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# High-pressure drop rates in solid-state batch one-step scCO<sub>2</sub> foaming of acrylic polymers: a way to stabilize the structure of micro-nano foams

Margaux Haurat<sup>1</sup>, Yannick Anguy<sup>2\*</sup>, Cécile Gaborieau<sup>2</sup>, Guillaume Aubert<sup>3</sup>, Cyril Aymonier<sup>3</sup>, Michel Dumon<sup>\*1</sup>

<sup>1</sup> Université de Bordeaux, UMR CNRS 5629, Bordeaux INP, LCPO, UMR 5629, ENSCBP 16 avenue Pey Berland, F-33600 Pessac, France

<sup>2</sup> Université de Bordeaux, UMR CNRS 5295 I2M, F-33405, Talence, France

<sup>3</sup> Université de Bordeaux, UMR CNRS 5026, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

\*Contact authors to whom correspondence should be addressed: [yannick.anguy@u-bordeaux.fr](mailto:yannick.anguy@u-bordeaux.fr) and [michel.dumon@u-bordeaux.fr](mailto:michel.dumon@u-bordeaux.fr)

## Abstract

One-step solid-state batch scCO<sub>2</sub> foaming is used with the target of achieving acrylic polymer micro-nano foams. Foaming is triggered by an average pressure drop (APDR), covering two decades, from 0.3 to 30 MPa.s<sup>-1</sup>. This study principally addresses the combined beneficial effects of block copolymer addition (BCP, here denoted as MAM) and high APDR. Numerous subtle kinetic parameters actually interplay and compete in the production of the final foams. In particular, the material effective temperature, the effective glass transition temperature of the plasticized system and the instantaneous PDR are physical quantities each having their own kinetics during foaming. The resulting foam morphologies are quantified by SEM microscopy and image analysis. A high APDR and the presence of BCP are shown to play a key role in the final structure of the foams. Over the scrutinized range of saturation temperature (40 °C to 60 °C *i.e.* rather 'low' temperatures in the CO<sub>2</sub> supercritical state), the APDR is the main factor for significantly reducing cell size and increasing nuclei density in foams from neat PMMA. In the block copolymer approach, increasing the APDR is of secondary importance as the targeted reduction of the porosity dimensions and augmentation of nuclei density are mostly the consequence of MAM presence. In this latter case, increasing the APDR still promotes the 'efficiency' of the BCP nucleants. A real efficient nucleation activity of MAM additive is observed at a very high APDR (30 MPa.s<sup>-1</sup>), leading to monomodal homogeneous distribution of tiny pores in nearly nanosized foams. At lower APDR, an interesting reproducible double porosity (foams containing intra-wall and inter-cell pores) is detected in PMMA/MAM systems. In such double porosity foams, benefits from the Knudsen effect achieved within well expanded local domains (showing micron-sized pores) may remain meaningful thanks to a locally poorly expanded nanoporous thick solid skeleton encapsulating these local domains. Thereby, the radiative thermal conduction can be minimized and does not override the conductive component at the sample scale. This work provides further insight on acrylic polymer BCP foams influenced by different kinetics.

38

39 **Keywords:** supercritical carbon dioxide; micro-nano foams; one-step batch foaming; high-pressure  
40 drop rate; acrylic polymers; quantitative structural analysis; foaming process; thermal insulation

## 41 **1. Introduction**

42 In recent years, polymer foams, and especially micro-nano foams obtained by a blowing (or foaming)  
43 agent, have raised the interest of industrials and academics due to their expected unusual  
44 combination of properties. Indeed, reducing the foam porosity dimensions from micro to nano range  
45 can lead to improved mechanical and thermal insulation properties (e.g. due to the Knudsen effect  
46 for the latter) [1],[2], or even filtration properties. However, when a blowing agent is used, the  
47 desired porosity size reduction is not easy to reach and requires optimization of the foaming process  
48 conditions (e.g. saturation pressure, temperature, and time, pressure drop rate) for each foaming  
49 agent – material – process combination.

50 The foaming agent is either chemical or physical. Chemical foaming requires use of a chemical  
51 blowing agent to generate a gas by thermal decomposition or by chemical reaction [3]. On the  
52 contrary, a physical blowing agent (e.g. an inert gas) is directly injected in the process [4],[5],[6]. In  
53 both cases, a thermodynamic instability is required to induce a phase separation between the gas  
54 and the material. At that point, foaming is initiated and the nucleation, growth and coalescence steps  
55 ensue. Depending on the foaming conditions, all three steps may, or not, partially overlap over time.  
56 In order to propose a more environmental responsible alternative than chemical foaming, carbon  
57 dioxide (CO<sub>2</sub>) is selected as the physical blowing agent. This non-toxic and low-cost blowing agent  
58 enters the supercritical state (scCO<sub>2</sub>) in rather easy conditions, with a critical point at  $P_C = 7.38 \text{ MPa}$   
59 and  $T_C = 31 \text{ }^\circ\text{C}$ . In these specific conditions, CO<sub>2</sub> offers a combination of liquid and gaseous  
60 properties *i.e.* good solubility and diffusivity in polymers (in comparison with other physical blowing  
61 agents, e.g. nitrogen) [7]. The supercritical specificities are thus favorable for polymer saturation and  
62 to some extent for polymer foaming (as pressure is released, the blowing agent leaves rapidly the  
63 supercritical state).

64 Considering the high CO<sub>2</sub>-philicity and the ability to foam with reduced porosity dimensions of acrylic  
65 polymers, they are good candidates for scCO<sub>2</sub>-assisted saturation/foaming [8],[9]. Both neat  
66 poly(methyl methacrylate) (PMMA) and blends of PMMA + MAM – the so-called MAM is a triblock  
67 copolymer PMMA-PBA-PMMA (where PBA is poly(butyl acrylate)) – have been largely studied in the  
68 literature and were selected for this study. In a 90/10 PMMA/MAM weight ratio solid precursor  
69 blend, MAM structures are typically nano micellar-like objects dispersed in the PMMA matrix. Due to  
70 the higher CO<sub>2</sub>-philicity of the soft PBA block, the micellar objects concentrate the CO<sub>2</sub> and act as  
71 CO<sub>2</sub>-reservoirs during saturation and foaming. In the foaming process, the micellar objects are

72 deemed to act as effective nucleation sites (as other additives [10]) and to improve PMMA foaming  
73 (foam homogeneity and cell size reduction) [6],[11],[12],[13].

74 Acrylic polymers can be saturated and foamed using various processes assisted with scCO<sub>2</sub>; one can  
75 quote extrusion [4],[14], injection [5],[15] and batch foaming (either one-step or two-step)  
76 [6],[11],[16]. So far, batch foaming (or autoclave foaming) is preferred over the other processes to  
77 produce foams with small porosities [12],[16]. Indeed, contrary to other processes, all batch  
78 saturation conditions (*i.e.* saturation pressure, temperature and time), are independently controlled  
79 [8]. In view of solid-state one-step batch foaming with reduced porosity dimensions, the roles of the  
80 saturation pressure and temperature upon acrylic polymers-foaming are well known [17],[18]. On the  
81 one hand, saturation pressure ( $P^{sat}$ ) has to be maximized to improve the sample saturation by  
82 increasing the CO<sub>2</sub>-solubility [9]. On the other hand, saturation temperature ( $T^{sat}$ ) has to be  
83 minimized to optimize the saturation step, while complying with the supercritical state, which also  
84 contributes to optimize the saturation step due to an advantageous combination of liquid and  
85 gaseous properties. The relation between  $T^{sat}$  and the speed at which the foam vitrifies (or  
86 stabilizes) is a complex issue, certainly overlooked in the literature. Indeed, as foaming is triggered  
87 e.g. by an adiabatic pressure *quench*, the effective temperature ( $T^{ef}$ ) of the plasticized system  
88 {polymer + CO<sub>2</sub>} is lower than  $T^{sat}$  and generally unknown. The vitrification speed is therefore  
89 determined, among others, by the interplay between *i)* the evolution of  $T^{ef}$  towards room  
90 temperature and *ii)* the rising kinetics of the effective glass transition temperature ( $T_g^{ef}$ ). Once the  
91 sample is vitrified ( $T_g^{ef} > T^{ef}$ ), cell growth and coalescence are stopped and one can expect to  
92 produce a foam with small cell dimensions.

93 At the beginning of foaming, another important parameter acts on the foam structure: the pressure  
94 drop rate (PDR). The pressure drop rate is typically defined as  $\Delta P/\Delta t$ , where  $\Delta P = p^{sat} - p^{ambient}$   
95 and  $\Delta t$  is the time to return to ambient pressure upon pressure release [19]. Several studies have  
96 shown that increasing the pressure drop rate is a relevant way to minimize foam cell size thereby  
97 improving the mechanical and thermal properties [19],[20],[21]. This trend has been observed using  
98 adapted devices (e.g. PP batch-foaming fitted with a window linked to a camera [22]) allowing  
99 observation of the foaming process from the early stages of cell growth. A PDR increase induces an  
100 increase of the nuclei formation rate [23]. At a certain stage, nucleation and growth may compete.  
101 More precisely, when cell nucleation and growth overlap, the later penalizes the former. When the  
102 PDR is increased, the nucleation rate is favored while growth is limited. Increasing the PDR also  
103 prevents coalescence by increasing the speed at which the effective glass temperature of the  
104 plasticized system {polymer + CO<sub>2</sub>} ( $T_g^{ef}$ ) is overcome (*i.e.*  $T^{ef} < T_g^{ef}$ ) [23],[24]. So, because of its

105 action upon the different foaming steps, the PDR has an influence upon both cell size and cell density  
106 [24],[25],[26],[27].

107 In batch foaming, a *classical* PDR value may be considered as  $0.5 \text{ MPa}\cdot\text{s}^{-1}$  [11]; other PDR values have  
108 been studied ( $30 \text{ MPa}\cdot\text{s}^{-1}$  [19];  $8.3 \text{ MPa}\cdot\text{s}^{-1}$  [24];  $0.4 \text{ MPa}\cdot\text{s}^{-1}$  [28]) by using vessels with a smaller  
109 capacity and/or by increasing the outlet pipe diameter to facilitate gas evacuation during foaming.  
110 Experimentally, the number of nucleated bubbles per unit volume of unfoamed material ( $N_0$ ) has  
111 been shown to depend linearly upon pressure drop rate in a bi logarithmic scale [24]. A classical PDR  
112 ( $\sim 0.5 \text{ MPa}\cdot\text{s}^{-1}$ ) is generally not sufficient to reach a very small pore size as it does not induce a  
113 sufficient number of nuclei or do not freeze the structure by a rapid enough thermal quench  
114 (consecutive to pressure quench). Simulations of PDR were carried out at an extremely high PDR  
115 ( $250 \text{ MPa}\cdot\text{s}^{-1}$ ) [20],[26]. As a matter of fact, both theoretical and experimental studies show that a  
116 PDR increment can increase the cell number density by 1 or 2 decades while cell size decreases by a  
117 moderate factor of 2 or 3. Furthermore, most of the systems studied in the literature are probably in  
118 a molten state (flowing state), and do not undergo a solid-state (non-flowing) foaming. Thus we may  
119 expect a greater influence of the PDR value when the system is solid (solid-state  $\text{CO}_2$  foaming).

