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1 **Polymerization of cellulose nanocrystals-based Pickering HIPE towards green**
2 **porous materials**

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15 **Abstract**

16 Porous materials were produced based on high internal phase emulsions (HIPE) formulation stabilized
17 by modified cellulose nanocrystals (CNCs). CNCs were first modified with bromoisobutryl bromide
18 and used as Pickering emulsion stabilizers to formulate highly concentrated inverse emulsions. Solid
19 foams with an open porosity were successively produced by free radical polymerization of
20 styrene/divinylbenzene continuous phase. The final materials were characterized regarding their cell
21 size distribution, porosity and mechanical properties and then compared with well-known
22 styrene/DVB polyHIPE stabilized either with usual surfactants or solid particles.

23

24 Keywords: cellulose nanocrystals; Pickering; High Internal Phase Emulsions (HIPE); Polymerized HIPE
25 (PolyHIPE)

26 **1. Introduction**

27 Highly porous, open-celled, low density polymer foams are very attractive materials for a wide range
28 of applications in many fields (Bhumgara, 1995; Gibson and Ashby, 2014; Yang et al., 2017), catalysis,
29 tissue engineering, acoustics, thermal insulator, filtration. Emulsion templating emerged as a way to
30 easily obtain such porous materials (Cameron, 2005; Cameron and Sherrington, 1996; Kimmins and
31 Cameron, 2011; Silverstein, 2014; Zhang and Cooper, 2005). This method is based on the use of highly
32 concentrated reverse emulsion, well-known under the HIPE acronym, for high internal phase emulsion,
33 as template followed by the polymerization of the continuous phase. A HIPE is obtained when the
34 dispersed phase represents more than 64%_v of the sample for a monodisperse emulsion and 71%_v for
35 a polydisperse one. Internal volume fraction of 64%_v corresponds to the random close packing of hard
36 spheres, which means that for higher volume fraction the droplets begin to deform (Cameron and
37 Sherrington, 1996). The resulting materials were first produced and called polyHIPE by Unilever in 1982
38 (Barby and Haq, 1982) for polymerized High Internal Phase Emulsions. This technique allows easily
39 accessing an open porosity with important interconnected structure (Lépine et al., 2008) (an example
40 of which is shown in Figure S1, SI). PolyHIPE exhibits complex morphologies. They possess cavities,
41 called cells or voids, and pores/holes/windows that interconnect these cells. To stabilize such large
42 volume of internal phase, usually large quantity of surfactant (often up to 30% of the continuous
43 phase) is solubilized in the organic phase (Silverstein, 2014). The main disadvantage when using
44 surfactants is the emulsion stability during the elaboration process. Indeed, as polymerization is often
45 thermally induced and since surfactants have low desorption energies (Leal-Calderon and Schmitt,
46 2008), heating may be sufficient to enhance desorption provoking evolution of the emulsion drop size
47 distribution during polymerization (Williams et al., 1990; Williams and Wroblewski, 1988). Large
48 amounts of surfactants molecules in the continuous phase that do not take part of the polymerization
49 may also affect polyHIPE properties.

50 Over the last two decades, the use of particles as stabilizers has increased in polyHIPE formulation
51 (Gurevitch and Silverstein, 2010; Ikem et al., 2011, 2010, 2008; Silverstein, 2014; Vílchez et al., 2011;

52 Yang et al., 2017). This kind of materials are called Pickering polyHIPE, by extension of the Pickering
53 emulsion denomination. In addition to the increased emulsion stability, with less than 5% of particles
54 upon the monomer content (*i.e.* with respect to the continuous phase), emulsion drop size can also be
55 easily controlled and tuned (Destribats et al., 2012). Nowadays, the most common particles used to
56 stabilize emulsions are inorganic particles (Destribats et al., 2012; Ikem et al., 2010, 2008; Vílchez et
57 al., 2011). Indeed, only few papers report the use of organic particles for HIPE stabilization (Cohen and
58 Silverstein, 2012; Liu et al., 2017; Pang et al., 2018; Yang et al., 2018). Among them, cellulose
59 nanocrystals (CNC) have gained increasing attention in recent years (Capron and Cathala, 2013; Li et
60 al., 2018; Liu et al., 2017; Tang et al., 2017; Tasset et al., 2014; Werner et al., 2019). CNC are particles
61 of growing interest because they are bio sourced, and highly available. They also have very good
62 mechanical properties (Cameron and Sherrington, 1997; Habibi, 2014; Klemm et al., 2011; Lavoine and
63 Bergström, 2017; Tang et al., 2017; Werner et al., 2018), and as demonstrated by Moon et al., they
64 may improve composite properties (Klemm et al., 2011; Postek et al., 2013). One can expect that the
65 addition of CNC in the emulsion formulation might increase the mechanical or optical properties of the
66 final materials. So far, only CNC stabilized-MIPE (Capron and Cathala, 2013) (medium internal phase
67 emulsion, for internal fraction above 50%) and HIPE (Liu et al., 2018) were obtained, and only one
68 attempt of polymerization of the water continuous phase of O/W HIPE was realized (Liu et al., 2017).
69 To our knowledge, no work reported the polymerization of the organic continuous phase of W/O HIPE
70 stabilized by modified CNC.

71 In previous contribution (Werner et al., 2019), we studied the stabilization of styrene-based direct,
72 inverse and double Pickering emulsions stabilized by CNC modified with appropriate α -
73 bromoisobutryl rates (CNC-Br) and their polymerization. However, only controlled radical
74 polymerization (AGET SI ATRP) was studied, and no quantitative link between the emulsion
75 characteristics and the polyMIPE properties was reported (in this study the dispersed phase
76 represented 60%, that enters the MIPE designation). Herein we prepared and studied a range of hybrid
77 polymer materials from free radical polymerization of styrene/divinylbenzene Pickering HIPE,

78 stabilized by modified-CNCs. In a first part, CNC modification for emulsion stabilization is presented.
79 Inverse emulsions stabilization is assessed and parameters varied to obtain different droplet sizes.
80 Then the continuous phase was polymerized leading to porous materials. Finally, the porosity and
81 mechanical properties were studied varying the CNC concentration and water phase content.

82 **2. Experimental**

83 **2.1 Materials**

84 Freeze-dried CNC isolated from sulfuric acid hydrolysis (Dong et al., 1998) of wood pulp were
85 purchased from The University of Maine. They present on their surface both sulfate functions (1.05%_{wt}
86 as data from the provider) and surface hydroxyl functions (3.10 ± 0.11 mmol.g⁻¹ of CNC (Brand et al.,
87 2017)). The initial CNC had rod-like shape with estimated dimension of 138 ± 47 nm in length and $25 \pm$
88 6 nm in width based on AFM analysis (Figure S2, SI).

89 Styrene (99%, St), Divinylbenzene (80%, DVB), Azobisisobutyronitrile (98%, AIBN), 4-
90 diméthylaminopyridine (99%, DMAP) and sodium chloride (NaCl) were purchased from Sigma Aldrich.
91 α -bromoisobutyryl bromide (98%, Bibb) was purchased from ABCR. Triethylamine (99%, TEA) was
92 purchased from Fisher Scientific. All reagents were used as received without further purification.

