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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 bromoisobutyryl 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 dispersed phase represents more than 64% of the sample for a monodisperse emulsion and 71% for 34 35 a polydisperse one. Internal volume fraction of 64%, 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 of which is shown in Figure S1, SI). PolyHIPE exhibits complex morphologies. They possess cavities, 40 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 Wrobleski, 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 of growing interest because they are bio sourced, and highly available. They also have very good 61 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 may improve composite properties (Klemm et al., 2011; Postek et al., 2013). One can expect that the 64 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 attempt of polymerization of the water continuous phase of O/W HIPE was realized (Liu et al., 2017). 68 69 To our knowledge, no work reported the polymerization of the organic continuous phase of W/O HIPE 70 stabilized by modified CNC.

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

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

82 **2. Experimental**

83 2.1 Materials

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

Styrene (99%, St), Divinylbenzene (80%, DVB), Azobisisobutyronitrile (98%, AIBN), 4diméthylaminopyridine (99%, DMAP) and sodium chloride (NaCl) were purchased from Sigma Aldrich.
α-bromoisobutyryl bromide (98%, Bibb) was purchased from ABCR. Triethylamine (99%, TEA) was
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.

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

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

107

Equation 1

108 With n_{OH} = 3.10 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 80/20wt/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
$$D_{3,2} = \frac{\sum i N_i \cdot D_i^3}{\sum i N_i \cdot D_i^2}$$

121

Equation 2

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

125
$$U = \frac{1}{\overline{D}} \cdot \frac{\sum_{i} |D_{i} - \overline{D}| \cdot D_{i}^{2}}{\sum_{i} D_{i}^{2}}$$

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

Infrared spectra of unmodified and brominated CNC were recorded using a Vertex 70 Bruker FT-IR
 spectrometer. CNC powder was analyzed thanks to an attenuated total reflectance ATR accessory.
 Each spectrum was recorded between 4000 cm⁻¹ and 400 cm⁻¹ with a resolution of 4 cm⁻¹ with 32 scans.

Materials morphology was characterized with SEM TM-1000 with acceleration voltage of 15 kV. The samples were stick onto support with silver lacquer and metallized with gold/palladium coating during 60 seconds. Slice of materials (70 nm) were obtained by cryo-ultramicrotomy with a Leica UC7 at -90°C and were observed at ambient temperature with a TEM Hitachi H7650.

The experimental porosity of the samples was determined by mercury intrusion porosimetry in a Micromeritics Autopore IV 9500 porosimeter with the following parameters: contact angle = 130°, mercury surface tension = 485 mN m⁻¹, maximum intrusion pressure = 124 MPa. The analysis was replicated at least 3 times for each set of parameters. A TA Instrument RSA3 (dynamic mechanical analysis, DMA) was used to study the mechanical properties of the samples, with a cylindrical shape of 20 mm diameter of 7.5 ± 1.5 mm thick. The compression test was performed in static mode at ambient temperature, during 10 s at a rate of 1mm/s until a force of 35 N is reached. Each set of experiments was replicated 5 times to insure the reproducibility of the analysis.

154 **3 Results and discussion**

155 3.1 CNC modification



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, etherification or by esterification (Eyley and Thielemans, 2014). Esterification reaction is known to be 160 161 fast and to offer a wide range of graft possibilities, therefore, this reaction was used in the following to graft Bibb function onto the CNC surface in order to modify the hydrophobic/hydrophilic balance of 162 the CNC (Figure 1). The use of Bibb allows providing hydrophobicity. In addition it may be useful as 163 164 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 extracted using Equation 1. Because of the material variability, initial amount of hydroxyl function was 169 eventually underestimated and therefore, substitution rate was overestimated. Further 170

171 characterization of the resulting crystals in terms of chemical modification and morphology is provided172 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%, 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 80/20wt/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 $83/17_{v/v}$.

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

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

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 \approx 0.3).

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

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

208

Equation 4

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 surface and volume of the particles in contact with the interface (calculated for a crystal of dimension 140x25x25 nm³), V_d the volume of the dispersed phase, and C the covering ratio.

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

217 3.3 Emulsions polymerization

218 **3.3.1 Study of a reference polyHIPE**

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 219 220 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 $122 \pm 23 \mu m$, 231 and the polyHIPE cell size $125 \pm 37 \mu m$ (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.



234

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

The morphology of the obtained polyHIPE (Figure 2) differs from usual open-cell polyHIPE stabilized by surfactant, but seems typical for a particle-stabilized Pickering polyHIPE. Indeed, conventional polyHIPE stabilized by surfactant and particle-stabilized Pickering polyHIPE present different types and aspects of porosity. The first category of polyHIPE usually presents an obvious open-cell structure with well242 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 Wrobleski, 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).

