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1 FTIR *in situ* measurement of swelling and CO₂ sorption in acrylic polymers at high CO₂ pressures

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7

8 **Keywords:** FTIR microscopy, CO₂ foaming, PMMA, MAM, CO₂ sorption, swelling

9

10 **Abstract**

11 A FTIR (Fourier Transform Infrared) microscope combined to a CO₂ high-pressure cell has been used
12 to determine simultaneously the CO₂ uptake and the swelling of several acrylic polymer systems,
13 precursors of CO₂-foamed polymers (PMMA), a triblock copolymer (MAM) and a PMMA/10 wt%
14 MAM blend. Samples were isothermally saturated with supercritical CO₂ (scCO₂) up to high- CO₂
15 pressures (5, 10, 30 MPa) at 40 °C and 130 °C. The behavior upon pressure increase is indeed
16 different at the two temperatures in the three systems, showing either a linear or a plateau shape.
17 These two types of regimes are analyzed in view of literature. Addition of 10 wt% MAM copolymer
18 led to a significant increase of CO₂ uptake (23 % for neat PMMA to 42 % for the blend, 40 °C, 30
19 MPa). Such data are useful to further find out the best routes to produce low-density and
20 nanoporous polymer foams, using scCO₂ as foaming agent.

21

22

23

24 1. Introduction

25 In the large field of porous materials, foams have been fabricated for a long time following
26 various methods, either chemical [1],[2], or physical [3],[4],[5]. On the one hand, chemical foaming
27 requires the use of chemical blowing agents (CBA). Once thermally degraded or thanks to a chemical
28 reaction, this agent generates a gas responsible of the so-called chemical foaming. On the other
29 hand, it is possible to directly inject a gas (or a supercritical fluid) in a process to create porosities by
30 gas expansion during the depressurization. For a few years, this solution (physical foaming) has been
31 largely studied in order to replace some traditional CBA that tend to be forbidden by REACH
32 regulation (e.g. azodicarbonamide).

33 Supercritical carbon dioxide (scCO₂) has been mostly used as an available, cheap and non-toxic
34 physical foaming agent in many polymers [6],[7],[8],[9]. Moreover, its critical point is rather “low” (31
35 °C and 7.4 MPa) so it is quite easy to reach the CO₂ critical state and take advantage of the
36 combination of gaseous and liquid properties: good diffusivity and a good solvent capability [10],[11].

37 In order to evaluate the foamability of a polymer (or a polymer blend) in presence of scCO₂
38 different parameters have to be evidenced : the CO₂ ability to diffuse in and out of the polymer
39 under supercritical conditions, sorption, desorption and polymer swelling (dilatation). In this article,
40 we will both focus on CO₂ sorption and polymer (and blends) swelling during the saturation step
41 before foaming.

42 CO₂ sorption into polymers can be characterized by various methods or devices : gravimetric
43 method [12],[13], quartz microbalance (QCM) [14],[15],[16] or magnetic suspension balance (MSB)
44 [17],[18]. All of them consist in calculating the mass variation before and after CO₂ saturation but the
45 fast desorption of the sample induces some errors on the % mass CO₂ determination.

46 This CO₂ uptake can also be determined with spectra recorded thanks to Fourier transform
47 infrared (FTIR) microscopy [11],[19],[20],[21],[22]. As shown in this study, the use of a FTIR
48 microscope set-up with a high-pressure cell, is a way to simultaneously measure swelling and CO₂

49 sorption at high pressures and at the desired temperatures. This *in situ* method provides information
50 about the behavior of the studied materials facing the CO₂ saturation, under given conditions (P, T)
51 selected to mimic CO₂ saturation in a foaming process. For example, in a batch process (“solid state
52 foaming”, represented by a typical temperature of 40 °C) or a continuous process (“melt foaming”,
53 represented by a typical temperature of 130 °C) - e.g. CO₂ extrusion -, foaming requires to optimize
54 scCO₂ saturation at several pressures. In this study, swelling and CO₂ sorption with increasing P and T
55 of acrylic polymer systems are studied inside the spectroscopic cell, mimicking different processes
56 saturating conditions.