93 **2.2 CNC-Br synthesis**

94 CNC-Br synthesis was first described by Zhang et al. (Meng et al., 2009) and Morandi et al. (Morandi et
95 al., 2009) and adapted by Werner (Werner et al., 2019). 1 g of CNC and 1 g of DMAP were introduced
96 in a reaction vessel. After a nitrogen purge, 50 mL of dry DMF were added. The solution was cooled to
97 0°C thanks to an ice bath and 4.25 g (0.74 mol/L) of Bibb (reactant) and 2.4 g (0.95 mol/L) of TEA, were
98 added to the solution under vigorous agitation. After 72 h of reaction, CNC-Br were precipitated in a
99 mixture of THF/ethanol (50/50_{v/v}), isolated by centrifugation (6000 rpm, 10 min, 15°C) and redispersed
100 in water. The crystals were washed several times with a mixture of water/THF/diethyl ether. The final
101 dispersion in water was freeze-dried to obtain a white powder.

102 The grafting was confirmed by CP MAS NMR (Figure S3, SI) and FT-IR by following the apparition of the
103 stretching bonds corresponding to the sulfate ester groups at 1760 cm^{-1} ($\nu(\text{C}=\text{O})$) and 1060 cm^{-1} ($\nu(\text{C}-$
104 $\text{O})$). The modification rates were evaluated by elemental analysis thanks to the mass percentage of
105 bromine and the amount of surface hydroxyl groups (Equation 1).

$$106 \quad \% \text{ substitution} = \frac{\text{mmol of Br by gram of CNCs}}{\text{mmol of surface hydroxyl functions by gram of CNCs}} = \frac{n_{\text{Br}}}{n_{\text{OH}}} \cdot 100$$

107 *Equation 1*

108 With $n_{\text{OH}} = 3.10\text{ mmol.g}^{-1}$

109 **2.3 Emulsification and characterization**

110 The organic phase, composed of 50/50_{wt/wt} of St/DVB, CNC-Br (from 3 to 20 g/L of dispersed phase)
111 and 1%_{wt} of AIBN was sonicated with a Bioblock vibra-cell equipped with an ultrasonic tip during 1 min
112 (cycles of 1 s “on” at 20% power and 1 s “off”). The aqueous phase, composed of deionized water and
113 sodium chloride (20 mM) was added to the organic phase in order to obtain 60/40_{wt/wt} of W/O. These
114 two phases were mixed with a rotor-stator, Ultraturrax®, at 15 000 rpm during 30 seconds in order to
115 obtain a pre-emulsion. Under agitation the aqueous phase was added dropwise to finally reach a ratio
116 of 80/20_{wt/wt}. These emulsions were characterized by optical microscopy. Because of the toxicity of the
117 St, samples were sealed between two microscope slides before observation. Size distribution was
118 obtained by measuring the diameter of a hundred of drops with ImageJ software. Then the surface
119 average diameter, or Sauter diameter $D_{3,2}$ was calculated following the definition:

$$120 \quad D_{3,2} = \frac{\sum i N_i \cdot D_i^3}{\sum i N_i \cdot D_i^2}$$

121 *Equation 2*

122 The surface uniformity was calculated in order to determine the polydispersity of the emulsions, where
123 \bar{D} is the median diameter that is to say the diameter for which the cumulative undersized volume
124 fraction is equal to 50%

125
$$U = \frac{1}{\bar{D}} \cdot \frac{\sum_i |D_i - \bar{D}| \cdot D_i^2}{\sum_i D_i^2}$$

126 *Equation 3*

127 In the following, an emulsion is considered as monodisperse if U is lower than 0.3.

128 **2.4 Polymerization and characterization**

129 Polymerization was carried out in 4 mL vials. The emulsions were heated to 70°C thanks to an oil bath,
130 the reaction was carried out during 24h. At the end of the polymerization, the material was removed
131 from the vial and washed several times with a Soxhlet apparatus, once during 24 h with ethanol and
132 then 6 h with acetone. The final materials were dried at 60°C in an oven. Materials morphology was
133 characterized by Scanning Electron Microscopy (SEM). Similarly to emulsions, Sauter diameter $D_{3,2}$ was
134 obtained with ImageJ software by measuring a hundred cells. Samples porosity was assessed by
135 mercury intrusion porosimetry. Mechanical properties were evaluated by extracting the compressive
136 modulus by Dynamic Mechanical Analysis (DMA).

137 **Instrumentation**

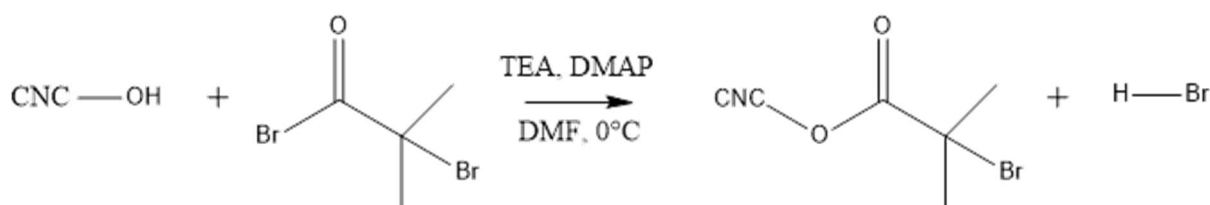
138 Infrared spectra of unmodified and brominated CNC were recorded using a Vertex 70 Bruker FT-IR
139 spectrometer. CNC powder was analyzed thanks to an attenuated total reflectance ATR accessory.
140 Each spectrum was recorded between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} with 32 scans.
141 Materials morphology was characterized with SEM TM-1000 with acceleration voltage of 15 kV. The
142 samples were stick onto support with silver lacquer and metallized with gold/palladium coating during
143 60 seconds. Slice of materials (70 nm) were obtained by cryo-ultramicrotomy with a Leica UC7 at -90°C
144 and were observed at ambient temperature with a TEM Hitachi H7650.

145 The experimental porosity of the samples was determined by mercury intrusion porosimetry in a
146 Micromeritics Autopore IV 9500 porosimeter with the following parameters: contact angle = 130°,
147 mercury surface tension = 485 mN m^{-1} , maximum intrusion pressure = 124 MPa. The analysis was
148 replicated at least 3 times for each set of parameters.

149 A TA Instrument RSA3 (dynamic mechanical analysis, DMA) was used to study the mechanical
150 properties of the samples, with a cylindrical shape of 20 mm diameter of 7.5 ± 1.5 mm thick. The
151 compression test was performed in static mode at ambient temperature, during 10 s at a rate of 1mm/s
152 until a force of 35 N is reached. Each set of experiments was replicated 5 times to insure the
153 reproducibility of the analysis.