120 No work actually states clearly if the mere fact to increase the pressure release rate can increase the  
121 cell density ( $\text{cells}\cdot\text{cm}^{-3}$ ) up to  $10^{15} \text{ cell}\cdot\text{cm}^{-3}$ , reduce cell size in the nanometer range and  
122 simultaneously lower the overall material density ( $\rho_f$ ) near or below  $0.2 \text{ g}\cdot\text{cm}^{-3}$ . However, in a one-  
123 step solid-state batch foaming, appropriate combinations of factors (high PDR, low saturation  
124 temperature and introduction of nucleating nano particles) may be beneficial. Such combinations are  
125 investigated in this work for neat PMMA and for PMMA/10 wt% MAM blend foams. PMMA and  
126 PMMA/10 wt% MAM are  $\text{CO}_2$ -saturated at temperatures ( $40 \text{ }^\circ\text{C}$  and  $60 \text{ }^\circ\text{C}$ ) and saturation pressures  
127 ( $20 \text{ MPa}$  and  $30 \text{ MPa}$ ) complying with the supercritical state before being foamed (one-step solid-  
128 state foaming) over a broad PDR range (from  $0.3 \text{ MPa}\cdot\text{s}^{-1}$  to  $30 \text{ MPa}\cdot\text{s}^{-1}$ ). Porous structures are  
129 investigated through a quantitative analysis of SEM images at different scales.

130

## 131 **2. Materials and Methods**

### 132 **2.1 Materials**

133 Neat poly(methyl methacrylate) (PMMA commercialized as V825T 101 Clear PMMA by Arkema)  
134 pellets and neat MAM (M53 grade commercialized by Arkema) triblock copolymer (poly(methyl  
135 methacrylate)-co-poly(butyl acrylate)-co-poly(methyl methacrylate)) pellets were supplied by  
136 Arkema (Lacq, France). The characteristics of these materials are well documented in literature  
137 [12],[18],[29].

### 138 **2.2 Unfoamed blend compounding**

139 To produce PMMA/10 wt% MAM blend, neat PMMA and MAM pellets were first dried at 80 °C for  
140 4 h in an oven. Then, the blend was compounded by CANOE (Pau, France) using a corotative twin-  
141 screw extruder (Labtech,  $\phi = 26 \text{ mm}$ ,  $L/D = 40$ ) with a temperature profile ranging from 250 °C to  
142 230 °C at a screw speed of 300 rpm. At the end of the extruder line, the blend was pelletized with a  
143 continuous cutting machine.

144 Neat PMMA and PMMA/10 wt% MAM pellets were dried again at 80 °C for 4 h in an oven. Then,  
145 transparent tensile test bars (ISO 180/U  $80 \times 10 \times 4 \text{ mm}^3$ ) of neat PMMA and PMMA/10 wt% MAM  
146 were injected with a classical injection-molding device (ENGEL ES 200-45 HL-V). The acrylic polymer  
147 and blend were injected at 230 °C at a screw speed of 300 rpm in a mold heated at 90 °C. All injected  
148 bulk bars were perfectly transparent.

### 149 **2.3 One-step batch foaming**

150 PMMA and PMMA/10 wt% MAM were foamed through scCO<sub>2</sub>-assisted one-step batch process at  
151 LCPO and ICMCB laboratories (Bordeaux, France). Varying the PDR over a wide range of values  
152 typically requires use of vessels of different capacities and/or outlet pipe diameter [19], [24], [28]. In  
153 this study, two vessels were used to vary the PDR by two order of magnitude (Table 1). These two  
154 vessels were especially necessary to be able to work with sufficiently large samples; and the bigger-  
155 sized vessel could in no way allow reaching  $30 \text{ MPa}\cdot\text{s}^{-1}$ .

156 The samples foamed at « low PDR » ( $0.3 \text{ MPa}\cdot\text{s}^{-1}$  and  $0.5 \text{ MPa}\cdot\text{s}^{-1}$ ) were produced in a high-pressure  
157 vessel provided by TOP Industrie (Vaux-le-Pénil, France). The vessel was filled with CO<sub>2</sub> at the desired  
158 pressure with a syringe pump Teledyne ISCO model 260 (Lincoln, USA). Because the outlet pipe  
159 diameter was fixed, the saturation pressure was set to 20 MPa or 30 MPa to enforce the target PDRs  
160 of 0.3 and  $0.5 \text{ MPa}\cdot\text{s}^{-1}$  (values in the range of low PDR). The saturation temperature (40 °C or 60 °C)  
161 was controlled with a heating collar. The CO<sub>2</sub> uptake (wt%) was measured in situ using a FTIR (Fourier  
162 Transform Infrared) microscope combined to a CO<sub>2</sub> high-pressure cell [9]; scCO<sub>2</sub> uptake was found to  
163 the same at 20 MPa and 30 MPa (the samples are already fully saturated at 20 MPa at both  
164 temperatures) [9]. Therefore, a saturation pressure spread of 10 MPa (20 vs. 30 MPa) had no impact  
165 upon the final foam structures. After saturation (during 24 h to ensure full saturation of the samples),  
166 the pressure was released with an on/off discharge valve model 910.10.00 provided by TOP Industrie  
167 (Vaux-le-Pénil, France).

168 Samples foamed at higher PDR ( $4 \text{ MPa}\cdot\text{s}^{-1}$  and  $30 \text{ MPa}\cdot\text{s}^{-1}$ ) were produced in a smaller-sized vessel  
169 (0.057 L) provided by Swagelok (Lyon, France). In this vessel, the PDR could be varied by adapting the  
170 geometry of the vessel (outlet pipe diameter; Table 1). After saturation (24 h), the pressure was  
171 released with an on/off discharge valve model SS-AFSS12 provided by Swagelok (Lyon, France).

172 **Table 1.** Batch set-up dimensions versus PDR

PDR (MPa.s <sup>-1</sup> )	Vessel capacity (cm <sup>3</sup> )	Outlet pipe internal diameter (cm)
0.3	300	0.2
0.5	300	0.2
4	57	2.36
30	57	13.51

173

## 174 2.4 Characterization techniques

### 175 i. Water pycnometer

176 Unfoamed materials density ( $\rho_s$ ) and foams density ( $\rho_f$ ) were determined with a water pycnometer  
 177 following the water displacement method, based on Archimedes' principle. Three measurements  
 178 were performed for each sample.

### 179 ii. Electron microscopy observations and image analysis

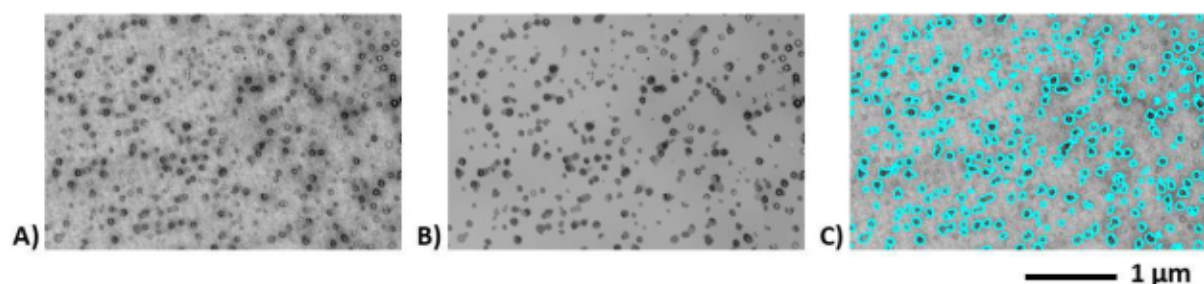
#### 180 • PMMA/10 wt% MAM dense precursor blend: TEM observations

181 The structure of the solid PMMA/10 wt% MAM blend precursor was observed through TEM. Before  
 182 observation, the solid blend was cut into a cryo-ultramicrotome LEICA EM UC7-FC7 (Wetzlar,  
 183 Germany) at -75 °C with a diamond knife at the Bordeaux Imaging Center (BIC, Bordeaux, France).  
 184 The thin cuts (80 – 100 nm thick) were collected on copper grids before being contrasted with an  
 185 aqueous solution containing 2 wt% phosphotungstic acid (PTA) + 2 wt% benzyl alcohol at ambient  
 186 temperature. As reported in the literature, PTA preferentially colors at ambient temperature the  
 187 CO<sub>2</sub>-philic PBA soft block (in black or dark grey on TEM images) over the PMMA more rigid block  
 188 (white or light grey on TEM images) [6],[11]. Benzyl alcohol acts as a dyeing assistant and helps PTA  
 189 coloration of PBA. TEM observations were performed at 80 kV at magnifications ranging from  
 190 X15 000 to X200 000 (Figure 1.A). The exhibited nanostructures can be qualified as micellar objects or  
 191 micelle-like objects.

#### 192 • Image analysis of TEM micrographs

193 TEM images captured at several magnifications were analyzed in order to quantify the micellar  
 194 objects and determine automatically their characteristics. To further improve the level of contrast  
 195 permitted by staining (Figure 1.A) and facilitate the subsequent segmentation of the micellar objects  
 196 (Figure 1.C), we adopted a multiscale (multiresolution) description of electronic images (thereafter  
 197 electronic images are denoted by  $u(\mathbf{x})$ , where  $u$  is the grey level intensity function at every pixel  $\mathbf{x} =$   
 198  $(x_1, x_2)$ ). Descriptions that depend on scale (or resolution) may be computed in several ways. We  
 199 retained the so-called *scale-space filtering* [30],[31]. In this approach, the original image  $u(\mathbf{x})$  (Figure  
 200 1.A) is embedded in a family of images  $u(\mathbf{x}, t)$  at coarser resolutions (larger scale levels) *cf* e.g. Figure  
 201 1.B. Such family of images  $u(\mathbf{x}, t)$  is obtained by filtering  $u(\mathbf{x})$  over increasing scales whose size is  
 202 parametrized by the increasing time  $t$  of a diffusion equation [32]. The resulting family of images  
 203  $u(\mathbf{x}, t)$  produced by varying continuously the scale-space parameter  $t$  is called the scale-space image.

204 Because information content decreases towards higher levels (at coarser resolutions), edges or  
 205 boundaries (the zero-crossings of the Laplacian of the image) are moved when sweeping out the  
 206 scale-space image. In this sense, we can say that the material is virtually reconstructed as illustrated  
 207 in Figure 1.B. With this multiscale (multiresolution) description, we could detect more readily image  
 208 features at different resolutions (e.g. Figure 1.B). In this approach, the key point is that images have  
 209 by nature a hierarchical organization composed of a small number of levels or scales [33]. There is a  
 210 natural range of resolutions, in other words intervals of the scale-space parameter  $t$ , corresponding  
 211 to each of these *semantic* levels of description, where the interphases and/or interfaces of interest  
 212 are better perceived and even reconstructed (Figure 1.B). As illustrated in Figure 1.B, the  
 213 reconstructed image tends to a piecewise constant solution representing a simplified image with  
 214 sharper boundaries, permitting to easily segment interphases e.g. by direct thresholding without  
 215 recourse to any complex treatment of image analysis. To achieve this, we followed the route paved  
 216 by Perona and Malik [34]. We relied on a nonlinear scale space, where blurring is locally adaptive to  
 217 image data: the diffusion process (blurring) mainly takes place in *flat* regions (PMMA matrix) where  
 218 the magnitude of the gradient  $\left(\nabla(\cdot) = \left(\frac{\partial(\cdot)}{\partial x_1}, \frac{\partial(\cdot)}{\partial x_2}\right)\right)$  of the grey level intensity  $\|\nabla u\|$  is low. On the  
 219 other hand, blurring does not affect region boundaries (micellar object boundaries), where  $\|\nabla u\|$  is  
 220 larger. Furthermore, in the neighborhood of marked discontinuities (boundaries), where  $\|\nabla u\|$  is  
 221 high across the level curve of the intensity  $u$ , the diffusion process is running locally backwards,  
 222 normal to the isoline of  $u$  *i.e.* normal to the boundary, which is thereby steepened (contrast  
 223 enhancement; Figure 1.B).