57 The final goal is to produce “nanofoams” by a continuous process namely extrusion foaming.
58 In acrylic systems CO₂ assisted extrusion (130 °C and 10 to 30 MPa) [23],[24] generally leads (at the
59 best) to micro cellular foams; whereas following a discontinuous process (batch foaming) in the same
60 pressure range but considerably lower temperatures (around 40 °C), it is proved to be easier to
61 obtain acrylic quasi nano foams [3]. Our study should help enhancing and optimizing conditions of
62 nano foaming. Foams, when reducing both cell size and density at the same time, are intended to
63 exhibit enhancement of several properties, such as high thermal insulation [25] or high performance
64 mechanical properties [26] (damping) or else useful for filtration [13].

65 The material’s choice is focused on an acrylic blend containing 90 wt% of poly(methyl
66 methacrylate), PMMA and 10 wt% of a triblock copolymer poly(methyl methacrylate)-co-poly(butyl
67 acrylate)-co- poly(methyl methacrylate), MAM (i.e. PMMA-PBA-PMMA, PBA is poly(butyl acrylate)).
68 This additive is more CO₂-philic than PMMA thanks to the butyl acrylate center block [27],[28],[29].
69 The neat PMMA matrix and neat MAM copolymer are also studied separately. Generally in the field
70 of polymer foams, these three acrylic polymers are considered as good CO₂-foamable candidates due
71 to their good affinity with CO₂ (thanks to the presence of the carbonyl groups), in comparison with
72 other kind of polymers [9].

73 Thus the present paper quantifies CO₂ sorption, swelling and identifies the trends when
 74 temperature and/or pressure increase ; especially in view of optimizing the CO₂ uptake in a short
 75 time, while maximizing expansion and controlling a high cell density.

76

77 2. Materials and Methods

78 2.1. Materials

79 Carbon dioxide N45 (purity 99 %) was supplied by Air Liquide. Pellets of poly(methyl methacrylate)
 80 (PMMA) and MAM (poly(methyl methacrylate)-co-poly(butyl acrylate)-co- poly(methyl methacrylate)
 81 triblock copolymer were kindly supplied by Arkema (Lacq, France). Details on the initial materials can
 82 be found in literature [27],[28],[30][4] and are summarized in Table 1.

83 For the preparation of the PMMA/10 wt% MAM blend, PMMA and MAM pellets, were first dried 4 h
 84 at 80 °C. Then the blend was compounded by CANOE (Pau, France) using a corotative twin screw
 85 extruder (Labtech $\varnothing = 26 \text{ mm}$, $L/D = 40$) with a temperature profile ranging from 250 to 230 °C at
 86 a screw speed of 300 rpm. Then, the blends were pelletized using a continuous cutting machine
 87 operating at the end of the line.

88 The PMMA, MAM and PMMA/10 wt% MAM thin films ($e \approx 0.5 \text{ mm}$; $L \approx 4 \text{ mm}$; $l \approx 1 \text{ mm}$) were
 89 made by dissolving pellets in tetrahydrofuran solvent (THF) at 60 °C and evaporated overnight at 85
 90 to 90 °C.

91 *Table 1: Characteristics of the polymers used*

Material	State at room temperature	M _n (g.mol ⁻¹)	M _w (g.mol ⁻¹)	Other characteristics	Density (g.cm ⁻³)	Aspect
PMMA V825T	glassy	43 000	83 000	use as	1.19	transparent
clear 101	amorphous solid			polymer matrix		
	rubbery center	82 000	128 000	used as an additive	1.03*	transparent

MAM M53	block +	triblock copolymer
	glassy end-blocks	PMMA-PBA-PMMA
		54 wt% PBA

92 * measured with a water pycnometer

93 **2.2. Infrared micro-spectroscopy**

94 **2.2.1. Experimental set-up (device, P, T, cell)**

95 A FTIR microscope (Perkin Elmer Spotlight 200) working in transfection mode was used to
 96 record infrared spectra of the studied materials. With this set-up it is possible to investigate the
 97 spectral range from 800 to 6500 cm^{-1} with a spatial resolution of 100 μm . Thanks to the microscope
 98 linked to the FTIR set-up, one can precisely focus the FTIR beam on the a specific part of the high-
 99 pressure cell (either in the sample or on a mirror as shown in Figure 1).