154 3 Results and discussion

155 3.1 CNC modification



156

157

Figure 1: CNC modification scheme

158 Because of surface hydroxyl functions, CNC are mainly hydrophilic. One big advantage is that this
159 surface is easily tuneable and new reactive functions can be grafted, by oxidation, carbamation,
160 etherification or by esterification (Eyley and Thielemans, 2014). Esterification reaction is known to be
161 fast and to offer a wide range of graft possibilities, therefore, this reaction was used in the following
162 to graft Bibb function onto the CNC surface in order to modify the hydrophobic/hydrophilic balance of
163 the CNC (Figure 1). The use of Bibb allows providing hydrophobicity. In addition it may be useful as
164 polymerization initiator (Meng et al., 2009; Morandi et al., 2009; Werner et al., 2019). As described by
165 Werner et al. (Werner et al., 2019), the highest grafting ratio was targeted so that the crystals would
166 present interfacial properties, and therefore could be used as inverse emulsion stabilizers (Figure S4,
167 SI). Bromine mass percentage was determined by elemental analysis (26%wt) and thanks to the initial
168 number of surface hydroxyl functions (3.10 mmol/g of CNC), a substitution rate of 105% could be
169 extracted using Equation 1. Because of the material variability, initial amount of hydroxyl function was
170 eventually underestimated and therefore, substitution rate was overestimated. Further

171 characterization of the resulting crystals in terms of chemical modification and morphology is provided
172 in SI (Figures S3, S5 and S6, SI).

173 **3.2 Emulsions formulation**

174 **3.2.1 High internal phase emulsion preparation**

175 The continuous organic phase of the inverse emulsions was composed of styrene and DVB and the
176 aqueous dispersed phase was composed of salted water (20 mM NaCl) ; these emulsions were
177 stabilized by the 100% modified CNC-Br, presented previously. We chose the most commonly studied
178 St/DVB system for polyHIPE synthesis (Cameron et al., 1996; Cameron and Sherrington, 1997; Ceglia
179 et al., 2012; Hainey et al., 1991; Ikem et al., 2011) in order to have a polymer matrix of reference. To
180 obtain HIPE, volume fraction of internal phase was set above 64%_v the random close packing of
181 monodisperse emulsions. More precisely, a W/O volume ratio of 79/21_{v/v} was chosen (equivalent to a
182 80/20_{wt/wt}), this fraction corresponds to the highest water content we could easily achieve. However,
183 more concentrated emulsions were obtained by centrifugation and removal of the organic
184 supernatant. The maximal ratio reached with this technique without destabilization under
185 centrifugation was 83/17_{v/v}.

186 Given the substitution rate of the CNC-Br, their aggregation make them difficult to redisperse in the
187 organic phase. As sonication is expected to improve dispersion of the CNC-Br in the organic phase, two
188 emulsions have been prepared: one with and the other without preliminary sonication of the CNC-Br
189 suspension.

190 Without sonication, the mean drop diameter was above 200 μm, whereas after sonication the drop
191 size was divided by a factor 2, around 100 μm (Figure S7, SI). This result shows that a better dispersion
192 of the CNC-Br leads to a better availability of the crystals resulting in a higher stabilizing efficiency; a
193 larger interfacial area can be stabilized, hence the drops diameter decreases. As a consequence in the
194 following, all the emulsions were prepared with prior sonication of the CNCBr in the organic phase.

195 **3.2.2 Influence of CNC-Br concentration on droplets diameter**

196 Emulsions were successfully prepared using different concentrations of CNC-Br in the range 3 g/L – 20
197 g/L with respect to the dispersed phase. The water volume fraction of 79/21_{v/v} was kept constant. The
198 droplet diameter varies with the CNC-Br concentration. The plot of 1/D_{3,2} versus the concentration of
199 CNC-Br showed a linear dependence between the two parameters which is consistent with the limited
200 coalescence phenomenon occurring for Pickering emulsions in the case of irreversible particle
201 adsorption and in the particle-poor domain (Arditty et al., 2003; Wiley, 1954) (Figure S8, SI). Indeed,
202 the higher CNC-Br concentration, the larger amount of stabilized interfacial area and thus the lower
203 the droplet diameter. In this linear domain, emulsion size is controlled by the amount of particles and
204 the way they pack at the interface. A relative narrow drops size distribution width is another
205 characteristic of this domain (U ≈ 0.3).

206 From the slope, the C parameter was extracted thanks to the following relation (Schmitt et al., 2014):

$$207 \quad \frac{1}{D_{3,2}} = \frac{m_p}{6 \cdot \rho_p \cdot V_d \cdot C} \cdot \frac{a_p}{v_p}$$

208 *Equation 4*

209 where m_p corresponds to the mass of particles, ρ_p their density (taken as 1.6 g/cm³), a_p and v_p the
210 surface and volume of the particles in contact with the interface (calculated for a crystal of dimension
211 140x25x25 nm³), V_d the volume of the dispersed phase, and C the covering ratio.

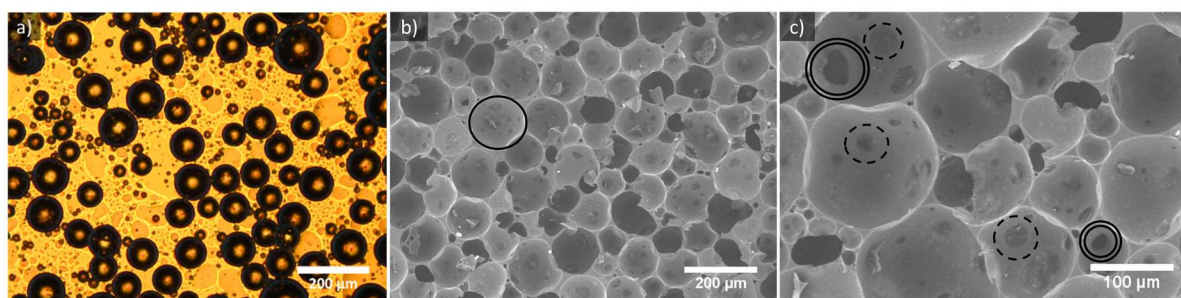
212 The C parameter is defined as the proportion of the interface that is covered by particles. Given the
213 almost rectangle parallelepiped shape of the particles, for a dense monolayer this parameter would
214 be equal to 1. If $C > 1$, then multi-layers are present at the interface and the number of layers n can be
215 estimated through: $C = n \times 100\%$. In the present case, $C \approx 5$, which means there are in average 5 layers
216 of CNC-Br on the droplets surface.

217 **3.3 Emulsions polymerization**

218 **3.3.1 Study of a reference polyHIPE**

219 The reference emulsion was composed of 79/21_{v/v} of W/O ratio, 50/50_{wt/wt} of St/DVB ratio, 8 g/L of
220 CNC-Br with respect to the dispersed phase. The Inverse emulsion was characterized 1 hour after
221 emulsification and remained stable for at least two days (Figure S9). Porous material was obtained
222 after free radical polymerization of the continuous phase by heating the HIPE at 70°C for 24 h. The
223 obtained material was white and cohesive forming a self-standing monolith (Figure S10, SI).
224 Furthermore, polymerization showed a good conversion of 85%. The conversion was obtained by
225 gravimetric measurement of the monolith, by measuring the monolith weight after washing and drying
226 and comparing it to the initial mass of the organic phase containing the monomers.

