Other hybrid
356 nanopapers also had superior water resistance as compared to the reference nanopaper.
357 CNF(1)PU, CNF(30)PU, CNF(60)PU had respectively 150%, 300% and 100% higher
358 modulus than the reference, respectively. The E_{dry}/E_{wet} values are presented in Table 2.
359 Similar trend was observed in tensile strength, yield strength and elongation with
360 CNF(10)PU outperforming the other samples.

361 The CNF side of the hybrid nanopapers did not show any significant improvement in
362 the wet state mechanical properties. Figure 6(b) shows a column graph of the elastic

363 modulus of the CNF(10)PU samples, which were wet from the CNF rich side along
 364 with the reference nanopaper. Elastic modulus of the hybrid nanopaper was marginally
 365 improved over wetted reference nanopaper indicating the susceptibility of cellulose
 366 when in contact with the water. Same hybrid nanopaper (CNF(10)PU) when wetted on
 367 the PU side, was able to maintain the stiffness and ended up at 4 GPa, indicating the
 368 advantage offered by PU when it comes to water resistance.



369

370 Figure 6 (a). Stress-strain curves of the wetted samples hybrid nanopapers (wetted on
 371 the PU rich side). All the hybrid nanopapers have superior mechanical properties superior
 372 to the reference nanopaper., (b). Comparison of the elastic moduli of the wetted
 373 CNF(10)PU (both sides) and the reference. Dry CNF(10)PU and dry reference modulus
 374 are also enlisted. The presence of PU is beneficial for safeguarding of elastic modulus
 375 under the influence of water

376 Table 2. Evolution of the elastic modulus of reference and hybrid nanopapers before and
 377 after wetting. E_{wet}/E_{dry} and % decrease is also enlisted.

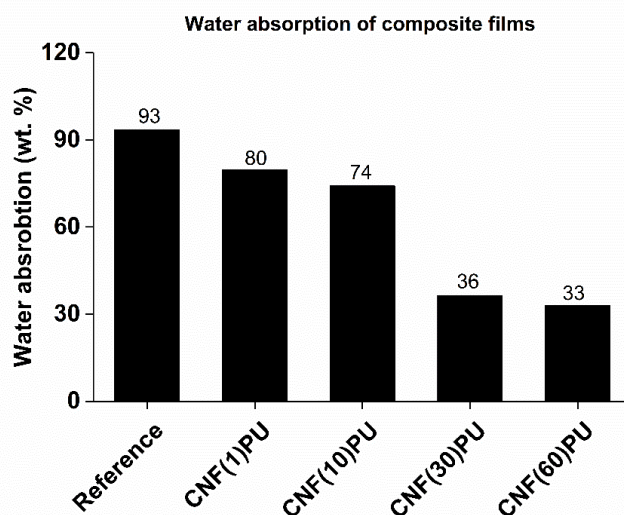
| Elastic Modulus | | | | |
|-----------------|----------------|---------------|-------------------|------------|
| | Before wetting | After wetting | E_{wet}/E_{dry} | % decrease |
| Reference | 7.8 | 0.8 | 0.1 | 90 |
| CNF(1)PU | 7.1 | 2 | 0.3 | 70 |
| CNF(10)PU | 6.2 | 3.9 | 0.6 | 35 |
| CNF(30)PU | 4.1 | 3.3 | 0.8 | 20 |
| CNF(60)PU | 2.3 | 1.7 | 0.75 | 25 |

378

379 (Sehaqui et al., 2014) used surface grafting of long chain carbon molecules to improve
380 the wet properties. Only the 16 carbon chain moiety showed a noticeable improvement
381 ($E_{wet}/E_{dry} = 0.5$). Other carbon chains gave E_{wet}/E_{dry} value less than 0.13. The method
382 reported in this study E_{wet}/E_{dry} values as high as 0.8 (and minimum 0.3) without the use
383 of hazardous reagents.