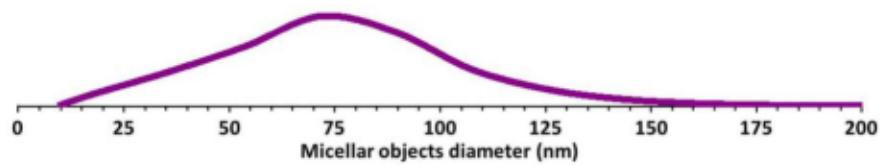
224  
 225 **Figure 1.** Illustration of the segmentation of micellar objects. **A)** Local close up in a TEM micrograph (X20 000)  
 226 showing dispersed micellar objects formed by MAM tri-block copolymers in a 90/10 PMMA/MAM solid blend  
 227 precursor. **B)** Enhanced image after applying to Figure 1.A a nonlinear directional diffusive filter. In this filtering  
 228 procedure, Gaussian blurring applies selectively to flat regions, which are dissipated, while the boundaries and  
 229 the contrast of the nanostructures of interest are clearly enhanced. **C)** Binarized (0 -1) counterpart of the grey  
 230 level image in Figure 1.B. In this display, the contours of the segmented nanostructures (labeled with a 1 value)  
 231 are displayed in cyan, superimposed upon the original image (Figure 1.A) rather than leaving in transparency  
 232 the 0-valued background matrix.

233 Before segmentation, the filtered image  $u(\mathbf{x}, t)$  was, when necessary, corrected for shading (uneven  
 234 background matrix). Touching/overlapping micellar objects were automatically separated before size



235 and shape measurements. To do so, we assumed, as others e.g. Canseco et al. [35], a systematic  
 236 region growing approach [36]. After disconnection of overlapping objects, the binary image (e.g.  
 237 Figure 1.C) was perfectly suited to the automatic measurement of the object size statistical  
 238 distribution (Figure 2). The effective diameter  $D$  of every micellar object was derived from the object  
 239 perimeter  $P$  measured by integrating for all affine lines in the plane the Euler-Poincaré characteristic  
 240 of the intersection of the line with the object [37].

241 The rather large distribution of the micellar objects diameter (Figure 2) suggests that the system is  
 242 not at equilibrium (a liquid micellar system would show a mono modal distribution). The non-  
 243 equilibrium state comes from several reasons: *i)* the macromolecular nature and chain polydispersity  
 244 of MAM, *ii)* the high viscosity and temperature quenching of the blend during the extrusion stage,  
 245 where the blend is sheared and cooled at the end of the die.



246

247 **Figure 2.** Nanostructure size distribution automatically determined from segmented objects (Figure 1.C). In this  
 248 display, the finite size interval bins of the original discrete frequency histogram of the object diameters are  
 249 schematically represented as a continuous distribution of the object percentile as a function of cell size. The  
 250 vertical full scale is set to the highest nanostructure percentile of the original frequency histogram.

251 Some of the characteristics derived from the nanostructure size distribution of the 10 wt% MAM  
 252 solid precursor (Figure 2) are listed in Table 2, namely the nanostructure number density  $N_s$   
 253 (objects.cm<sup>-3</sup>), the nanostructure average diameter  $\bar{D}_s$  and the aggregation number  $N_{aggregation}$   
 254 (number of copolymer molecules per nanostructure). Assuming that all the copolymer lies inside the  
 255 micellar objects, an upper bound of the aggregation number was estimated as:

$$256 \quad N_{aggregation} = \frac{w N_a \rho_s}{M_n N_s} \quad Eq. 1$$

257 where  $w$  is the amount of copolymer (wt%) and  $N_a = 6.02 \cdot 10^{23} \text{ mol}^{-1}$  the Avogadro's number,  $M_n$   
 258 number average molar mass.

259 **Table 2.** Characteristics of PMMA/10 wt% MAM solid precursors.

Solid sample ID	Nanostructure density $N_s$ (objects.cm <sup>-3</sup> )	Nanostructure average diameter $\bar{D}_s$ (nm)	Density of the solid blend $\rho_s$ (g.cm <sup>-3</sup> )	Predicted aggregation number $N_{aggregation}$
PMMA/10 wt% MAM	$2.4 \cdot 10^{14} \pm 0.2 \cdot 10^{14}$	$68 \pm 8$	$1.19 \pm 0.07$	3700

260 Compared to the literature, the micellar objects average diameter is consistent with previous  
261 determinations. Nevertheless, the number density of  $2.4 \cdot 10^{14}$  objects.cm<sup>-3</sup> seems an insufficient  
262 nucleating density to provide true nano foams (requiring an order of magnitude of  $10^{15}$  to  
263  $10^{16}$  objects.cm<sup>-3</sup> [38]).

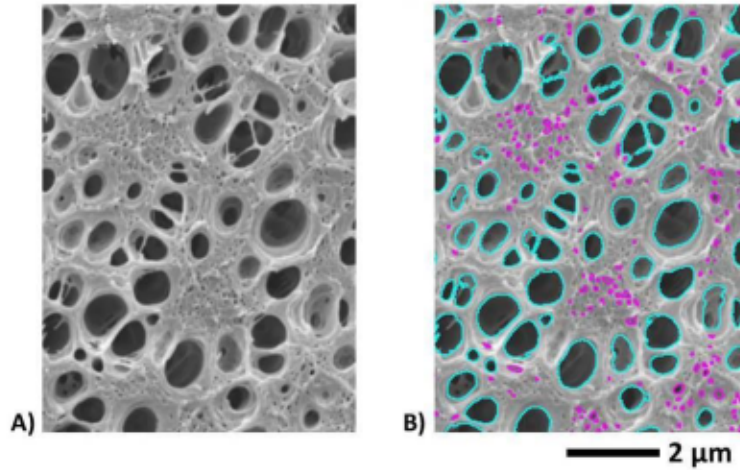
264 • PMMA and PMMA/10 wt% MAM foams: SEM observation

265 PMMA and PMMA/10 wt% MAM foam structures were observed on micrographs acquired with an  
266 environmental scanning electron microscope (E-SEM), a Quanta FEG 250 from FEI/ThermoFisher.  
267 Before observation, the foamed samples were frozen in liquid nitrogen, fractured (perpendicularly to  
268 the height) and sputter-coated with a thin layer of gold. All samples were imaged at low acceleration  
269 voltage (< 5 keV) and current (a few pA to a few tens of pA) (not to damage the foam structure with  
270 the primary electron beam). Images were formed by collecting the secondary electron (SE) emission.  
271 In this situation, contrast is said topographical and is made of three contributions: the inclination  
272 contrast, the shading contrast and the ridge contrast. Each sample was imaged at several  
273 magnifications (from X100 to X100 000). Figure 3.A illustrates over a local area the structure of a  
274 foam sample produced from the 90/10 PMMA/MAM blend at a saturation temperature of 60 °C, and  
275 a pressure drop rate of 0.3 MPa.s<sup>-1</sup>.

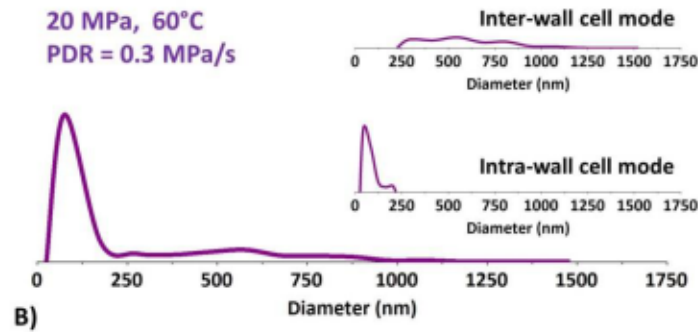
276 • Image analysis of SEM image

277 In micrographs formed in secondary electron mode, both shading and ridge contrasts promote  
278 darker foam cells than the polymeric background solid lattice. Yet, dependence of the secondary  
279 emission upon the incident angle of the primary electron beam (inclination contrast) may work  
280 locally *the other way around*, depending on the local geometry of the sample. Thus, there is again a  
281 need to further increase contrast in order to develop a sound automatic method for the  
282 determination of the cell size distribution. We took again advantage of the nonlinear directional  
283 diffusive filter described earlier to reach a suitable level of (enhanced) contrast. After this contrast  
284 augmentation, the segmentation of smooth and darker foam cells standing out from a brighter solid  
285 lattice could be accomplished via a simple threshold. The object sets segmented thereby, like the one  
286 illustrated in Figure 3.B, were suited for the automatic determination of the object diameter  
287 statistical distribution (Figure 4), the diameter of every object being derived from measurement of its  
288 perimeter.

289



290  
 291 **Figure 3. A)** Cellular structure produced from a PMMA/10 wt% MAM blend saturated with  $scCO_2$  at 60 °C and  
 292 then foamed in one-step batch-foaming with a pressure release rate of  $0.3 \text{ MPa}\cdot\text{s}^{-1}$ . **B)** The segmented object set  
 293 (cell set) includes inter skeletal pores (in cyan) and intra skeletal pores (in magenta).



294  
 295 **Figure 4.** Cell size distribution of the foam sample locally illustrated in Figure 3. The vertical full scale is set to  
 296 the highest cell % of the frequency histogram. The foam sample shows two scales of porosity (Figure 3). The  
 297 intra- and inter-wall cell size modes of the global (bimodal) size distribution (lower curve) were further specified  
 298 by filtering the segmented object set (cell set). Filtering consisted in removing those objects from an object set  
 299 whose filter size attribute (e.g. object diameter or area) fell outside a specified range. The chosen object size  
 300 attribute threshold value was that one which partitioned unequivocally the cell set in two classes of porosity:  
 301 small-sized intra-wall cells (in magenta) versus much larger inter-wall cells (in cyan) (Figure 3).

302 Several important characteristics were derived from the cell size distributions including the cell  
 303 number density ( $N_{cell}$ ,  $\text{cell}\cdot\text{cm}^{-3}$ ), the cell nucleation density ( $N_0$ ,  $\text{nuclei}\cdot\text{cm}^{-3}$ ) and the mean cell size  
 304 ( $\bar{D}_{cell}$ ). The cell number density in the porous material ( $N_{cell}$ ) was calculated using Equation (2).

305 
$$N_{cell} = \left(\frac{m}{A}\right)^{3/2} \quad \text{Eq. 2}$$

306 where  $m$  is the number of cells segmented in an image (collection of images) and  $A$  is the area of the  
 307 digital image (collection of digital images) in  $\text{cm}^2$ .

308 The cell nucleation density in the foamed material ( $N_0$ ) represents the number of pores formed per  
 309 cubic centimeter of the unfoamed dense blend precursor making implicitly the hypothesis that there  
 310 is no coalescence during the stabilization of the foam structure.  $N_0$  was calculated using Equation (3).

311 
$$N_0 = N_{cell} \times \frac{\rho_s}{\rho_f} \quad Eq.3$$

312  $N_0$  can be paralleled to the micellar objects density ( $N_s$ ) measured in the dense blend precursor.  
313 Those values should be ideally as close as possible.

314 SEM images at different scales and their quantitative analysis revealed two scales of pores in several  
315 of the foams produced from the 90/10 PMMA/MAM blend *cf* e.g. Figure 3 namely, inter-skeletal  
316 micropores (voids separated by cell walls as defined by Kaneko et al. in a general review on solid  
317 porous materials [39]) and intra-skeletal much smaller nanopores, located inside the cell walls. In this  
318 instance three average diameters were calculated:  $\bar{D}_{cell}$  the global mean cell diameter,  
319  $\bar{D}_{inter-wall\ cell}$  the inter skeletal pore mean diameter and  $\bar{D}_{intra-wall\ cell}$  the intra skeletal pore  
320 mean diameter. When intra skeletal pores are present,  $\bar{D}_{cell}$  contains information (weighted  
321 average) from  $\bar{D}_{inter-wall\ cell}$  and  $\bar{D}_{intra-wall\ cell}$ ; while  $\bar{D}_{cell} \equiv \bar{D}_{inter-wall\ cell}$  when there is no  
322 intra skeletal pores. The size distributions (including the inter wall and intra wall cell modes in case of  
323 bimodal distribution *cf* e.g. Figure 4) of all studied foam samples are provided and discussed in the  
324 next section.