227 Comparison of the emulsion before and after polymerization showed that no destabilization occurred
228 during the process. Indeed, cells were clearly observed by SEM with diameter matching the original
229 emulsion drop sized obtained by optical microscopy. Comparison between the emulsion and the
230 polyHIPE (Figure 2) revealed identical sizes within error, between the emulsion droplets $122 \pm 23 \mu\text{m}$,
231 and the polyHIPE cell size $125 \pm 37 \mu\text{m}$ (Table 2, sample PPH-1). The good agreement between drop
232 and cell sizes and the absence of fracture in the monolith also indicates that no coalescence neither
233 contraction occurred during polymerization.



235 *Figure 2: a) Microscopic pictures 79/21_{v/v} HIPE, with 10 g/L of CNCBr with respect to the aqueous phase with sonication,*
236 *diluted, b) c) SEM pictures of corresponding solid dried material with the cell (straight line), open pores (double line) and*
237 *closed pores (dashed line)*

238 The morphology of the obtained polyHIPE (Figure 2) differs from usual open-cell polyHIPE stabilized by
239 surfactant, but seems typical for a particle-stabilized Pickering polyHIPE. Indeed, conventional polyHIPE
240 stabilized by surfactant and particle-stabilized Pickering polyHIPE present different types and aspects
241 of porosity. The first category of polyHIPE usually presents an obvious open-cell structure with well-

242 defined pores. A large number of paper has been devoted to the study of structure-properties
243 relationship of these porous materials among which the mechanism of the pore formation in polyHIPE.
244 The hypothesis that pores result of the cracking of polymer film during the purification process
245 (Cameron et al., 1996) was ruled out thanks to Gilti et al. (Gitli and Silverstein, 2008). The most common
246 explanations are that the formation of the cells interconnections is due to mechanical rupture of the
247 polymer film during the polymerization step (Menner and Bismarck, 2006; Williams and Wroblewski,
248 1988) where the water droplets are the closest and the polymer the thinnest, which can be supported
249 by Ceglia et al. work showing a very good adequacy between the dimension of the liquid film separating
250 two emulsion drops (that depends on the drops size and the dispersed phase volume fraction) and the
251 size of the interconnexions (Ceglia et al., 2012). Alternatively, for Barby and coll. (Barby and Haq, 1982)
252 the formation of pores is due to the removal of surfactant from the two emulsion phases during the
253 washing step (Lépine et al., 2008). Finally, Stubenrauch and Drenckan also discussed the role of the
254 initiator locus in the pore formation for surfactant stabilized polyHIPE showing an influence of the
255 phase in which it is solubilized (Quell et al., 2016). With regards to Pickering polyHIPE, Cameron et al.
256 explained that the monomer contraction during polymerization was restricted to the gel point so that
257 a film would be formed instead of an open pore, which could eventually rupture submitted to vacuum
258 process (Kimmins and Cameron, 2011). Therefore, for organic Pickering polyHIPE no open-cell
259 structure was evidenced so far (Ikem et al., 2010, 2008; Menner et al., 2007a, 2007b), but some
260 attempts to produce an open-cell structure were realized by adding small amounts of non-ionic
261 surfactant as co-stabilizer (Ikem et al., 2011).

262 Therefore, it was not surprising observing in our samples some open pores (dotted line), but mostly
263 pores covered by a thin polymeric film (Figure 2 dashed lines). In order to assess the closed or open
264 structure of the polyHIPE, one can compare the monolith density also given by mercury intrusion
265 porosimetry and the one estimated either through the mass to volume ratio of the macroscopic
266 monolith or estimated from the monolith composition. In the later calculus, the density of
267 poly(styrene-DVB) has been taken equal to 1.06 g/cm^3 , density of CNC as 1.6 g/cm^3 and for different

268 monomers conversions (Figure S11, SI). The estimated porosity from the composition was taken equal
 269 to the initial volume fraction of water within the HIPE. The porosity estimated from the mass to volume
 270 ratio was deduced from the as-measured density in comparison with the density of the matrix
 271 composed of styrene, DVB and CNC. All three set of density and porosity were compared (Table 1).

	Density (g/cm ³)	Porosity (%)
Estimated from the composition (100% conversion)	0.21	79
Estimated from the composition (85% conversion)	0.18	88
Estimated from the mass to volume ratio	0.12	81 ± 2
Mercury porosimetry measurement	0.18	

272 *Table 1: Features estimated and measured by porosimetry of reference polyHIPE*

273 Estimated values of density and porosity are very close to the measured ones especially those issuing
 274 from the composition taking into account the 85% conversion of the monomer. Values from the mass
 275 to volume ratio are a bit different probably due to a lack of precision of the way measuring the volume.
 276 The good agreement indicates that the whole monolith is accessible therefore that the porosity is
 277 open. This was verified with the full data given by the mercury porosimetry analysis, plotting the
 278 mercury intrusion as a function of the pressure (Figure 4). Two ranges of mercury intrusion were
 279 identified from Figure 4 a-b, one at low pressure, around 0.02 MPa and another around 2 MPa. This
 280 observation is in agreement with the hypothesis of a double population of holes: one corresponding
 281 to holes easily accessible to mercury, and the other more difficult to access. Through Washburn
 282 equation, pores diameter can be obtained from mercury pressure values, Equation 5:

$$283 \quad D = -\left(\frac{1}{P}\right) 4 \cdot \gamma \cdot \cos\varphi$$

284 *Equation 5*

285 where D is the hole diameter, P the mercury pressure, γ the surface tension of the mercury (taken
 286 equal to 485 mN/m) and φ the wettability angle of mercury (130°).

287 Intrusion at low pressure was attributed to large pore sizes (110 μm) (Figure 4 b), corresponding to the
 288 cells of the polyHIPE (125 μm). At higher pressures, a second population of holes (< 1 μm) with a much

289 higher mercury intrusion value was identified though difficult to observe by SEM and showed to be
290 responsible for the open porosity of the material (Figure 4 a). However, if the second pore population
291 would directly result from the contact films between the drops one would expect holes between the
292 cells with 39 μm in diameter for 79%_v (see Figure S12 (Ceglia et al., 2012)). These values are far from
293 the measured ones around 0.66 μm . This seems indicating either that CNC-Br induce a repulsion at a
294 much larger scale than the thickness of 5 CNC layers between the drops or that the interconnections
295 do not result from the contact zones between initial drops. The presence of this second smaller
296 population of pores is in agreement and supports the hypothesis made by Silverstein et al. (Gurevitch
297 and Silverstein, 2010), for polyHIPE stabilized with silica nanoparticles, believing in the existence of an
298 interconnectivity within Pickering polyHIPE at a smaller scale in spite of a seemingly closed-cell
299 structure. As for the described materials, the polyHIPE presented here were easily washed and dried,
300 the ability to easily remove water being another argument in favor of an open-cell structure (Gurevitch
301 and Silverstein, 2010). It is worth noticing here that washing and drying were performed in mild
302 conditions (avoiding use of vacuum) to avoid any material structure modification. Furthermore, as the
303 majority of the porosity was accessed at high pressure above 1 MPa, and given the mechanical strength
304 of the polymer which should have undergone breakage below 1MPa, it was assumed that no breakage
305 of the solid foam occurred during the mercury porosimetry analysis, validating the open porosity
306 conclusion.