384 3.6 Swelling studies

385 The water resistance of the hybrid nanopapers was confirmed by the swelling studies.
386 The results are presented in Figure 7. All the hybrid nanopapers had lower water
387 absorption than the reference indicating that the presence of PU is making hybrid
388 nanopapers water-resistant. CNF(30)PU and CNF(60)PU absorbed the least amount of
389 water: 36% and 33% respectively, which is approximately 60% less than the reference.
390 The difference is more prominent in CNF(30)PU and CNF(60)PU as PU has properly
391 embedded the CNFs (as seen in Figure 1). On the other hand, PU Matrix is not clearly
392 visible in CNF(10)PU. The reason behind the reduced water absorption might be that
393 the presence of PU that is separating a fraction of the CNFs from the environment,
394 which makes them impervious to water. The findings from the swelling studies indicate
395 the basic tendency of the hybrid nanopapers to constrain the water uptake by the CNFs.

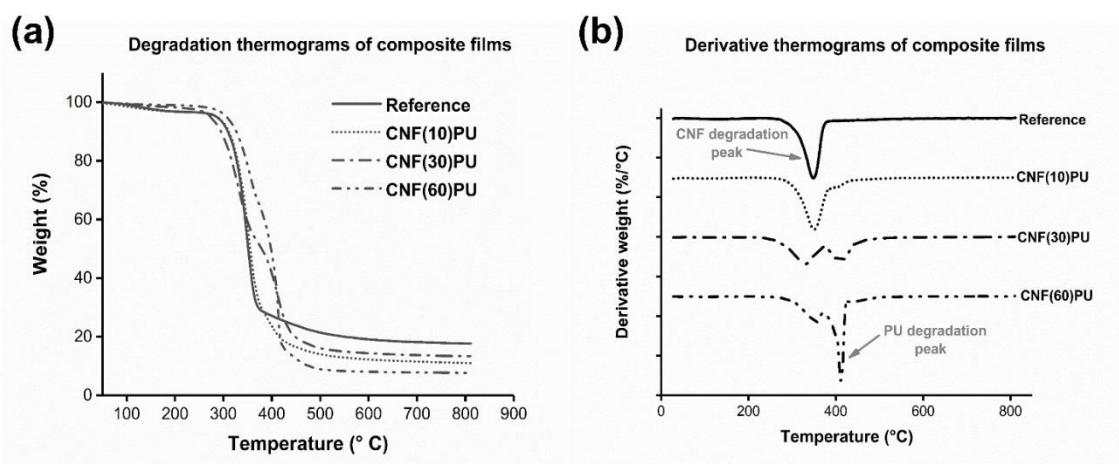


396

397 Figure 7. Water absorption of the hybrid and reference nanopapers. All the composites
 398 nanopapers have less water absorption than reference.
 399

400 3.7 Thermal Stability

401 The CNF(60)PU and CNF(30)PU hybrid nanopapers are more thermally stable than the
 402 reference, as seen in Figure 8(a), which presents the thermograms from the
 403 thermogravimetric analysis (TGA). The thermal properties of CNF(10)PU are
 404 comparable with those of the reference. Quantitatively, the reference is losing 48% of
 405 its weight between 0 and 350°C. CNF(60)PU on the other hand, lost only 22% of its
 406 weight at the same temperature, indicating its superior thermal properties. CNF(10)PU
 407 and CNF(30)PU, respectively lost 42% and 41% of their weight, which is better than
 408 the reference. The influence of the presence of PU is more clearly observed in Figure
 409 8(b), which presents the differential weight loss thermograms indicating the percent
 410 weight loss per degree Celsius. The CNF has the highest rate of degradation around 350
 411 °C, PU on the other hand has it at 410 °C. As the amount of PU is increasing, the
 412 degradation peak of PU is becoming higher, indicating that more material is degrading
 413 above 400 °C. It also confirms the presence of two separate phases: one PU rich and the
 414 other CNF rich.