100 In order to maintain the sample in an area saturated with CO_2 at high pressure, it was placed
 101 between a mirror and a sapphire window constituting the high-pressure cell as shown in Figure 1.

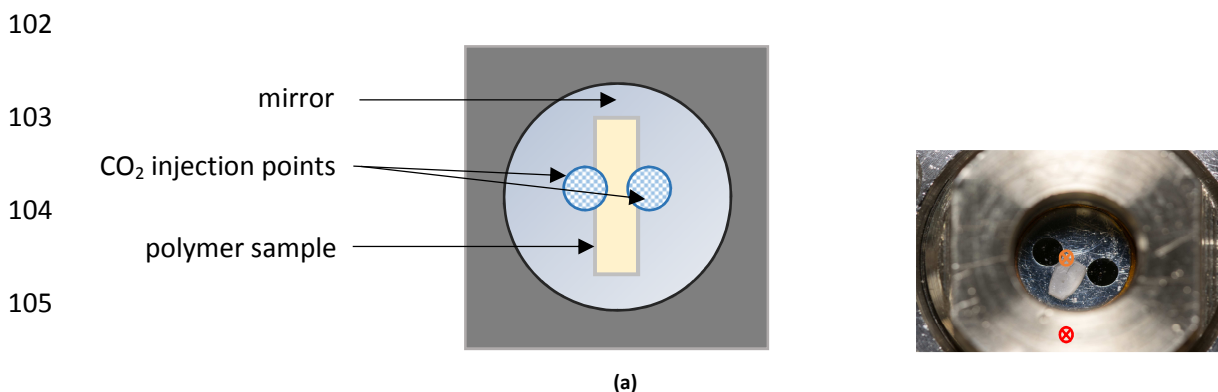


Figure 1: FTIR CO_2 high-pressure cell used to measure the polymer absorbance (red arrow location) or the CO_2 absorbance (orange arrow location); a) scheme of top view, b) photograph of a sample inside the high-pressure cell

106 This cell was CO_2 powered at the desired pressure (up to 40 MPa) thanks to a stainless-steel capillary
 107 linked to a hydraulic pressurizing system. The temperature in the cell was regulated thanks to 4
 108 cartridge heaters distributed all around the cell and was measured with 2 thermocouples
 109 respectively located close to the sample area and close to a cartridge heater (Figure 2). For each

110 pressure or temperature modification, a stabilization time was necessary and evaluated by recording
111 several consecutive spectra.