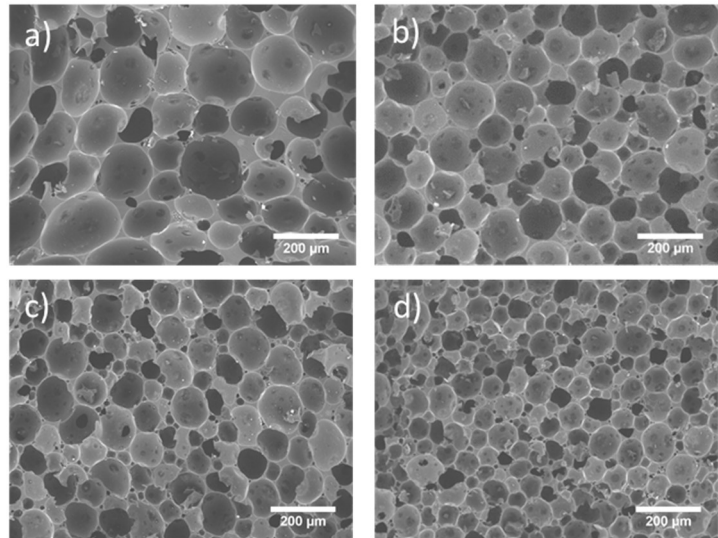
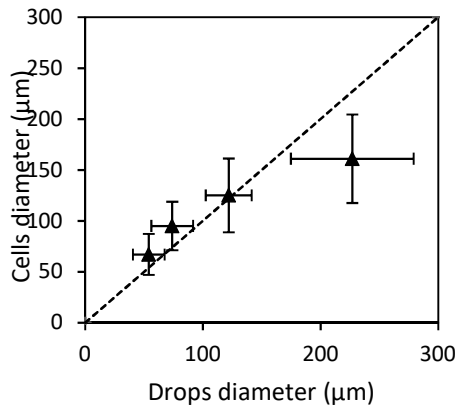
307 The mechanical properties of polyHIPE were studied by compression measurements at room
308 temperature. Compressive moduli (that we'll call Young modulus even if the experiments were not
309 performed under traction) were extracted from the slope of the linear region of the stress-strain curve
310 (Figure S13, SI). Three different domains were identified: the linear domain, where the deformation
311 was reversible and from which the modulus was extracted, the plateau and the densification domains,
312 where the material fell apart. The compression modulus for the reference monolith reached 2 MPa,
313 which was lower than expected for polyHIPE reinforced with particles. Typical values of compressive
314 moduli for St/DVB polyHIPE stabilized by surfactants were estimated around 10 MPa (Gitli and

315 Silverstein, 2008; Tai et al., 2001) and Pickering polyHIPE stabilized solely with titania nanoparticles
316 showed an enhancement of the compressive modulus up to 65 MPa in similar conditions. The low
317 compressive modulus found for CNC-stabilized polyHIPE was surprising, given the high aspect ratio and
318 strength of the CNC (Klemm et al., 2011; Tang et al., 2017). However, successful reinforcement
319 required homogeneous repartition of the fillers, with adhesion of the particles to the matrix which was
320 likely not the case for the studied system since CNC-Br were not reactive and accumulated at the
321 interface (forming 5 layers around the drops). This corroborates the hypothesis of Bismarck et al. when
322 they proposed that particles agglomerate at the interface acts as flaws instead of reinforcing the
323 polymer matrix (Ikem et al., 2010).

324 **3.3.2 CNC-Br concentration impact at fixed water/organic phase ratio**

325 The influence of the cell size was studied by varying the CNC-Br concentration. Four concentrations of
326 CNC-Br were tested: 5 g/L, 8 g/L, 12 g/L and 16 g/L with respect to the dispersed phase keeping all
327 other parameters constant. First, emulsion size was preserved after polymerization (Figure 3 left). At
328 lower CNC-Br concentration, no destabilization phenomenon was observed (coagulum, demixing...)
329 upon polymerization, however drops diameter differed from cells diameter. This deviation from the
330 slope $y=x$ might be explained by deformed SEM pictures harder to analyze (Figure 3 a).

331 Successful materials were synthesized based on these emulsions and characterized by SEM (Figure 3
332 a-d). All the materials were homogeneous regarding their cell size distribution, with a decrease of the
333 cell diameter with the concentration of CNC-Br (Table 2) as expected according to the limited
334 coalescence phenomenon. Each sample exhibited also the presence of pores between the cells
335 covered with polymeric films as discussed previously.



336

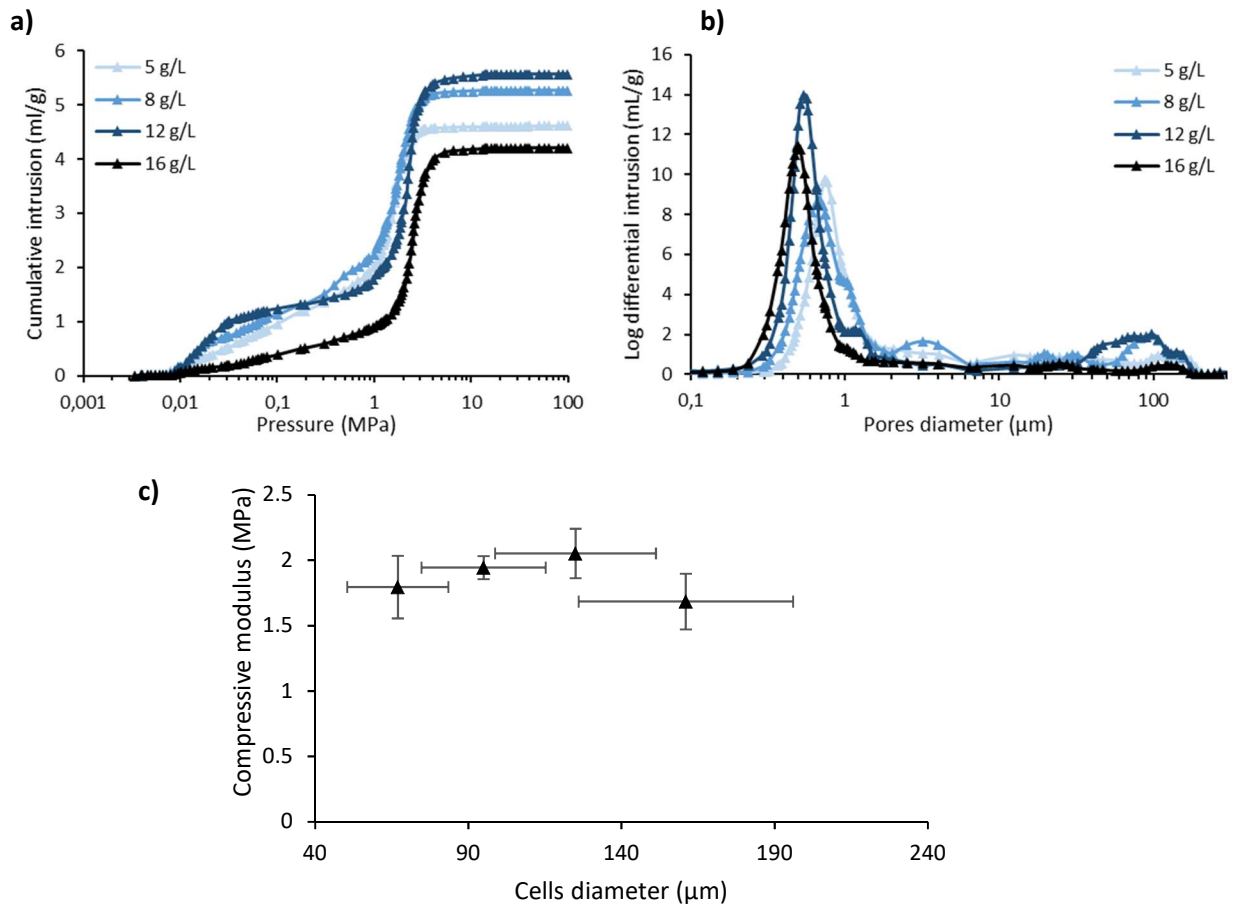
337 *Figure 3: Left, Evolution of the foam cell size determined from SEM observations, as a function of initial water drops size*
 338 *determined by optical microscopy. The dashed line with slope of 1 corresponding to equality is plotted as a guide to the eye.*
 339 *Right, Scanning Electron Micrographs of the final obtained monoliths after washing and drying with initially a) 5 g/L of CNC-*
 340 *Br b) 8 g/L of CNC-Br c) 12 g/L of CNC-Br and d) 16 g/L of CNC-Br with respect to the organic phase*