415

416 Figure 8 (a). Degradation thermograms of the reference and hybrid nanopapers
417 indicating the thermal stability of hybrid films. (b). Derivative thermograms of
418 reference and hybrid nanopapers indicating the peak degradation temperature of CNF
419 and PU phase. CNF phase degrades around 350°C and PU phase around 410°C.

420 **4 Conclusion**

421 This research provides an eco-friendly water based approach to prepare hybrid
422 nanopapers from PU and CNFs. Nanopapers with PU content as high as 60% were
423 prepared from commercially available PU latex. Interestingly, the PU particles were
424 migrating, through the CNF web, towards the applied vacuum due to a spherical
425 morphology and a small particle size (200 nm). This resulted in formation of gradient
426 interpenetrating network due to preferential accumulation of PU towards one of the
427 surfaces, resulting in separate PU rich and CNF rich phases. The PU rich surface was
428 water resistant with the CNF(10)PU sample retaining its mechanical properties under
429 wet conditions. The modulus of wetted CNF(10)PU was 400% of that of the wetted
430 reference, though originally the reference had a higher modulus. It was found that
431 CNF(10)PU has the most optimal properties achieved with the lowest possible
432 concentration of non-degradable PU. The introduction of PU also led to an increase of
433 thermal stability. Further work studying the use of different polymers such as PMMA
434 and the effect of polymer particle size is at a planning stage.

435 **5 Acknowledgements**

436 The authors acknowledge the contribution of Tommi Kokkonen and Santtu Heinilehto
437 for their contribution in TGA and XPS respectively. This research did not receive any
438 specific grant from funding agencies in the public, commercial or non-profit sectors.

439 440 **6 References**

441 Barnes, D. K. a, Galgani, F., Thompson, R. C., & Barlaz, M. (2009). Accumulation and
442 fragmentation of plastic debris in global environments. *Philosophical Transactions*

- 443 *of the Royal Society of London. Series B, Biological Sciences*, 364(1526), 1985–
444 1998. <http://doi.org/10.1098/rstb.2008.0205>
- 445 Benítez, A. J., Torres-Rendon, J., Poutanen, M., & Walther, A. (2013). Humidity and
446 multiscale structure govern mechanical properties and deformation modes in films
447 of native cellulose nanofibrils. *Biomacromolecules*, 14(12), 4497–4506.
448 <http://doi.org/10.1021/bm401451m>
- 449 Chang, M. T., Lee, J. Y., Rwei, S. P., Wu, W. Y., Chiang, W. Y., Chang, S. M., & Pan,
450 Y. H. (2017). Effects of NCO/OH ratios and polyols during polymerization of
451 water-based polyurethanes on polyurethane modified polylactide fabrics. *Fibers
452 and Polymers*, 18(2), 203–211. <http://doi.org/10.1007/s12221-017-6382-x>
- 453 Chun, S. J., Lee, S. Y., Doh, G. H., Lee, S., & Kim, J. H. (2011). Preparation of
454 ultrastrength nanopapers using cellulose nanofibrils. *Journal of Industrial and
455 Engineering Chemistry*, 17(3), 521–526. <http://doi.org/10.1016/j.jiec.2010.10.022>
- 456 Eichhorn, S. J., Dufresne, a., Aranguren, M., Marcovich, N. E., Capadona, J. R.,
457 Rowan, S. J., ... Peijs, T. (2010). *Review: Current international research into
458 cellulose nanofibres and nanocomposites. Journal of Materials Science* (Vol. 45).
459 <http://doi.org/10.1007/s10853-009-3874-0>
- 460 Gamadi, T. D., Elldakli, F., & Sheng, J. J. (2014). Compositional simulation evaluation
461 of EOR potential in shale oil reservoirs by cyclic natural gas injection. In
462 *Unconventional Resources Technology Conference*. Unconventional Resources
463 Technology Conference.
- 464 Greene, K. L., & Tonjes, D. J. (2014). Degradable plastics and their potential for
465 affecting solid waste systems. *WIT Transactions on Ecology and the Environment*,
466 180, 91–102. <http://doi.org/10.2495/WM140081>