325

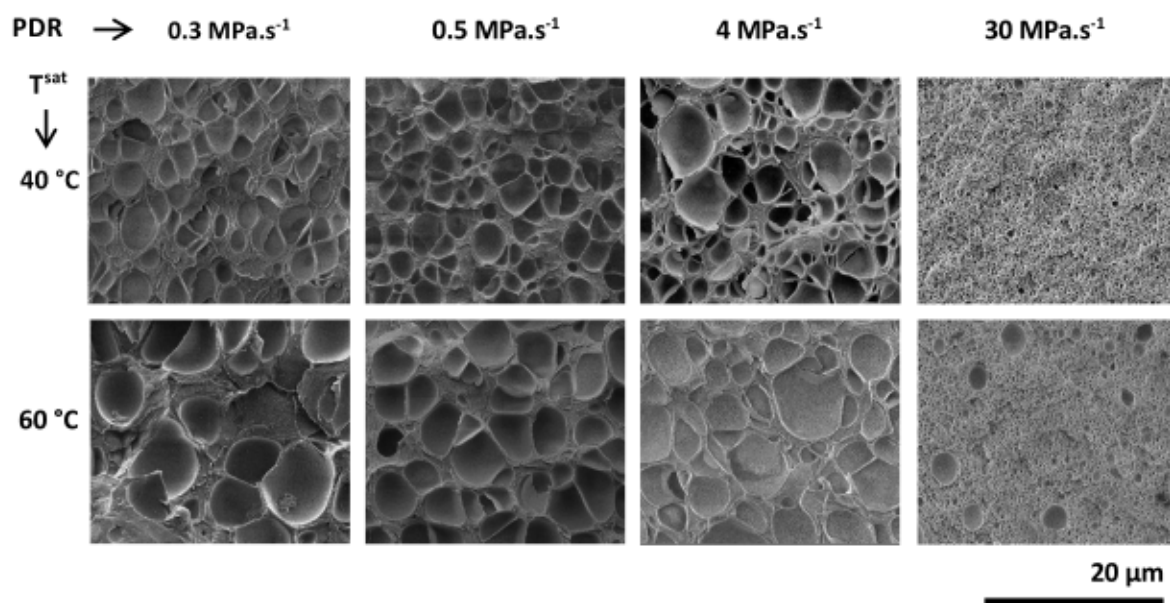
### 326 **3. Results and discussion**

#### 327 **3.1 Porous structures after one-step batch foaming (SEM Imaging)**

328 This section (3.1) describes qualitatively the different morphologies observed on SEM micrographs  
329 and outlines general trends. The next section (3.2) deals with the quantification of the structural  
330 information contained in the SEM micrographs.

##### 331 **3.1.1 PMMA foam structures**

332 Neat PMMA samples were foamed at PDR ranging from 0.3 MPa.s<sup>-1</sup> to 30 MPa.s<sup>-1</sup>. The influence of  
333 the saturation temperature and the PDR on the structure of the final PMMA foams is illustrated in  
334 Figure 5.



335

336 **Figure 5.** SEM images of neat PMMA saturated at either 40 °C or 60 °C ( $P^{sat} = 20$  MPa or 30 MPa) at a PDR  
 337 ranging from 0.3 MPa.s<sup>-1</sup> to 30 MPa.s<sup>-1</sup> (in a one-step batch foaming process)

338

339 At a fixed saturation temperature (either 40 °C or 60 °C), PMMA foamed at low to moderate PDR (*i.e.*  
 340 between 0.3 MPa.s<sup>-1</sup> and 4 MPa.s<sup>-1</sup>) are comparable. In other words, at a given temperature, the  
 341 foam cell size is not significantly influenced by the PDR value (Figure 5). Although the foam cells of  
 342 the samples scCO<sub>2</sub>-saturated at 40 °C appear a little smaller than those of the samples saturated at  
 343 60 °C, the cell dimension remains in the same order of magnitude at low to moderate PDR.

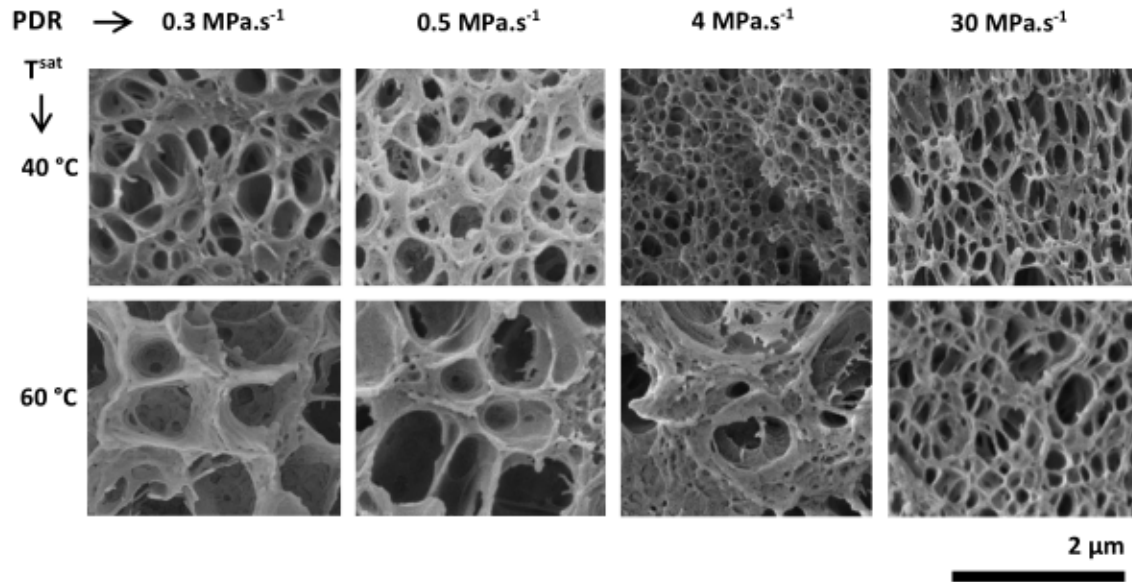
344 Only a high PDR of 30 MPa.s<sup>-1</sup> induces a true change towards much smaller cells. Moreover, the  
 345 sample foamed at 30 MPa.s<sup>-1</sup> after a saturation at 60 °C contains two types of porosities, while the  
 346 sample saturated at 40 °C is monomodal (only small pores).

347 As a first global summary for PMMA foams, the cell dimension is mainly governed by the saturation  
 348 temperature at low to moderate PDR, while cell dimension is principally governed by PDR at  
 349 30 MPa.s<sup>-1</sup>.

350

### 351 3.1.2 PMMA/10 wt% MAM foam structures

352 PMMA/10 wt% MAM blend samples were foamed in the same conditions as for neat PMMA (Figure  
 353 6). As observed in the case of PMMA, saturation temperature and PDR are competing to determine  
 354 the PMMA/10 wt% MAM final foam structure.



355

356 **Figure 6.** SEM images of PMMA/10 wt% MAM blend foamed after saturation at 40 °C and 60 °C ( $P^{sat} = 20$  MPa  
 357 or 30 MPa) using a PDR ranging from 0.3 MPa.s<sup>-1</sup> to 30 MPa.s<sup>-1</sup> (in one-step batch foaming process).

358

359 At fixed temperature, PMMA/10 wt% MAM samples foamed at low PDR (0.3 to 0.5 MPa.s<sup>-1</sup>) are not  
 360 significantly affected by the PDR value (Figure 6). But, over that PDR range, the scCO<sub>2</sub> saturation  
 361 temperature plays a more important role upon the inter-wall cell size: the lower the saturation  
 362 temperature is, the smaller is the inter-wall cell size.

363 At the moderate PDR of 4 MPa.s<sup>-1</sup>, both the saturation temperature and the PDR impact cell size. At  
 364 40 °C, the 4 MPa.s<sup>-1</sup> PDR leads to a much smaller cell size than at lower PDR, while at 60 °C, the inter-  
 365 wall cell size is still comparable to that observed at lower PDR.

366 Samples foamed at the highest PDR (30 MPa.s<sup>-1</sup>) contain small cells of the same size independently of  
 367 the saturation temperature, which no longer impacts the final foam structure.

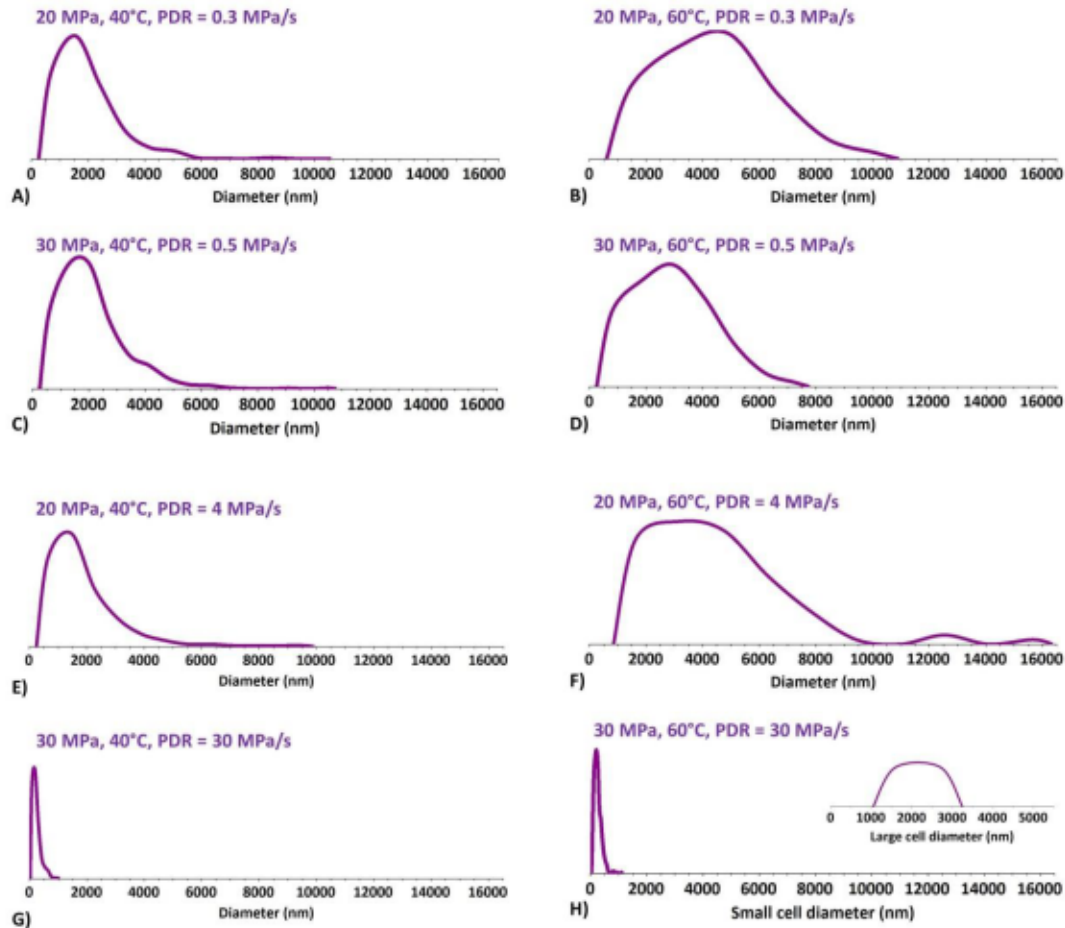
368 Whatever the thermodynamic conditions are ( $P^{sat}$ ,  $T^{sat}$ ,  $t^{sat}$ , PDR), the addition of MAM in PMMA  
 369 systematically induces smaller porosity dimensions than in neat PMMA foams (note that Figure 6 is  
 370 shown at a scale ten times smaller than in Figure 5). This trend of cell size reduction, already  
 371 reported in the literature, can be explained in terms of CO<sub>2</sub> local concentration, heterogeneous  
 372 nucleation and increased cell density [7],[8],[9],[10],[11].

373 As a first conclusion, in a one-step solid-state foaming, if the material formulation always influences  
 374 the foam structure, a high PDR acts as a supplementary beneficial variable to efficiently achieve the  
 375 targeted cell size reduction as observed by SEM imaging.