sample	Water/oil wt/wt ratio	Equivalent v/v ratio	[CNC] (g/L)	D _{3,2} HIPE (μm)	D _{3,2} polyHIPE (μm)	Secondary pores diameter (μm)	Porosity (%)	Foam density (g/cm ³)	Skeletal density (g/cm ³)	E (MPa)
PPH-1	80/20	79/21 _{v/v}	8	122 ± 23	125 ± 37	0.66	81 ± 2	0.18	0.97	2.05 ± 0.19
PPH-2	80/20	79/21 _{v/v}	5	227 ± 53	164 ± 39	0.74	79 ± 2	0.19	0.93	1.68 ± 0.21
PPH-3	80/20	79/21 _{v/v}	12	74 ± 18	95 ± 23	0.57	80 ± 2	0.20	0.98	1.94 ± 0.09
PPH-4	80/20	79/21 _{v/v}	16	54 ± 14	67 ± 22	0.55	80 ± 2	0.19	0.94	1.79 ± 0.24

341

Table 2: PolyHIPE characteristics varying the CNCBr concentration

342 Mercury intrusion porosimetry results were consistent with an open-cell structure for all CNC-Br
 343 concentrations as it was shown for the reference polyHIPE sample (Figure 4 a-b). Two populations of
 344 holes were identified: the largest corresponding to the cells and a second one smaller, corresponding
 345 to a much higher mercury intrusion pressure, similarly to the reference sample, and suggested to be
 346 responsible for the overall interconnectivity. Interestingly, the second population diameter decreases
 347 with increasing amount of CNC-Br used to stabilize the polyHIPE (Table 2) at constant drop coverage
 348 by the particles (since the samples belong to the limited coalescence domain where the coverage is
 349 constant).



350

351

352 *Figure 4: a) b) Mercury intrusion as function of pores diameter for different size diameter, c) compressive modulus of porous*
 353 *materials as function of cells diameter*

354 Mechanical analyses were performed on the four samples and compressive moduli were extracted. As
 355 shown in Figure 4 c, there was no significant difference between the four samples, the moduli varying
 356 in the range 1.5 MPa – 2 MPa. As a result, no dependence of the modulus with the cell size was
 357 assessed for these porous materials. This behaviour was expected, and even predicted by the Gibson
 358 and Ashby model (Gibson and Ashby, 2014), which is often used to describe polyHIPE behaviour
 359 (Gibson and Ashby, 2014). This model states that the elastic modulus does not depend on the cell size,
 360 but only varies with the fraction of continuous phase which is here kept constant. This model is based
 361 on the double hypothesis that the material has an open porosity and is homogeneous, and the lack of
 362 one implies deviation from the model as it was observed by Ceglia et al. with polyHIPE stabilized by
 363 surfactants (Ceglia et al., 2012). First hypothesis was verified by previously described mercury intrusion
 364 porosimetry analysis. Concerning the homogeneity of the matrix, this hypothesis was verified by cryo-

365 TEM observations of 70 nm thick slices cut in the material. Cryo-TEM pictures showed a homogeneous
366 polymer matrix even at low scale (see Figure S14, SI).

367 Contrary to surfactants, the concentration of CNC-Br did not show any influence over the
368 interconnectivity of the polyHIPE or the mechanical properties of the sample. Even samples with low
369 concentration of CNC-Br (5 g/L) did present an open-cell structure, which remained at high
370 concentration (16 g/L). The increase in stabilizer concentration neither did affect the global structure
371 of the formed material, since self-standing monoliths were produced for all concentrations contrary to
372 what was observed by Williams and Wroblewski (Williams and Wroblewski, 1988) for polyHIPE stabilized
373 with sorbitan monooleate. As it was explained for the reference polyHIPE sample, no improvement of
374 the mechanical properties was obtained by the presence of CNC-Br nor by increasing the particle
375 content in this range of concentration (Figure 4 c). But yet, the increase of particle content did not
376 reduce the young modulus as it was observed for titania nanoparticles (Ikem et al., 2010).

377 **3.3.3 W/O ratio impact at a fixed drop size**

378 From the Gibson and Ashby model, the foam fraction or continuous phase fraction is expected to
379 influence the polyHIPE properties following Equation 6 (Ceglia et al., 2012).

$$380 \quad \frac{E^*}{E_s} \propto \left(\frac{\rho^*}{\rho_s}\right)^2 = (1 - \phi_{foam})^2$$

381 *Equation 6*

382 Where E^* and ρ^* are respectively the compressive modulus and the density of the polyHIPE, E_s and ρ_s
383 respectively the Young's modulus and the density of the material constituting the solid (poly(styrene-
384 co-divinylbenzene)) and ϕ_{foam} the foam volume fraction or equivalently the water volume fraction of
385 the initial emulsion as no contradiction was observed. E_s is taken as 500 GPa as reported in the
386 literature for similar polymers (Ceglia et al., 2014; Graeber, 2013).

387 Here, the study focused on three distinct ratios, keeping a water volume fraction above 64%_v to remain
388 in the HIPE denomination: 74/26_{v/v}, 79/21_{v/v} and 83/17_{v/v}. As the amount of CNC-Br determines the

389 drop size, we chose to maintain the ratio of the amount of CNC-Br to the amount of dispersed phase
 390 constant (see Equation 4). This value is fixed at a value of 8 g/L with regards to the dispersed phase for
 391 all samples. After optical observation, the droplets diameter was measured to be around 125 μm for
 392 all three formulations (Table 3). The last ratio (83/17_{v/v}) was reached thanks to centrifugation of the
 393 emulsion and removal of the organic supernatant.