- 467 Henriksson, M., & Berglund, L. A. (2007). Structure and properties of cellulose
468 nanocomposite films containing melamine formaldehyde. *Journal of Applied*
469 *Polymer Science*, 106(4), 2817–2824. <http://doi.org/10.1002/app.26946>
- 470 Henriksson, M., Berglund, L. A., Isaksson, P., Lindström, T., & Nishino, T. (2008).
471 Cellulose nanopaper structures of high toughness. *Biomacromolecules*, 9(6), 1579–
472 1585. <http://doi.org/10.1021/bm800038n>
- 473 Huang, J., Zhou, Y., Zhang, L., & Zhou, Z. (2018). Study on the electrical properties of
474 nanopaper made from nanofibrillated cellulose for application in power equipment.
475 *Cellulose*, 25(6), 3449–3458. <http://doi.org/10.1007/s10570-018-1782-7>
- 476 Isogai, A. (2018). Development of completely dispersed cellulose nanofibers.
477 *Proceedings of the Japan Academy, Series B*, 94(4), 161–179.
- 478 Kim, Y. J., & Park, O. O. (1999). Miscibilities and biodegradability properties of
479 poly(butylene succinate)-poly(butylene terephthalate) blends. *Journal of*
480 *Environmental Polymer Degradation*, 7(1). [http://doi.org/10.1002/\(SICI\)1097-](http://doi.org/10.1002/(SICI)1097-4628(19990516)7:7<945::AID-APP10>3.0.CO;2-0)
481 [4628\(19990516\)7:7<945::AID-APP10>3.0.CO;2-0](http://doi.org/10.1002/(SICI)1097-4628(19990516)7:7<945::AID-APP10>3.0.CO;2-0)
- 482 Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., & Dorris,
483 A. (2011). Nanocelluloses: A new family of nature-based materials. *Angewandte*
484 *Chemie - International Edition*, 50(24), 5438–5466.
485 <http://doi.org/10.1002/anie.201001273>
- 486 Koga, H., Nogi, M., Komoda, N., Nge, T. T., Sugahara, T., & Suganuma, K. (2014).
487 Uniformly connected conductive networks on cellulose nanofiber paper for
488 transparent paper electronics. *NPG Asia Materials*, 6(3), e93.
489 <http://doi.org/10.1038/am.2014.9>
- 490 Lee, H.-L., & Flynn, N. T. (2006). X-ray photoelectron spectroscopy. In *Handbook of*

- 491 *Applied Solid State Spectroscopy* (pp. 485–507). Springer.
- 492 Lee, H. J., Lee, H. K., Lim, E., & Song, Y. S. (2015). Synergistic effect of
493 lignin/polypropylene as a compatibilizer in multiphase eco-composites.
494 *Composites Science and Technology*, *118*, 193–197.
495 <http://doi.org/10.1016/j.compscitech.2015.08.018>
- 496 Li, S., & Lee, P. S. (2017). Development and applications of transparent conductive
497 nanocellulose paper. *Science and Technology of Advanced Materials*, *18*(1), 620–
498 633. <http://doi.org/10.1080/14686996.2017.1364976>
- 499 Li, S., Qi, D., & Huang, J. (2017). Natural cellulose based self-assembly towards
500 designed functionalities. *Current Opinion in Colloid & Interface Science*.
- 501 Liao, Q., Su, X., Zhu, W., Hua, W., Qian, Z., Liu, L., & Yao, J. (2016). Flexible and
502 durable cellulose aerogels for highly effective oil/water separation. *RSC Adv.*,
503 *6*(68), 63773–63781. <http://doi.org/10.1039/C6RA12356B>
- 504 Lipatov, Y. S., & Karabanova, L. V. (1995). Gradient interpenetrating polymer
505 networks. *Journal of Materials Science*, *30*(10), 2475–2484.
- 506 Mittal, N., Ansari, F., V, K. G., Brouzet, C., Chen, P., Larsson, P. T., ... Kotov, N. A.
507 (2018). Multiscale Control of Nanocellulose Assembly : *ACS Nano*.
508 <http://doi.org/10.1021/acsnano.8b01084>
- 509 Peresin, M. S., Kammiovirta, K., Heikkinen, H., Johansson, L. S., Vartiainen, J., Setälä,
510 H., ... Tammelin, T. (2017). Understanding the mechanisms of oxygen diffusion
511 through surface functionalized nanocellulose films. *Carbohydrate Polymers*, *174*,
512 309–317. <http://doi.org/10.1016/j.carbpol.2017.06.066>
- 513 Product center coatings Covestro. (2018). Bayhydrol® UH 240. Retrieved February 12,
514 2018, from