376

### 3.2 Structural quantification by image analysis

377 This section presents the structural quantification of PMMA and PMMA/10 wt% MAM foams by  
 378 image analysis. For each foam sample, several SEM images captured at various magnifications were  
 379 automatically segmented according to the procedure presented in *Section 2.4* in order to determine  
 380 a representative cell size statistical distribution *cf* e.g. Figure 7 for neat PMMA.



381 **Figure 7.** Cell size distributions of the foams produced from neat PMMA. As discussed further below, the sample  
 382 saturated at 60°C and foamed using a PDR of 30 MPa.s<sup>-1</sup> is bimodal (see Figure 5). The two modes (small vs.  
 383 large size) of the cell size distribution were specified relying on a filtering procedure similar to that described in  
 384 the legend of Figure 4.

385

386 Morphological characteristics of the foams from neat PMMA including average cell size, cell number  
 387 density and nuclei number density were derived from the calculated cell size distributions in Figure 7.  
 388 These characteristics are compiled in Table 3.

389

390 **Table 3.** Neat PMMA foams morphological characteristics determined by quantitative image analysis.

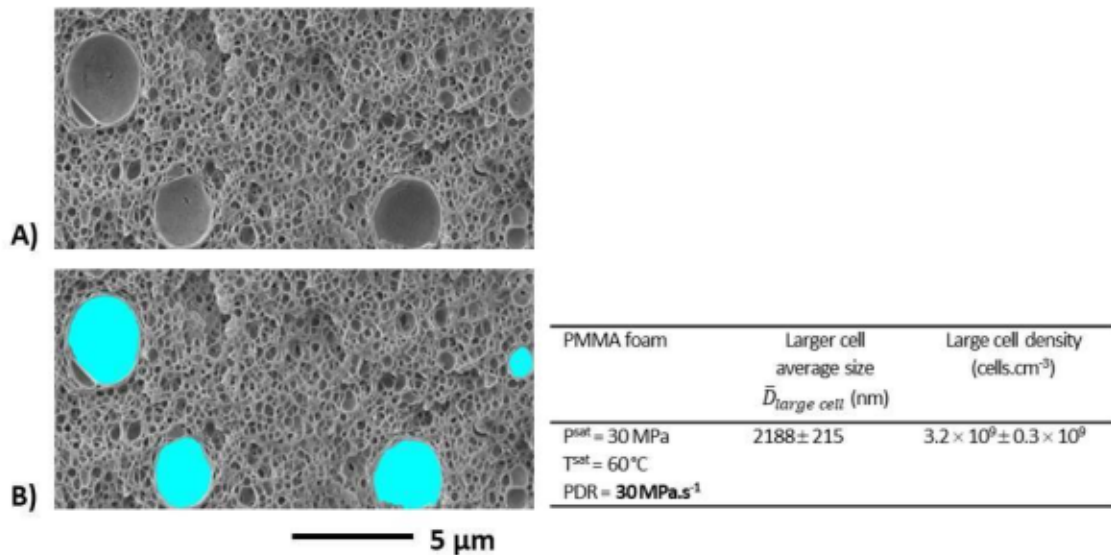
PMMA Foam	Foam density $\rho_f$ (g.cm <sup>-3</sup> )	Average cell size $\bar{D}_{cell}$ (nm)	Cell density $N_{cell}$ (cells.cm <sup>-3</sup> )	Nuclei density $N_0 = N_{cell} \times \rho_s / \rho_f$ (nuclei.cm <sup>-3</sup> )
$P^{sat} = 20$ MPa $T^{sat} = 40$ °C PDR = 0.3 MPa.s <sup>-1</sup>	$0.78 \pm 0.05$	$1900 \pm 46$	$3.2 \times 10^{10} \pm 0.6 \times 10^{10}$	$4.8 \times 10^{10} \pm 1.2 \times 10^{10}$

$P^{sat} = 20 \text{ MPa}$ $T^{sat} = 60 \text{ }^\circ\text{C}$ <b>PDR = 0.3 MPa.s<sup>-1</sup></b>	$0.81 \pm 0.03$	$4340 \pm 119$	$4.2 \times 10^9 \pm 0.3 \times 10^9$	$6.1 \times 10^9 \pm 0.7 \times 10^9$
$P^{sat} = 30 \text{ MPa}$ $T^{sat} = 40 \text{ }^\circ\text{C}$ <b>PDR = 0.5 MPa.s<sup>-1</sup></b>	$0.76 \pm 0.09$	$2070 \pm 43$	$3.3 \times 10^{10} \pm 0.1 \times 10^{10}$	$5.1 \times 10^{10} \pm 0.8 \times 10^{10}$
$P^{sat} = 30 \text{ MPa}$ $T^{sat} = 60 \text{ }^\circ\text{C}$ <b>PDR = 0.5 MPa.s<sup>-1</sup></b>	$0.6 \pm 0.02$	$2892 \pm 60$	$1.6 \times 10^{10} \pm 0.2 \times 10^{10}$	$3.1 \times 10^{10} \pm 0.5 \times 10^{10}$
$P^{sat} = 20 \text{ MPa}$ $T^{sat} = 40 \text{ }^\circ\text{C}$ <b>PDR = 4 MPa.s<sup>-1</sup></b>	$0.64 \pm 0.01$	$1867 \pm 61$	$5.9 \times 10^{10} \pm 2.0 \times 10^{10}$	$1.1 \times 10^{11} \pm 0.4 \times 10^{11}$
$P^{sat} = 20 \text{ MPa}$ $T^{sat} = 60 \text{ }^\circ\text{C}$ <b>PDR = 4 MPa.s<sup>-1</sup></b>	$0.52 \pm 0.003$	$4373 \pm 299$	$4.9 \times 10^9 \pm 2.0 \times 10^9$	$1.1 \times 10^{10} \pm 0.5 \times 10^{10}$
$P^{sat} = 30 \text{ MPa}$ $T^{sat} = 40 \text{ }^\circ\text{C}$ <b>PDR = 30 MPa.s<sup>-1</sup></b>	$0.53 \pm 0.003$	$231 \pm 10$	$2.1 \times 10^{13} \pm 0.2 \times 10^{13}$	$4.6 \times 10^{13} \pm 0.5 \times 10^{13}$
$P^{sat} = 30 \text{ MPa}$ $T^{sat} = 60 \text{ }^\circ\text{C}$ <b>PDR = 30 MPa.s<sup>-1</sup></b>	$0.6 \pm 0.01$	$250 \pm 8$	$1.8 \times 10^{13} \pm 0.1 \times 10^{13}$	$3.5 \times 10^{13} \pm 0.1 \times 10^{13}$

391

392 The PMMA foams imaged in Figure 5 are essentially « homogeneous » i.e. their cell size distributions  
393 (Figure 7) are monomodal, apart from one sample saturated at 60 °C and foamed at 30 MPa.s<sup>-1</sup>. This  
394 sample shows two porosity populations: numerous small-sized cells and far less numerous much  
395 larger cells, both dispersed in the solid lattice. For this foam, the mean cell size listed in Table 3 (last  
396 row) is the weighted average of the two populations. Aided by the marked difference in size of the  
397 two populations, the average size and number density of the larger cells were assessed (Figure 8) by  
398 applying a connected filter (an opening by reconstruction) to the segmented/binarized image. More  
399 precisely, a large-sized morphological erosion followed by a geodesic dilation of infinite size, was  
400 used to discard the small cell population (Figure 8.B). This discrete (in number) large cell population  
401 shall be paralleled to the systematic large cells observed at 60 °C at lower PDR (0.3 to 4 MPa.s<sup>-1</sup>). In  
402 other words, in the case of homogenous nucleation, a PDR as high as 30 MPa.s<sup>-1</sup> is not high enough  
403 to suppress totally the impact of temperature upon the final foam structure. As mentioned earlier,  
404 the situation is different in the case of heterogeneous nucleation, where the saturation temperature  
405 no longer influences the final foam structure, which is only controlled by such a high PDR (30 MPa.s<sup>-1</sup>).  
406 <sup>1</sup>).

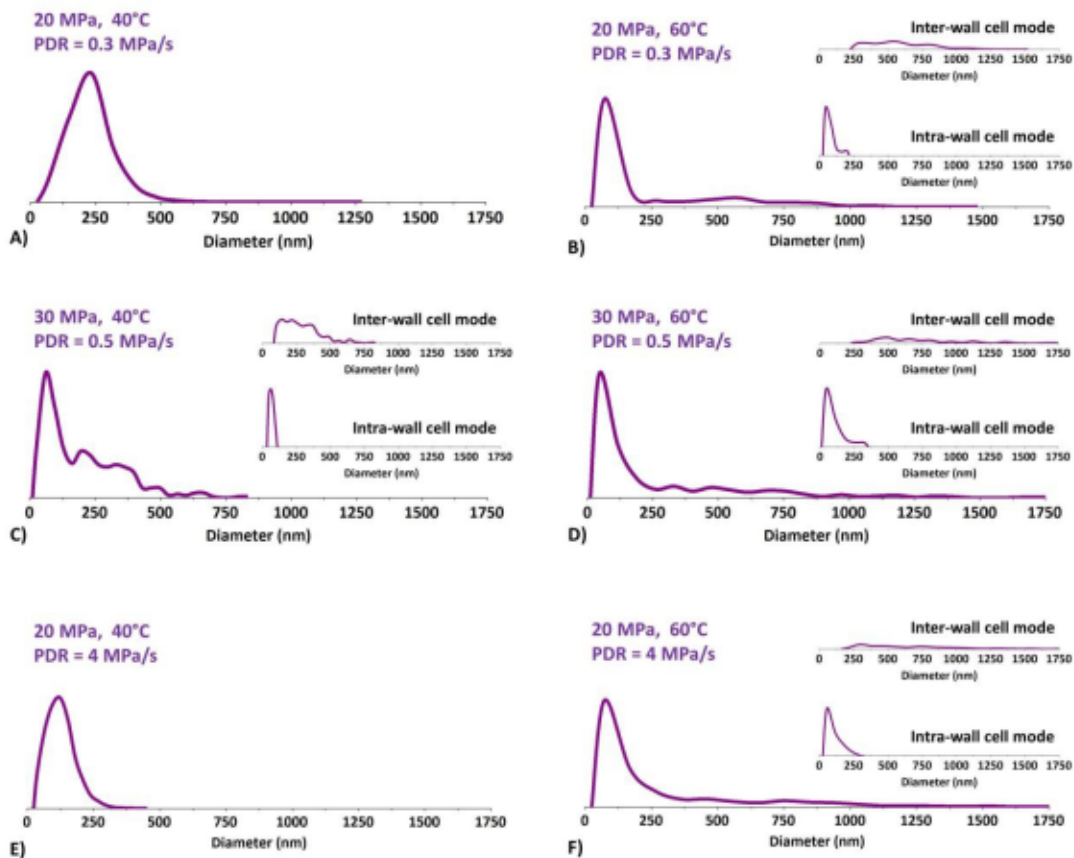


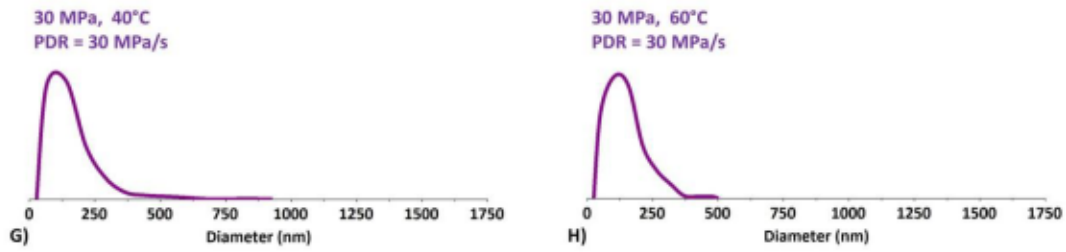


407

408 **Figure 8.** Local illustration of the segmentation (binarization) of the large cell population of the PMMA foam  
 409 saturated at 60 °C and foamed at a high PDR of 30 MPa.s<sup>-1</sup>.