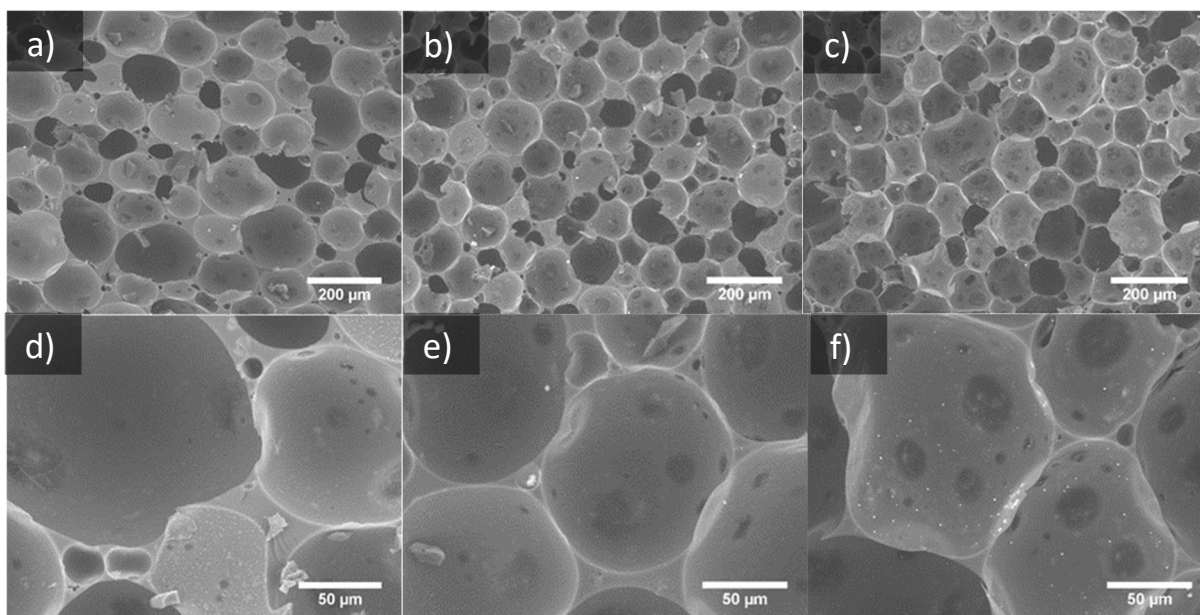
sample	Water/oil wt/wt ratio	Equivalent v/v ratio	[CNC] (g/L)	D _{3,2} HIPE (μm)	D _{3,2} polyHIPE (μm)	Secondary pores diameter (μm)	Porosity (%)	Foam density (g/cm ³)	Skeletal density (g/cm ³)	E (MPa)
PPH-1	80/20 _{wt/wt}	79/21 _{v/v}	8	122 \pm 23	125 \pm 37	0.66	81 \pm 2	0.18	0.97	2.05 \pm 0.19
PPH-5	75/25 _{wt/wt}	74/26 _{v/v}	8	120 \pm 25	122 \pm 36	0.50	75 \pm 2	0.24	0.96	2.08 \pm 0.31
PPH-6	85/15 _{wt/wt}	83/17 _{v/v}	8	150 \pm 38	127 \pm 34	1.22	85 \pm 2	0.12	0.81	1.48 \pm 0.36

394

395 *Table 3: PolyHIPE characteristics varying the W/O fraction*

396 As previously noticed, homogeneous self-standing monoliths were obtained, but SEM micrographs
 397 (Figure 5) revealed an inner structural difference. As expected, when the volume of water increased,
 398 the polyHIPE cells deformation increased until to reach almost polyhedral shapes. This evolution
 399 originates from the higher packing of the drops, leading to an increase of the contact surface between
 400 two adjacent cells, as can be seen from Figure 5, forming larger interconnections.

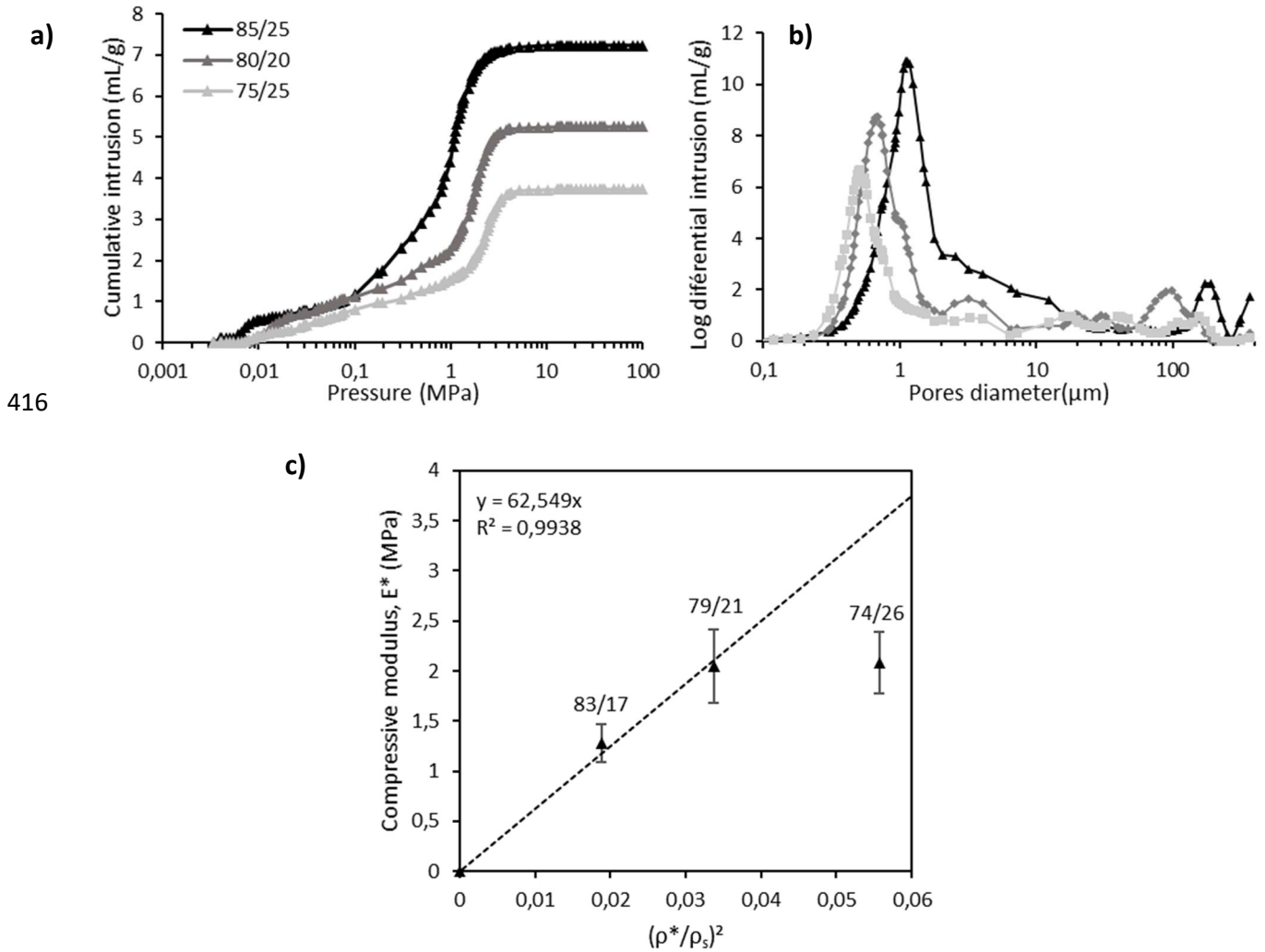
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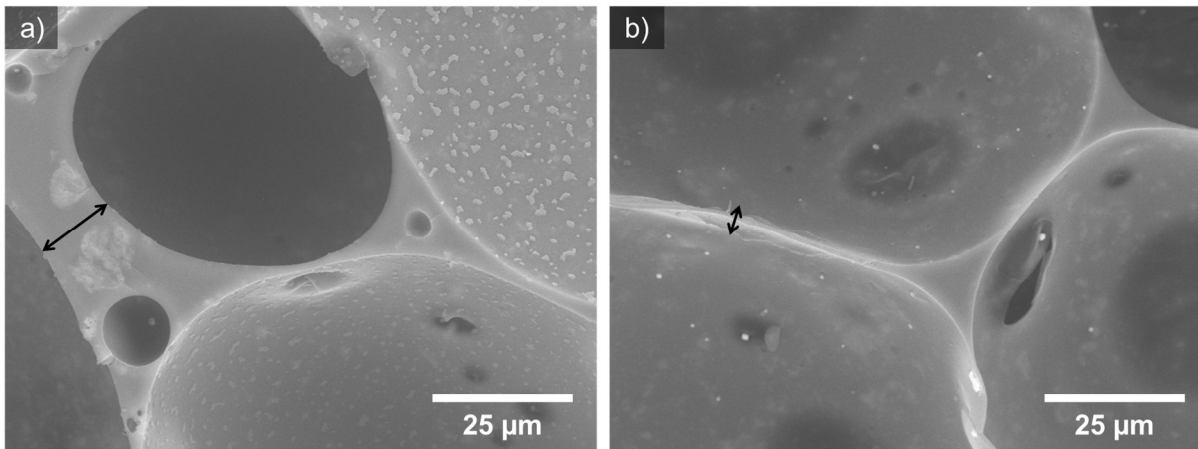
402 *Figure 5: Scanning Electron Micrographs of the solid dried material with ratio W/O of a) 74/26_{v/v} b) 79/21_{v/v} and c) 83/17_{v/v}*
 403 *and d) e) f) respective zoom into the cells*