112 In this study the experiments were conducted at 40 °C or 130 °C and in a pressure range from 5 MPa
113 to 30 MPa.

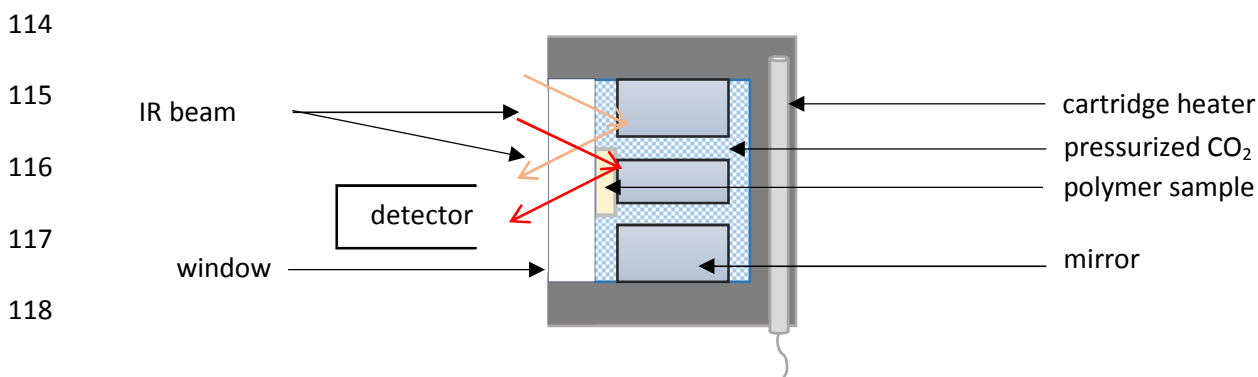


Figure 2: Experimental FTIR set-up

119

120

121 2.2.2. Experimental procedure

122 As shown in Figure 1, the thin polymer sample (about 0.5 mm) was centered between the
123 two CO₂ arrivals before being fixed between a stainless-steel polished mirror and the window of the
124 cell. Under these conditions, the CO₂ can diffuse inside the cell and saturate the studied sample.
125 Samples are allowed to swell on their non-constrained edges. Although in a batch configuration the
126 swelling is possible in all 3 dimensions (3D), we emphasize that the polymers under investigation are
127 isotropic in nature and we do not expect to have any influence on the swelling of the polymer even if
128 the polymer can swell in only 2 dimensions in our IR microscopy configuration. This expected
129 behavior was checked by Champeau et al. [21] on swelling and CO₂ sorption measurement in
130 Polyethylene Oxide (PEO). The results obtained using a 2D configuration with Infrared microscopy
131 were in a good agreement with literature data that were obtained under experimental conditions
132 where the polymer could swell in 3D configuration. Finally, some of the results obtained in this study

133 are found to be in a rather good agreement with literature data obtained in 3D configuration. The
134 discrepancies observed between the different set of data are mainly due to the experimental errors
135 that are inherent to the different methods used in the literature.

136 After sample positioning, the cell was heated up to the chosen temperature (40 °C or 130 °C). Once
137 the temperature was reached, a first spectrum was recorded without CO₂ (red location shown in
138 Figure 1). Then, CO₂ was injected at the desired pressure (5 – 10 – 20 – 30 MPa). During the pressure
139 stabilization a spectrum was recorded every 5 min to follow the CO₂ sorption in the material over
140 time.

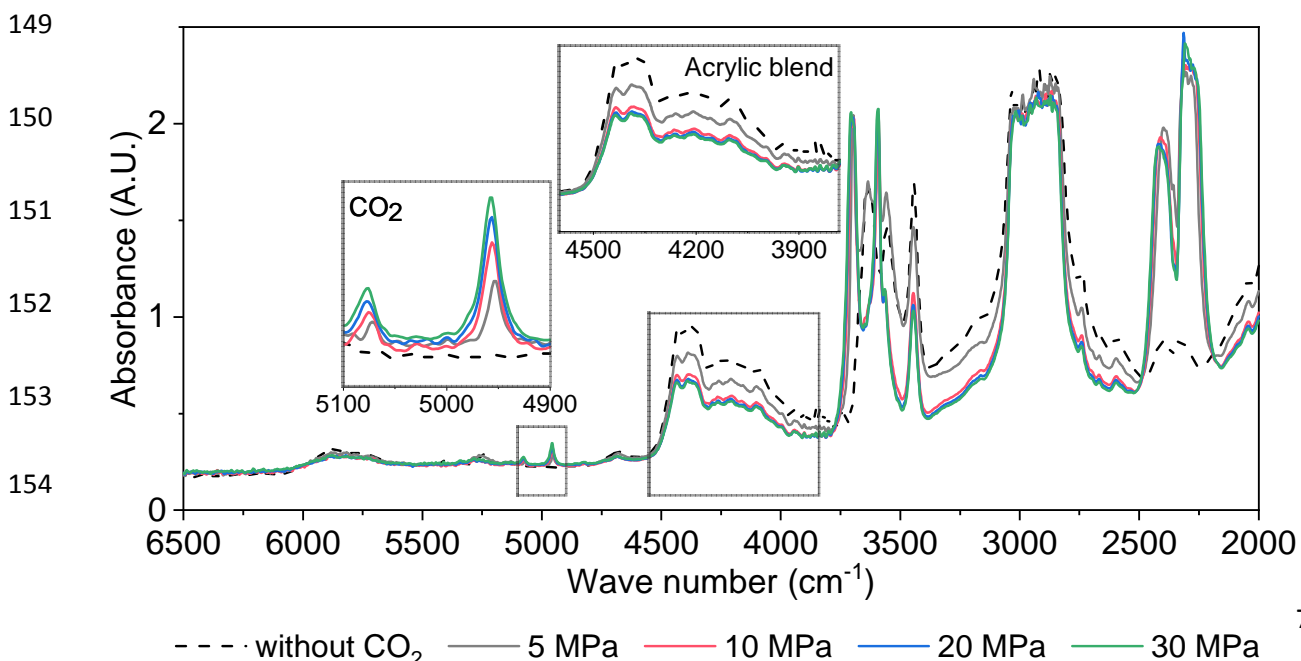
141 In this study, the equilibrium was generally reached after 30 to 90 min. At the end of the experiment,
142 samples were taken out of the cell as transparent pieces (unfoamed) or slightly white pieces (close to
143 the beginning of foaming when the cell was quickly depressurized).