410 Quite interestingly, PMMA/10 wt% MAM foams reveal a cell size bimodality in the majority of the  
 411 samples up to a PDR of 4 MPa.s<sup>-1</sup>. The cell size distributions (Figure 9) and associated morphological  
 412 characteristics (Table 4) were first determined considering all cells with no distinction.





413

414 **Figure 9.** Cell size distributions of the foams produced from 90/10 PMMA/MAM blends. Refer to Figure 4 for a  
 415 more complete legend.

416 Then, for bimodal samples, small porosities, referred to as intra skeletal pores, localized within locally  
 417 thicker struts and inter-cell walls were distinguished from inter skeletal pores. Using the image  
 418 analysis procedures described in Section 2.4 cf e.g. Figure 3.B, the two modes of the global cell size  
 419 distributions were determined (Figure 9). The mean diameter of each cell mode is given in Table 5  
 420 along with the inter-wall cell fraction (%).

421 **Table 4.** PMMA 10 wt% MAM foams morphological characteristics determined by quantitative image analysis.

PMMA/10 wt% MAM Foam	Foam density $\rho_f$ (g.cm <sup>-3</sup> )	Average cell size $\bar{D}_{cell}$ (nm)	Cell density $N_{cell}$ (cells.cm <sup>-3</sup> )	Nuclei density $N_0 = N_{cell} \times \rho_s / \rho_f$ (nuclei.cm <sup>-3</sup> )	Number of modes
$P^{s:st} = 20$ MPa $T^{s:st} = 40$ °C PDR = <b>0.3 MPa.s<sup>-1</sup></b>	$0.85 \pm 0.002$	$228 \pm 3$	$1.2 \times 10^{13} \pm 0.1 \times 10^{13}$	$1.7 \times 10^{13} \pm 0.2 \times 10^{13}$	Very slightly bimodal*
$P^{s:st} = 20$ MPa $T^{s:st} = 60$ °C PDR = <b>0.3 MPa.s<sup>-1</sup></b>	$0.67 \pm 0.01$	$206 \pm 5$	$1.0 \times 10^{13} \pm 0.2 \times 10^{13}$	$1.8 \times 10^{13} \pm 0.5 \times 10^{13}$	<b>Bimodal</b>
$P^{s:st} = 30$ MPa $T^{s:st} = 40$ °C PDR = <b>0.5 MPa.s<sup>-1</sup></b>	$0.66 \pm 0.01$	$193 \pm 4$	$3.6 \times 10^{13} \pm 0.2 \times 10^{13}$	$6.5 \times 10^{13} \pm 0.8 \times 10^{13}$	<b>Bimodal</b>
$P^{s:st} = 30$ MPa $T^{s:st} = 60$ °C PDR = <b>0.5 MPa.s<sup>-1</sup></b>	$0.53 \pm 0.01$	$239 \pm 57$	$1.5 \times 10^{13} \pm 0.5 \times 10^{13}$	$3.4 \times 10^{13} \pm 1.4 \times 10^{13}$	<b>Bimodal</b>
$P^{s:st} = 20$ MPa $T^{s:st} = 40$ °C PDR = <b>4 MPa.s<sup>-1</sup></b>	$0.59 \pm 0.01$	$126 \pm 4$	$5.2 \times 10^{13} \pm 2.1 \times 10^{13}$	$1.0 \times 10^{14} \pm 0.5 \times 10^{14}$	Monomodal
$P^{s:st} = 20$ MPa $T^{s:st} = 60$ °C PDR = <b>4 MPa.s<sup>-1</sup></b>	$0.52 \pm 0.02$	$260 \pm 20$	$1.4 \times 10^{13} \pm 0.4 \times 10^{13}$	$3.2 \times 10^{13} \pm 1.2 \times 10^{13}$	<b>Bimodal</b>
$P^{s:st} = 30$ MPa $T^{s:st} = 40$ °C PDR = <b>30 MPa.s<sup>-1</sup></b>	$0.52 \pm 0.004$	$152 \pm 6$	$7.9 \times 10^{13} \pm 0.6 \times 10^{13}$	$1.8 \times 10^{14} \pm 0.3 \times 10^{14}$	Monomodal
$P^{s:st} = 30$ MPa $T^{s:st} = 60$ °C PDR = <b>30 MPa.s<sup>-1</sup></b>	$0.51 \pm 0.001$	$143 \pm 3$	$9.3 \times 10^{13} \pm 1.3 \times 10^{13}$	$2.2 \times 10^{14} \pm 0.4 \times 10^{14}$	Monomodal

422 \*Foam samples produced at 40 °C and at the lowest pressure drop (0.3 MPa.s<sup>-1</sup>) were very locally typified by thick walls and struts  
 423 showing a discrete nano-scaled porosity. Such local areas being so few, those samples were considered as (essentially) monomodal.

424

425 **Table 5.** Some of the foams produced from 90/10 PMMA/MAM solid blend showed clearly two scales of  
 426 porosity i.e. nano-sized intra-wall cells versus micro-sized inter-wall cells. The inter-wall cell fraction was  
 427 calculated as the inter-cell number to total cell number.

PMMA/10 wt% MAM Foam	Average intra-wall cell size $\bar{D}_{intra-wall cell}$ (nm)	Average inter-wall cell size $\bar{D}_{inter-wall cell}$ (nm)	Inter-wall cell fraction (%)
----------------------	---	---	------------------------------

$P^{sat} = 20 \text{ MPa}$ $T^{sat} = 60 \text{ }^\circ\text{C}$ <b>PDR = 0.3 MPa.s<sup>-1</sup></b>	$76 \pm 4$	$572 \pm 6$	$24 \pm 1$
$P^{sat} = 30 \text{ MPa}$ $T^{sat} = 40 \text{ }^\circ\text{C}$ <b>PDR = 0.5 MPa.s<sup>-1</sup></b>	$65 \pm 5$	$277 \pm 3$	$60 \pm 1$
$P^{sat} = 30 \text{ MPa}$ $T^{sat} = 60 \text{ }^\circ\text{C}$ <b>PDR = 0.5 MPa.s<sup>-1</sup></b>	$95 \pm 4$	$671 \pm 18$	$25 \pm 9$
$P^{sat} = 20 \text{ MPa}$ $T^{sat} = 60 \text{ }^\circ\text{C}$ <b>PDR = 4 MPa.s<sup>-1</sup></b>	$95 \pm 4$	$658 \pm 21$	$29 \pm 2$

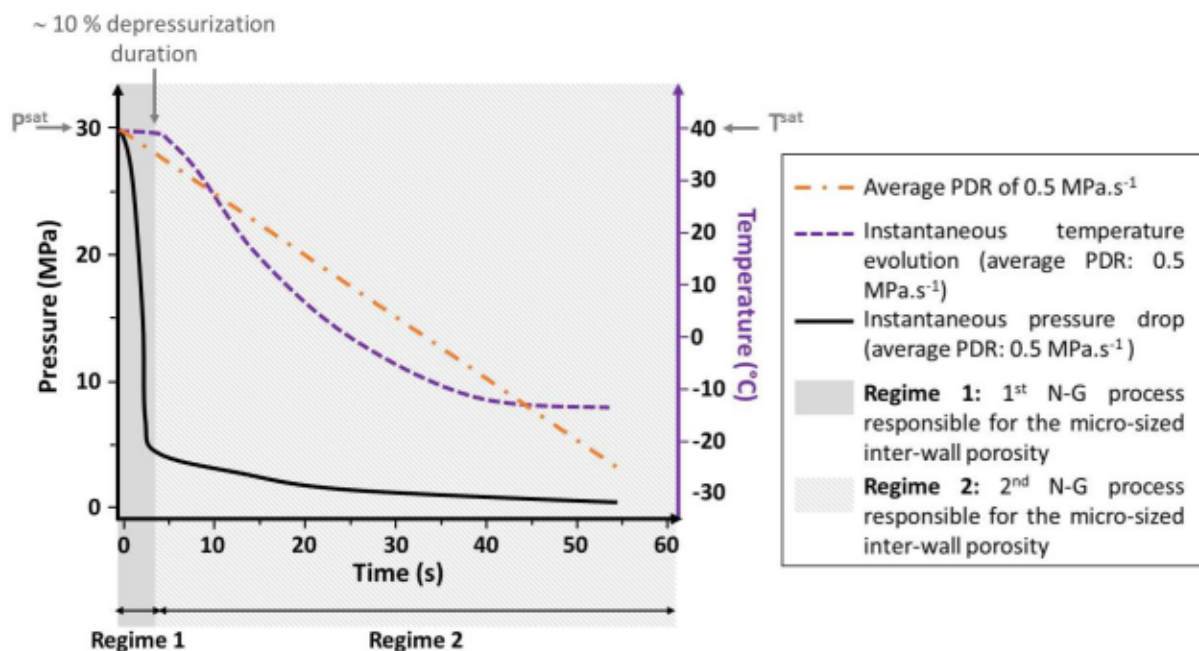
428

429 To the authors' knowledge, this is the first time such a double porosity is mentioned and quantified  
430 in PMMA/MAM acrylic micro-nano foams. The intra-skeletal pores appear as a reproducible sub  
431 population of nano pores with an average diameter ranging from 65 to 95 nm (Table 5). One  
432 candidate explanation may be that bimodal foams are formed by a twofold separation process *i.e.* two  
433 successive nucleation growth (N-G) processes. The first to occur is the expected or « classical » N-G process.  
434 The second N-G process would occur during a subsequent second foaming step inside still CO<sub>2</sub>-filled MAM  
435 micellar objects within the walls. In other words, residual CO<sub>2</sub> in micellar objects enables a second  
436 foaming and therefore, an intra skeletal true nano porosity. The reason for this may be that the PDR  
437 at which the pressure is released is actually uncontrolled and shall be regarded as an average PDR. To  
438 be more precise, a PDR of 0.5 MPa.s<sup>-1</sup> shall read as *an average* PDR (APDR) of 0.5 MPa.s<sup>-1</sup>. Using an  
439 APDR of 0.5 MPa.s<sup>-1</sup>, Pinto et al. [40] have measured the evolution of the instantaneous pressure and  
440 temperature during the depressurization stage (see Figure 8 of their paper). During the early stages  
441 (in the first seconds) of the depressurization, the system temperature stays around  $T^{sat}$ , while  
442 pressure decreases abruptly at an instantaneous rate far higher (by almost one order of magnitude)  
443 than the APDR (Figure 10). These early stages, typified by a high temperature and a high  
444 instantaneous PDR, originate the aforementioned first expected N-G process (whereby MAM  
445 nanostructures act as effective nucleants) responsible for the inter-skeletal cell population. After  
446 these early stages, the depressurization stage continues with a regular drop of the vessel  
447 temperature (down to values below  $RT$ ), while instantaneous pressure decreases (towards ambient  
448 pressure) at a much slower instantaneous rate, say one order of magnitude lower than the APDR  
449 (Figure 10). Where the first N-G process occurred, the effective glass transition temperature of the  
450 PMMA matrix  $T_g^{ef}$  has rapidly raised (due to CO<sub>2</sub> release during the first N-G process) and the system  
451 is therefore locally vitrified. The second N-G process responsible for the intra-skeletal nano-cell  
452 population is going to develop independently of the first N-G process, in local areas where residual  
453 CO<sub>2</sub> is still available. The slow instantaneous PDR, the effective temperature and the effective glass  
454 temperature are less favorable. Cell growth is thus minimized. Due to the very low effective

455 (instantaneous) PDR (Figure 10), only MAM nanostructures still concentrating the blowing agent can  
 456 nucleate [8]. Recall that using scCO<sub>2</sub> Arora et al. [41] produced bimodal foams from a polystyrene  
 457 precursor by reducing the pressure in stages. The marked slope change in instantaneous pressure  
 458 decrease that typifies the pressure release in our study (*i.e.* steep decrease during the early stage of  
 459 the depressurization followed by an almost asymptotic behavior down to ambient pressure (Figure  
 460 10)) shall be paralleled to a pressure reduction in stages.