405 These observations were verified by mercury intrusion porosimetry (Figure 6 a-b). As previously
406 observed samples showed a double population of holes, one with larger diameters resulting from the
407 emulsion droplets, and another at a smaller scale. As expected, porosity increased with the water
408 volume fraction, with good adequacy between initial emulsion composition and porosimetry
409 measurements (Table 3). When the water volume fraction increased the mercury intrusion into the
410 sample was facilitated. This phenomenon was mainly observed as intrusion pressure decreased,
411 shifting the small holes population diameter towards larger values. These results were in good
412 adequacy with the observation made by SEM (Figure 5). Indeed, Figure 5 shows the presence of larger
413 holes in samples with higher water volume fractions: $1.2\ \mu\text{m}$ for the highest water content (84/16_{v/v}),
414 decreasing to $0.7\ \mu\text{m}$ for the intermediate water content (79/21_{v/v}) reaching $0.5\ \mu\text{m}$ for the smallest
415 water volume fraction (74/26_{v/v}).



420 Mechanical analysis were performed and the compressive moduli were extracted. As described by
 421 Equation 6, the compressive modulus was plotted against the square of the relative density (Figure 6
 422 c), and showed a linear dependence according to Equation 6. However, a deviation can be observed at
 423 the lowest studied water volume fraction (highest density). Several explanations could be proposed to
 424 explain this behaviour: at least one of the two hypothesis of the Gibson and Ashby model might not
 425 be verified anymore. The open-porosity hypothesis was verified by mercury intrusion porosimetry,
 426 therefore rather questioning the homogeneity of the matrix. Indeed, cell-to-cell wall thickness
 427 increases with decreasing water content, the localisation of the CNC-Br at the interface might induce

428 a non-negligible inhomogeneous composition of the wall. This hypothesis was confirmed by a closer
429 look at SEM micrographs of samples PPH-5 (74/26_{v/v}) and PPH-6 (83/17_{v/v}), Figure 7 .



430

431 *Figure 7: Impact of W/O ratio on polymer film (continuous line), (a) for low water ratio 74/26_{v/v} and (b) for high water ratio*
432 *83/17_{v/v}*

433 Thickness of polymer films were measured and the results are compared to the estimated thickness of
434 the CNC-Br envelope present at each cell surface. Given the fact that an average of 5 layers of CNC-Br
435 was calculated to be present at each cell surface, a minimum of 125 nm is to be considered for a dense
436 packing of the rods. Therefore, a homogeneous polymer matrix could only be assumed if the polymer
437 film thickness does not exceed 250 nm, maximal value when two CNC-Br envelopes of neighbouring
438 cells come into contact. The film thickness deduced from the SEM picture in the case of the highest
439 concentrated emulsion-base polyHIPE PPH-6 (83/17_{v/v}) was about 609 nm, which is of the same order
440 of magnitude (factor 2.4) as the double CNC-Br envelop, while the film thickness of the polyHIPE issuing
441 from the emulsion with the lowest water content PPH-5 (74/26_{v/v}) was measured about 2094 μm which
442 is one order of magnitude larger than this double envelope size. Therefore, we think that the polymeric
443 matrix of PPH-5 (74/26_{v/v}) cannot be assumed homogeneous enough to fit in Gibson and Ashby model,
444 contrary to the two other samples.

445

446 **Conclusion**

447 We have shown in the current paper that cellulose nanocrystals modified with a hydrophobic function
448 (CNC-Br) could stabilize High internal phase emulsions (W/O) with water content of 80%_{wf} that could
449 be easily polymerized to promote materials with an open porosity. Indeed, The HIPE were effectively
450 polymerized without destabilization, and polyHIPE reflected the original HIPE as measured emulsion
451 and cell size were identical. All materials synthesized showed an open porosity, confirmed by mercury
452 intrusion porosimetry analysis and by the fact that all the water caught was evaporated without the
453 use of vacuum and lead to adequate density. Using the limited coalescence phenomenon, monoliths
454 with a wide range of cell diameters were synthesized with both constant density and CNC-Br coverage
455 of 5 layers. Emulsion drop size showed to have no influence over the Young modulus, as predicted by
456 Gibson and Ashby model for porous materials. The use of the model was made possible as the material
457 had an open porosity and by verifying the homogeneity of the polymer matrix by cryo-TEM
458 observation. Also, variation of the density by changing the volume fraction at fixed drop size showed
459 a good dependence of the Young modulus except for high densities. This behaviour was explained by
460 increasing film thickness in-between adjacent cells questioning the matrix homogeneity necessary to
461 apply Gibson and Ashby model. In general, the pore diameter didn't match the calculation made for
462 interconnections resulting from the contact zones between cells. The presence of smaller pores than
463 expected could be explained by the existence of especially thick films.

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469

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