144

145 2.3. Infrared spectra and data analysis

146 2.3.1. Near-infrared absorption spectra (i.e. 6500 – 2000 cm⁻¹)

147 For each sample, the infrared spectrum of the polymer or blend swelled by CO₂ was recorded at 40 °C
148 and at 130 °C for pressures ranging between 5 and 30 MPa.



155

156

157 *Figure 3: Infrared spectra of MAM at 40 °C without CO₂ and with CO₂ at P = 5-10-20-30 MPa, showing the spectral regions*
158 *used for quantitative analysis*

159 As shown in Figure 3, the CO₂ addition leads to spectra modifications. Different peaks associated with
160 fundamental and combination modes of CO₂ can be observed at different wavenumbers (see Table
161 2). In order to determine the CO₂ mass uptake and swelling of our polymers and blend both CO₂ and
162 polymers peaks were studied.

163 *Table 2: IR spectral contributions of CO₂ in the spectral range 2000-5100 cm⁻¹ [11]*

164	Peak wavenumber (cm ⁻¹)	CO ₂ contribution
165	2350	v ₃
166	3590	2v ₂ + v ₃
167	3695	v ₁ + v ₃
168	4950	v ₁ + 2v ₂ + v ₃
169	5030	2v ₁ + v ₃
	4850	4v ₂ + v ₃

170 v₁: symmetric stretching mode; v₂: CO₂ bending mode; v₃: antisymmetric stretching mode

171 For a quantitative analysis, we have selected non saturated (to avoid neither a too large absorbance,
172 e.g. A > 1, nor too weak absorbance, e.g. A < 0.1) significant peaks associated with the polymer and
173 the sorbed CO₂ at both 40 °C and 130 °C over a pressure range from 5 to 30 MPa. Then, these peaks
174 were integrated from different onsets and endsets, and several areas were calculated (more details
175 in Supporting Information). Finally, each set of values was used for the calculation of the CO₂
176 sorption, C_{CO₂} (mol.L⁻¹), the CO₂ mass uptake (%) and the swelling, S (%) (see details in paragraph
177 below). Considering all the sources of errors associated with our methodology (baseline correction,

178 molar extinction coefficient, thickness of the sample, signal to noise ratio, spectrometer stability), we
179 have evaluated a relative standard uncertainty of about $\pm 10\%$ on our results.

180

181 **2.3.2. Data analysis**

182 **2.3.2.1. Polymer swelling**

183 As proposed by Guadagno et al. [20], and shown by Flichy et al. [22], it is possible to
184 determine polymer swelling using the absorbance of a specific band of polymer before and after
185 exposure to CO_2 , according to the Beer-Lambert law:

$$A_0 = \varepsilon \cdot l \cdot C_0 \quad \#(1)$$

$$A = \varepsilon \cdot l \cdot C \quad \#(2)$$

186 with A_0 and A the absorbances before and after exposure to CO_2 ; ε the molar extinction coefficient
187 of the polymer band ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$); l the sample pathlength (cm); C and C_0 the concentrations of
188 polymer before and after exposure to CO_2 ($\text{mol}\cdot\text{L}^{-1}$).

189 If V is the volume of the polymer before exposure to gas and $V + \Delta V$ is the volume of the polymer
190 after exposure to the gas, one can write:

$$\frac{C_0}{C} = \frac{V + \Delta V}{V} \quad \#(3)$$

$$1 + \frac{\Delta V}{V} = 1 + S \quad \#(4)$$

191 By combining these equations (1) to (4), it is possible to determine the swelling (S) with the following
192 Equation (5) [22]:

$$S = \frac{A_0}{A} - 1 \quad \#(5)$$

193 For this study, the broad profile centered at about 4250 cm⁻¹ (combination of the C-H stretching and
194 bending modes) have been selected to determine the swelling of both 100 % MAM, at 40 and 130 °C
195 ; PMMA/10 wt% MAM at 40 and 130 °C and PMMA at 130 °C. The integrated absorbance was
196 calculated with a baseline fixed at 4600-3780 cm⁻¹.