- 515 <https://www.coatings.covestro.com/en/Products/Bayhydrol/ProductListBayhydrol/>
516 [201503030528/Bayhydrol-UH-240](https://www.coatings.covestro.com/en/Products/Bayhydrol/ProductListBayhydrol/201503030528/Bayhydrol-UH-240)
- 517 Sehaqui, H., Ezekiel Mushi, N., Morimune, S., Salajkova, M., Nishino, T., & Berglund,
518 L. A. (2012). Cellulose nanofiber orientation in nanopaper and nanocomposites by
519 cold drawing. *ACS Applied Materials and Interfaces*, 4(2), 1043–1049.
520 <http://doi.org/10.1021/am2016766>
- 521 Sehaqui, H., Zimmermann, T., & Tingaut, P. (2014). Hydrophobic cellulose nanopaper
522 through a mild esterification procedure. *Cellulose*, 21(1), 367–382.
523 <http://doi.org/10.1007/s10570-013-0110-5>
- 524 Sethi, J., Farooq, M., Sain, S., Sain, M., Sirviö, J. A., Illikainen, M., & Oksman, K.
525 (2018). Water resistant nanopapers prepared by lactic acid modified cellulose
526 nanofibers. *Cellulose*, 25(1), 259–268. <http://doi.org/10.1007/s10570-017-1540-2>
- 527 Sethi, J., Oksman, K., Illikainen, M., & Sirviö, J. A. (2018). Sonication-assisted surface
528 modification method to expedite the water removal from cellulose nanofibers for
529 use in nanopapers and paper making. *Carbohydrate Polymers*, 197(October), 92–
530 99. <http://doi.org/10.1016/j.carbpol.2018.05.072>
- 531 Subramani, S., Cheong, I. W., & Kim, J. H. (2004). Chain extension studies of water-
532 borne polyurethanes from methyl ethyl ketoxime/ε-caprolactam-blocked aromatic
533 isocyanates. *Progress in Organic Coatings*, 51(4), 329–338.
534 <http://doi.org/10.1016/j.porgcoat.2004.08.004>
- 535 Tennebroek, R., van der Hoeven-van Casteren, I., Swaans, R., van der Slot, S., Stals, P.
536 J. M., Tuijtelars, B., & Koning, C. (2018). Water-based polyurethane dispersions.
537 *Polymer International*.
- 538 Yang, X. F., Vang, C., Tallman, D. E., Bierwagen, G. P., Croll, S. G., & Rohlik, S.

- 539 (2001). Weathering degradation of a polyurethane coating. *Polymer Degradation*
540 *and Stability*, 74(2), 341–351. [http://doi.org/10.1016/S0141-3910\(01\)00166-5](http://doi.org/10.1016/S0141-3910(01)00166-5)
- 541 Yoon Jang, J., Kuk Jhon, Y., Woo Cheong, I., & Hyun Kim, J. (2002). Effect of process
542 variables on molecular weight and mechanical properties of water-based
543 polyurethane dispersion. *Colloids and Surfaces A: Physicochemical and*
544 *Engineering Aspects*, 196(2–3), 135–143. [http://doi.org/10.1016/S0927-](http://doi.org/10.1016/S0927-7757(01)00857-3)
545 [7757\(01\)00857-3](http://doi.org/10.1016/S0927-7757(01)00857-3)
- 546