461 *As always*, the depressurization step most likely induces local temperature and pressure gradients.  
 462 The information recorded by *punctual* pressure and temperature sensors, as schematically  
 463 represented in Figure 10, is by definition sensitive to such gradients. Yet, the main trends discussed  
 464 in this work *i.e.* *i)* a first regime typified by a nearly constant effective temperature  $T^{ef}(t)$  and an  
 465 instantaneous PDR  $\frac{dP(t)}{dt}$  one order of magnitude higher than the APDR and *ii)* a second regime  
 466 characterized by a regular drop of  $T^{ef}(t)$  and a pressure decrease  $\frac{dP(t)}{dt}$  one order of magnitude  
 467 smaller than the APDR, remain true at the sample-scale, irrespective of local gradients.

468 As the APDR is increased, the first N-G process implies more and more MAM nanostructures so that  
 469 ultimately (at 30 MPa.s<sup>-1</sup> in our work) there is no MAM nucleants left for a second N-G process.



470  
 471 **Figure 10.** Schematic representation of the instantaneous (true) pressure and temperature evolution during a  
 472 depressurization process of average PDR (APDR) equal to 0.5 MP.s<sup>-1</sup>. Modified from original experimental work  
 473 by Pinto et al. [40] using the same high-pressure vessel and the same operating conditions than in this study.

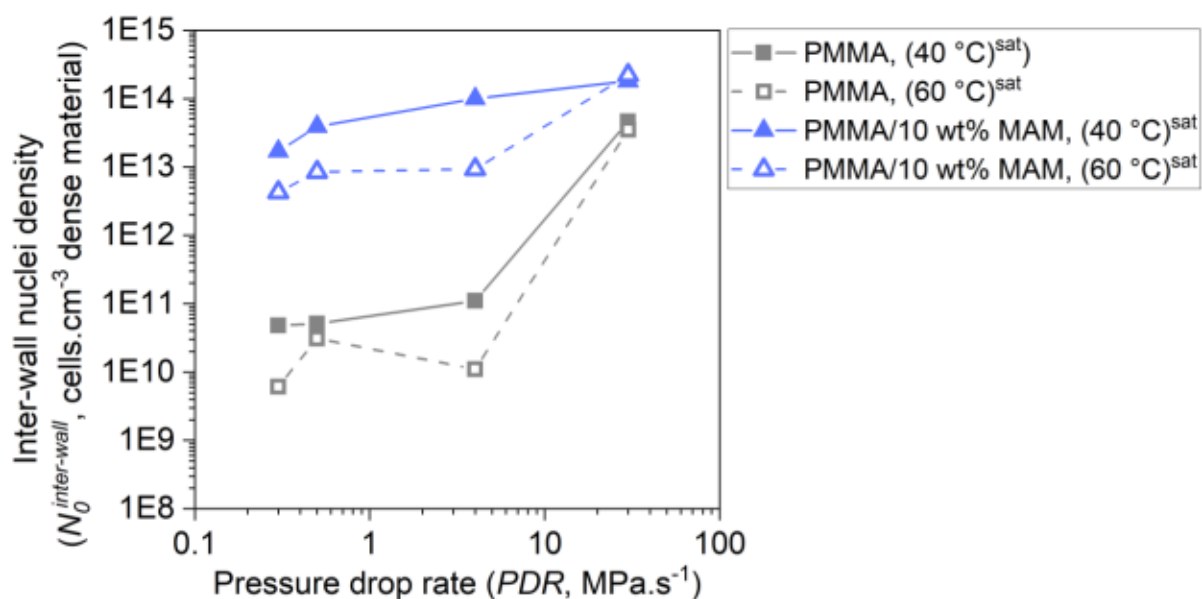
474

475 In our view, the bimodal blend foams observed in this study essentially when using an average PDR in  
 476 the range 0.3 – 4 MPa.s<sup>-1</sup> shall not be designated as « heterogeneous ». They should rather be  
 477 described as « doubly homogeneous ». Indeed, the dynamics of the vessel pressure and temperature  
 478 evolution during the depressurization step produces two N-G processes that develop in two  
 479 successive stages, independently of one another. In each N-G process, the block copolymer (BCP)  
 480 does homogenize the foam structure.

481

482 In Figure 11, the inter-wall nuclei density, noted  $N_0^{inter-wall}$  (see the legend of Figure 11), is plotted  
 483 as a function of the average PDR (APDR) using a bi logarithmic scale.  $N_0^{inter-wall}$  increases as the  
 484 APDR is incremented with a threshold effect at 4 MPa.s<sup>-1</sup>. The threshold effect is less marked in the  
 485 foams from 90/10 PMMA/MAM blend saturated at 40°C. The rise of  $N_0^{inter-wall}$  as the APDR is  
 486 increased is much smoother in the foams from PMMA/MAM than in the foams from neat PMMA.  
 487 This demonstrates again the homogenizing role of an organic BCP such as MAM, which triggers high  
 488 inter-wall nuclei densities even at low APDR. Using PS or PS/talc systems, Tammaro et al. [24] made  
 489 similar log-log plots in which the nuclei density linearly increases with APDR. The smoothing effect  
 490 observed with MAM organic additive is less pronounced with talc inorganic additive. This may be  
 491 related to the fact that in Tammaro et al. [24], the PS or PS/talc systems are in molten (flowing) state,  
 492 while our PMMA and PMMA/MAM systems are in a true (non-flowing) solid state.

493



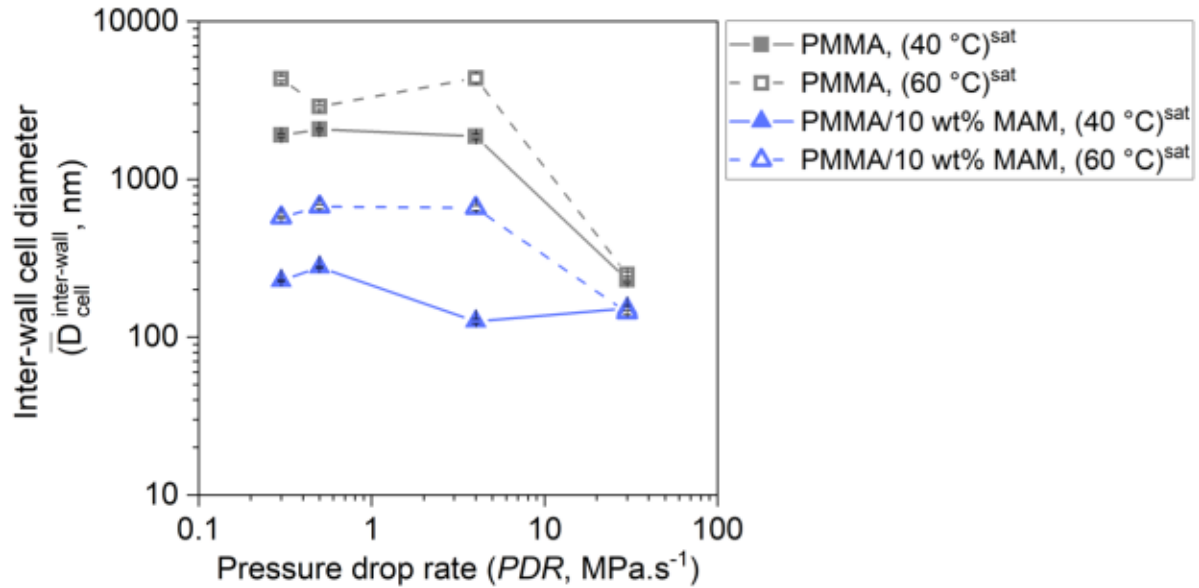
494

495 **Figure 11.** Inter-wall nuclei density (noted  $N_0^{inter-wall}$ ) as a function of average PDR (APDR) over 2 decades  
 496 ranging from 0.3 MPa.s<sup>-1</sup> to 30 MPa.s<sup>-1</sup> in a bi logarithmic scale. In monomodal samples, the inter-wall nuclei  
 497 density is the usual nuclei density referred to as  $N_0$  in Table 3 and Table 4. In bimodal foam samples (produced  
 498 from 90/10 PMMA/MAM blend),  $N_0^{inter-wall}$  is equal to  $N_0$  multiplied by the Inter-wall cell fraction (Table 5).  
 499 Saturation temperature is 40 °C or 60°C.

500

501 As for the inter-wall nuclei density, the inter-wall cell mean diameter ( $\bar{D}_{inter-wall\ cell}$ ) (Figure 12) is  
502 discriminated by APDR, saturation temperature and MAM presence.

503



504

505 **Figure 12.** Mean inter-wall cell size as a function of average PDR (APDR); saturation temperature 40 °C or 60 °C,  
506 PMMA and PMMA/10 wt% MAM. In monomodal foam samples, the inter-wall cell mean diameter  
507  $\bar{D}_{inter-wall\ cell}$  is the average cell diameter  $\bar{D}_{cell}$  listed in Table 3 and Table 4.

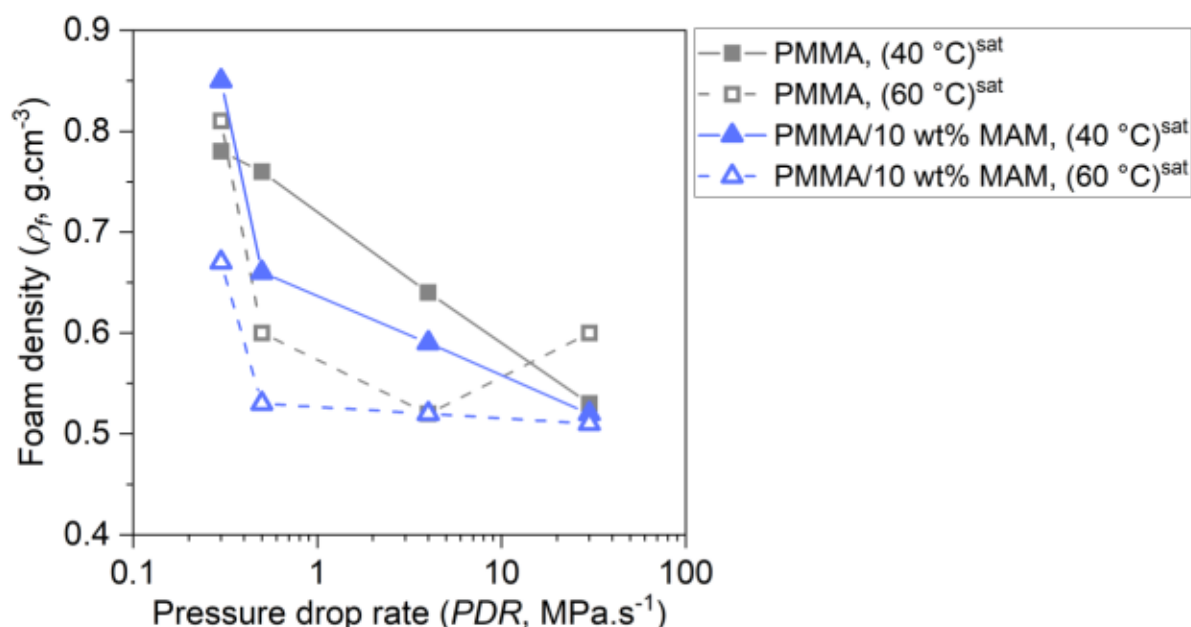
508

509 Over low to intermediate APDR (0.3 to 4 MPa.s<sup>-1</sup>), MAM enables a gain of 3 decades in  $N_0^{Inter-wall}$   
510 and a gain of one decade in  $\bar{D}_{inter-wall\ cell}$  at fixed saturation temperature (read from the bottom  
511 up Figures 11 and 12). Without MAM addition, the APDR is the main factor (the driving force)  
512 explaining the reduction by two orders of magnitude of the inter-wall cell diameter (read from left to  
513 right Figure 12). With MAM, the APDR appears of secondary importance in the reduction of the  
514 porosity dimensions (at a fixed temperature, the inter-wall cell diameter being reduced no more than  
515 by a factor two or three; read from left to right Figure 12).