197 For the 100 % PMMA sample at 40 °C, the 4250 cm⁻¹ centered profile was close to the saturation.
198 This is why we have used the broad band at about 6000 cm⁻¹ (overtone of the C-H stretching modes)
199 with a baseline fixed at 6260-5470 cm⁻¹ to determine the integrated absorbance and calculate the
200 polymer swelling. For the other samples, this band centered around 6000 cm⁻¹ was unusable due to
201 the too low signal strength.

202 **2.3.2.2. CO₂ sorption**

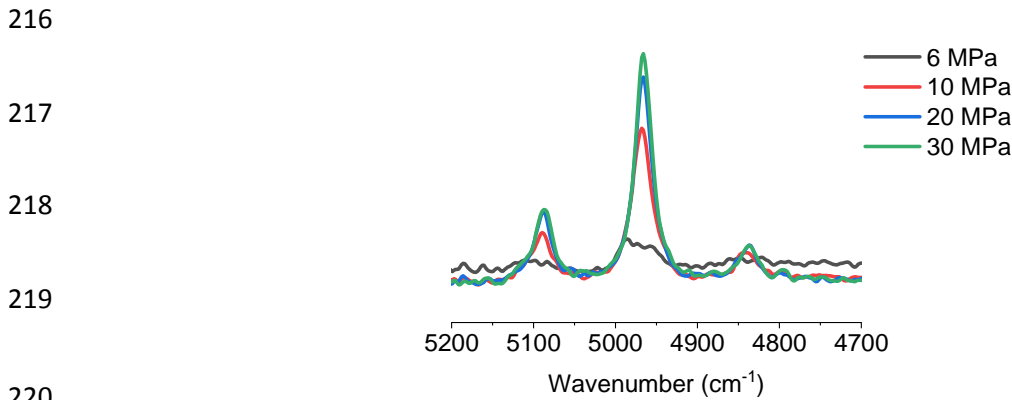
203 The Beer-Lambert law was applied to the CO₂ peaks in order to determine the concentration of CO₂
204 sorbed into the polymer. Equation (2) has been adapted to give CO₂ concentration in each polymer
205 and blend in g.cm⁻³:

$$C_{CO_2} = \frac{A}{\varepsilon \cdot l} \times M_{CO_2} \times 10^{-3} \#(6)$$

206 with A the absorbance of the CO₂ band; ε the molar extinction coefficient of the CO₂ band (L.mol⁻¹
207 ¹.cm⁻¹); l the sample pathlength (cm) and $M_{CO_2} = 44 \text{ g.mol}^{-1}$ the CO₂ molar mass.

208 In this study, the CO₂ band centered at 4950 cm⁻¹ was chosen. In this case, the molar extinction
209 coefficient considered is $\varepsilon_{4950\text{cm}^{-1}} = 0.25 \text{ L.mol}^{-1}.\text{cm}^{-1}$ [11],[21],[31]. The other peaks (2300;
210 3590; 3695; 4850 and 5030 cm⁻¹) were not used because they were either saturated or too weak and
211 produced large errors linked to the choice of baseline during the determination of both height and
212 integrated area.