Therefore, it was not surprising observing in our samples some open pores (dotted line), but mostly pores covered by a thin polymeric film (Figure 2 dashed lines). In order to assess the closed or open structure of the polyHIPE, one can compare the monolith density also given by mercury intrusion porosimetry and the one estimated either through the mass to volume ratio of the macroscopic monolith or estimated from the monolith composition. In the later calculus, the density of poly(styrene-DVB) has been taken equal to 1.06 g/cm³, density of CNC as 1.6 g/cm³ 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	, 5		
Estimated from the mass to volume ratio	0.12	88		
Mercury porosimetry measurement	0.18	81 ± 2		

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
$$D = -(\frac{1}{P}) 4.\gamma .\cos\varphi$$

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 μ m) (Figure 4 b), corresponding to the 288 cells of the polyHIPE (125 μ m). At higher pressures, a second population of holes (< 1 μ m) 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 μ m in diameter for 79%, (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 that the thickness of 5 CNC layers between the drops or that the interconnections 295 do not results 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

The influence of the cell size was studied by varying the CNC-Br concentration. Four concentrations of 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 other parameters constant. First, emulsion size was preserved after polymerization (Figure 3 left). At lower CNC-Br concentration, no destabilization phenomenon was observed (coagulum, demixing...) upon polymerization, however drops diameter differed from cells diameter. This deviation from the slope y=x might be explained by deformed SEM pictures harder to analyze (Figure 3 a).

Successful materials were synthesized based on these emulsions and characterized by SEM (Figure 3 a-d). All the materials were homogeneous regarding their cell size distribution, with a decrease of the cell diameter with the concentration of CNC-Br (Table 2) as expected according to the limited coalescence phenomenon. Each sample exhibited also the presence of pores between the cells 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 e. 339 IC-

determined by optical microscopy. The dashed line with slope of 1 corresponding to equality is plotted as a guide to the ey
Right, Scanning Electron Micrographs of the final obtained monoliths after washing and drying with initially a) 5 g/L of CN
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/cm³)	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

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 holes were identified: the largest corresponding to the cells and a second one smaller, corresponding 344 345 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 with increasing amount of CNC-Br used to stabilize the polyHIPE (Table 2) at constant drop coverage 347 by the particles (since the samples belong to the limited coalescence domain where the coverage is 348 349 constant).



350

Figure 4: a) b) Mercury intrusion as function of pores diameter for different size diameter, c) compressive modulus of porous
 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 cryoTEM observations of 70 nm thick slices cut in the material. Cryo-TEM pictures showed a homogeneous
 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 Wrobleski (Williams and Wrobleski, 1988) for polyHIPE stabilized 373 with sorbitan monoleate. 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

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

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

381

Equation 6

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

Here, the study focused on three distinct ratios, keeping a water volume fraction above 64% to remain 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 drop size, we chose to maintain the ratio of the amount of CNC-Br to the amount of dispersed phase constant (see Equation 4). This value is fixed at a value of 8 g/L with regards to the dispersed phase for all samples. After optical observation, the droplets diameter was measured to be around 125 μ m for all three formulations (Table 3). The last ratio (83/17_{v/v}) was reached thanks to centrifugation of the 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/cm³)	Skeletal density (g/cm ³)	E (MPa)
PPH-1	80/20 _{wt/wt}	79/21 _{v/v}	8	122 ± 23	125 ± 37	0.66	81 ± 2	0.18	0.97	2.05 ± 0.19
PPH-5	75/25 _{wt/wt}	74/26 _{v/v}	8	120 ± 25	122 ± 36	0.50	75 ± 2	0.24	0.96	2.08 ± 0.31
PPH-6	85/15 _{wt/wt}	83/17 _{v/v}	8	150 ± 38	127 ± 34	1.22	85 ± 2	0.12	0.81	1.48 ± 0.36

394



Table 3: PolyHIPE characteristics varying the W/O fraction

As previously noticed, homogeneous self-standing monoliths were obtained, but SEM micrographs (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 form 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.





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) $83/17_{v/v}$ 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 μ m for the highest water content (84/16_{v/v}), 414 decreasing to 0.7 μ m for the intermediate water content (79/21_{v/v}) reaching 0.5 μ m for the smallest 415 water volume fraction $(74/26_{v/v})$.



418 Figure 6: a) b) Mercury intrusion as function of pores diameter for different W/O ratio, c) Compressive modulus evolution 419 with relative density (Gibson and Ashby model prediction in dotted line)

420 Mechanical analysis were performed and the compressive moduli were extracted. As described by Equation 6, the compressive modulus was plotted against the square of the relative density (Figure 6 421 422 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 microcrographs of samples PPH-5 (74/26_{v/v}) and PPH-6 (83/17_{v/v}), Figure 7.



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
 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 μ m 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.

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%wt 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 increasing film thickness in-between adjacent cells questioning the matrix homogeneity necessary to 460 461 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 expected could be explained by the existence of especially thick films. 463

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469

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