516 At very high APDR (30 MPa.s<sup>-1</sup>), the inter-wall nuclei density (Figure 11) and the inter-wall cell  
517 diameter (Figure 12) both tend towards similar values without and with MAM addition. This  
518 convergence actually expresses different physical phenomena in the case of neat PMMA and in the  
519 case of the PMMA/MAM blend. In the former instance, the nuclei density is augmented by a physical  
520 phenomenon *i.e.* a steep pressure drop. In the latter case, nucleation is essentially promoted by the  
521 concentrating effect of MAM on scCO<sub>2</sub>.

522 To our knowledge, the above influence of the APDR upon the final foam structure has been only  
 523 reported in foaming experiments from the molten state, and not from the solid state as is the case  
 524 here.

525 As the APDR is increased, the density ( $\rho_f$ ) of our acrylic foams also decreases moderately in a  
 526 comparable manner regardless of the system and the saturation temperature (Figure 13). Although  
 527 the density remains rather high for foams ( $> 0.5 \text{ g.cm}^{-3}$ ), the concomitant decrease of cell diameter  
 528 (Figure 12) and  $\rho_f$  (Figure 13) in a one-step solid-state foaming of *amorphous* acrylics may be viewed  
 529 as a novelty to the best of our knowledge.



530  
 531 **Figure 13.** Evolution of the foam density with the average pressure drop rate (APDR) for neat PMMA and  
 532 PMMA/10 wt% MAM at two saturation temperatures (40°C and 60 °C).

533  
 534 Altogether, the trends contained in Figure 11, Figure 12 and Figure 13 can be attributed to the  
 535 interplay of several kinetics or kinetic factors whose respective effects cannot be unraveled:  
 536 evolution with time of  $T^{ef}$  and that of  $T_g^{ef}$ . More precisely, in a one-step procedure, foaming occurs  
 537 inside the autoclave and the sample effective temperature ( $T^{ef}$ ) is not controlled right after foaming  
 538 is triggered. Indeed, depressurization induces a rapid decrease of the sample temperature ( $T^{ef}$ ), the  
 539 kinetics of which is not controlled [6],[42],[43] (Figure 10). However, at a certain time of cells  
 540 development, the actual temperature ( $T^{ef}$ ) crosses inevitably the effective glass transition  
 541 temperature of the system ( $T_g^{ef}$ ), either up or down. At foaming,  $T_g^{ef}$  can be much lower than that of  
 542 neat PMMA before saturation [44]. When  $T^{ef} < T_g^{ef}$ , the cells are stabilized, this is the vitrification  
 543 kinetics. Other kinetics may be interfering: phase separation and growth kinetics, kinetics of gas

544 diffusion (either through the bulk matrix phase, but also through interfaces, once MAM nodules are  
545 created).

546 Among the above described numerous triggers for one-step foaming, a « low » CO<sub>2</sub> saturation  
547 temperature complying with the supercritical state ( $T^{sat} = 40\text{ °C}$  or  $60\text{ °C}$ ), a PMMA/MAM  
548 combination material formulation and a high APDR should be obviously preferred.

549

### 550 3.3 Implications for high thermal insulation

551 Microsized and nanosized porous polymer foams, in particular those produced using scCO<sub>2</sub> as physical  
552 foaming agent, are promising thermal insulation *green* materials [1],[2],[45],[46],[44],[47],[48] and for a  
553 large variety of applications, including clothing and footwear industries.

554 The conventional route towards improving thermal insulation of polymer foams (porous materials made of  
555 cells/walls/struts) generally consists in *i*) reducing cell size to the nanometer range in order to benefit from  
556 the Knudsen effect and *ii*) increasing the expansion ratio (or porosity) since air conductivity is far lower than  
557 that of the polymeric lattice [46], [47],[2],[49],[50],[51],[48],[52],[53]. This strategy aims at minimizing the  
558 conductive component of the foam effective conductivity  $k_{ef}$ . Yet, decreasing cell size and increasing the  
559 expansion ratio requires a high number density of cells leading to very thin struts and cell walls which,  
560 unfortunately, increase ultimately the radiative transmittivity [54],[55],[48],[52]. Such an increase in the  
561 radiative component of the foam effective conductivity  $k_{ef}$  often *erases* the performance gain (reduction of  
562 the conductive component of  $k_{ef}$ ) permitted by the Knudsen effect and a high gas fraction [48],[52].

563 Therefore, the lowered gas conductivity achieved thanks to the Knudsen effect successfully reduces the  
564 effective conductivity  $k_{ef}$  only in foams showing a relatively high density (e.g  $\sim 0.3\text{-}0.5\text{ g/cm}^3$ ) *i.e.* a rather  
565 low expansion ratio [52]. The monomodal foams produced in this work from PMMA/10 wt% MAM  
566 precursor at high APDR ( $30\text{ MPa}\cdot\text{s}^{-1}$ ) after scCO<sub>2</sub> saturation at  $40\text{ °C}$  or  $60\text{ °C}$  and at moderate APDR ( $4\text{ MPa}\cdot\text{s}^{-1}$ )  
567 after saturation at  $40\text{ °C}$  (Figure 6) exhibit nanosized alveolar cells ( $\bar{D}_{cell} < 150\text{ nm}$ ) and a somewhat high  
568 density ( $\sim 0.5\text{ g}\cdot\text{cm}^{-3}$ ) (table 4). According to the literature cited above and particularly in the line with  
569 Buahom et al. [48] and Pang et al. [52], these foams shall show a low effective thermal conductivity.

570 Using a comprehensive predictive model validated by published experimental data in the literature, Buahom  
571 et al. conclude that in low density monomodal foams, the optimal cell-size minimizing the radiative  
572 transmittivity (so that the lowered gas conductivity remains meaningful) lies in the micrometer range.

573 In our view, the bimodal foams produced in our work at low to moderate APDR ( $0.3\text{ MPa}\cdot\text{s}^{-1}$  to  $4\text{ MPa}\cdot\text{s}^{-1}$ )  
574 after scCO<sub>2</sub> saturation at  $40\text{ °C}$  and/or  $60\text{ °C}$  (Figure 6 and table 5) shall represent a potential innovative  
575 solution towards reducing drastically heat transfer. These bimodal samples show locally a porous solid



576 skeleton made up of thick walls and struts and including numerous well apart intra-skeleton nanopores (of a  
577 size comparable to that of the micellar nanostructures in the precursor). This locally thick skeleton  
578 encapsulates local domains of relatively high-expansion ratio. These local domains are formed either by  
579 several adjacent submicrometer-sized cells or reduce to a single submicrometer-sized cell (referred above as  
580 inter-wall pores). Within these local domains typified by a high porosity, a submicrometer cell size at which  
581 the Knudsen effect starts to take place, the (local) conductive thermal conduction shall be low. At the  
582 immediate periphery of these local domains, the larger amount of matter and the well apart nanopores  
583 within the thick skeleton shall lower transmittivity (radiative conduction) and the conductive solid  
584 conduction<sup>1</sup>, respectively. Heat transfer shall be further minimized by the higher tortuosity of the thick  
585 skeleton bordering local domains of higher expansion ratio [56],[57],[48]. In addition, the nanosized cells  
586 within the thick nanoporous skeleton shall enhance phonon scattering, which increases the solid thermal  
587 resistance thereby reducing the solid conductivity [58],[59],[60],[61].

588 Thus, in this series of bimodal acrylic foams, the benefit from the Knudsen effect within well expanded local  
589 domains showing porosity dimensions in the submicrometer range remains meaningful thanks to a locally  
590 poorly expanded nanoporous thick solid skeleton *encapsulating* these local domains and preventing  
591 radiative thermal conduction from overriding the conductive component at the sample scale.

592 This suggests that micro-nano bimodal foams may represent better candidates for improved thermal  
593 insulation than « all nanosized » foams.

594 The next step will be to measure the effective conductivity of these thermal insulator polymeric foams. Yet,  
595 as recently stressed by Sánchez-Calderón et al. [62], the accurate measurement of the thermal conductivity  
596 of micro-nanocellular polymers is quite a challenge which is beyond the scope of the current contribution.

597

#### 598 **4. Conclusion**

599 With the target of achieving micro-nano foams, this study principally addresses the combined  
600 beneficial effects of block copolymer (BCP) addition and high average pressure drop rate (APDR) in  
601 one-step solid-state batch scCO<sub>2</sub> foaming. Producing micro-nano foams is a multi-factorial issue,  
602 where numerous subtle parameters interplay and compete; one can quote the saturation conditions  
603 *i.e.*  $P^{sat}$  and  $T^{sat}$ , the material effective temperature during foaming  $T^{ef}(t)$ , the effective glass  
604 transition temperature of the plasticized system  $T_g^{ef}(t)$ , the APDR value, and the presence of block  
605 copolymer.

606 APDR and BCP are two key triggering factors. Either parameter may become prevalent for ruling the  
607 cell size and the overall density. Over the scrutinized range of saturation temperature (40 °C and 60

---

<sup>1</sup> Heat conduction in the solid is reduced by the significant Knudsen effect in well apart nanopores.

608 °C), the APDR is the main factor for significantly reducing cell size and increasing nuclei density in  
609 foams from neat PMMA. In the block copolymer approach, increasing the APDR appears of secondary  
610 importance as the targeted reduction of the porosity dimensions and augmentation of the nuclei  
611 density are essentially the consequence of the MAM presence. Yet, in this latter case, increasing the  
612 APDR still promotes the « efficiency » of BCP nucleants. In particular, a real efficient nucleation  
613 activity of MAM additive is observed at very high average APDR (30 MPa.s<sup>-1</sup>), leading to unimodal  
614 homogeneous distribution of tiny pores, typically 150 nm in diameter, in nearly nanosized foams.  
615 Next, in our saturation conditions ('low' temperature complying with the supercritical state for CO<sub>2</sub>), a  
616 high APDR tends to reduce also foam density (although in a moderate way, 0.8 down to 0.5 g.cm<sup>-3</sup>).  
617 Let us insist again on the fact that in the block copolymer approach, the average PDR (APDR) plays  
618 only 'a supporting role' in the final structure of the foam. More precisely, a APDR increment  
619 promotes the efficiency of the BCP nucleants. This interplay between BCP and APDR, combined with  
620 the underlying instantaneous dynamics  $dP/dt$  of the apparent average APDR  $\Delta P/\Delta t$ , which can be  
621 paralleled to a two-stage pressure reduction, can be used to produce bimodal foams where a truly  
622 intra-wall/intra-strut nanosized porosity is distinguished from the inter-wall micro-sized pores.  
623 Indeed, the evolution with time of the uncontrolled instantaneous depressurization rate  $dP/dt$   
624 (Figure 10) leads to two serial nucleation-growth (N-G) processes. Such two N-G processes develop  
625 independently of one another. As the (apparent) average PDR ( $\Delta P/\Delta t$ ) is higher (as nucleation occurs  
626 over a shorter time interval), the earliest N-G process is all the more important to the detriment of  
627 the second N-G process, which ends by running out at very high APDR 30 (MPa.s<sup>-1</sup>). Last we provide  
628 some arguments in favor of the superiority of these twofold porosity foams (rather than 'all nano  
629 foams') in applications requiring thermal insulation. Indeed, in these double porosity foams, benefit  
630 from the Knudsen effect, achieved within well expanded local domains showing submicrometer  
631 pores, would remain meaningful thanks to a locally poorly expanded nanoporous thick solid skeleton  
632 encapsulating these local domains. Such local encapsulation prevents radiative thermal conduction  
633 from overriding the conductive component at the sample scale.

634

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637

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