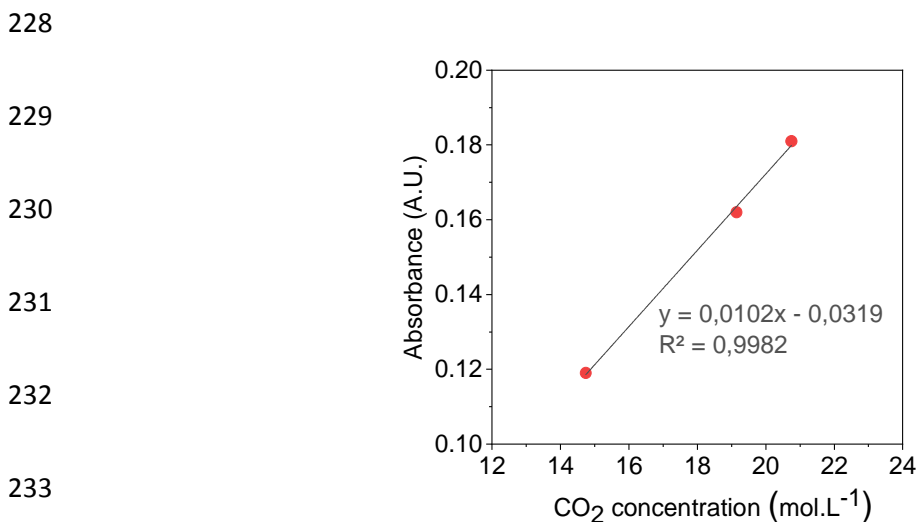
213 The sample thickness was evaluated thanks to spectra of neat CO₂ taken next to the polymer sample
214 in the cell (i.e. on a mirror, orange location represented in Figure 1), at 4 different pressures (Figure
215 4).



221 *Figure 4: Infrared spectra of CO₂ at T = 40 °C and various pressures ranging from P = 6 MPa (gaseous CO₂) to P = 10-20-30*
 222 *MPa (supercritical CO₂)*

223 Indeed, by plotting the absorbance (A_{CO_2}) of one of the characteristic peak of CO₂ (4950 cm⁻¹ in this
 224 study) as a function of CO₂ concentration in the cell (C_{CO_2}), it is possible to determine the pathlength
 225 (l) thanks to the following Beer-Lambert equation (Equation (7)). Because C_{CO_2} varies with the
 226 saturation pressure and temperature conditions, its value, for each couple of conditions, will be
 227 found in the literature tables [32].

$$l = \frac{A_{CO_2}}{\varepsilon \times C_{CO_2}} \#(7)$$



234 *Figure 5: Integrated peak of neat CO₂ absorbance (around 4950 cm⁻¹), as a function of CO₂ concentration in the polymer, at*
 235 *40 °C (data obtained in the cell out of the sample, during the experiment done with the MAM sample)*

236

237 As shown in Figure 5, it is possible to determine the pathlength by plotting the absorbance as a
 238 function of the CO₂ concentration. Indeed, the slope of the straight line is equal to $\varepsilon \cdot l$ and we know
 239 $\varepsilon_{4950cm^{-1}} = 0.25 L \cdot mol^{-1} \cdot cm^{-1}$. The pathlength thus determined for each samples saturated at
 240 (P,T) is representative of the sample thickness. Same procedure was performed for all samples
 241 (Figure 3).

242 *Table 3: Samples thicknesses calculated with equation (7)*

	<i>l</i> sample at 40 °C	<i>l</i> sample at 130 °C
	(mm)	(mm)
neat PMMA	0.428	0.292
neat MAM	0.408	/
PMMA/10 wt% MAM	0.892	0.38

248 Finally, the weight percentage of CO₂ (% mass CO₂) sorbed into the polymer was calculated with the
 249 following equation:

$$\% \text{ mass } CO_2 = \frac{C_{CO_2}}{C_{CO_2} + \frac{\rho_{pol}}{1+S}} \#(8)$$

250 with C_{CO_2} the concentration of CO₂ in the polymer sample (calculated following equation (2)); ρ_{pol}
 251 the initial polymer density (g.cm⁻³) and S the polymer swelling.

253 3. Results and discussion

254 3.1. CO₂ sorption through FTIR spectra recovery

255 The *in situ* CO₂ sorption equilibrium values at 40 °C and 130 °C, for respectively neat PMMA, neat
 256 MAM, PMMA/10 wt% MAM blend, at 5 MPa, 10 MPa and 30 MPa, are presented in Figure 6.

257 A low temperature (40 °C), and pressures up to 30 MPa are typically representative of the conditions
 258 that can be used in CO₂ batch foaming for acrylic materials [3]. In the same pressure range, a high
 259 temperature (130 °C) is representative of the conditions that can be used in CO₂ extrusion foaming
 260 for these kind of PMMA-based materials [24].

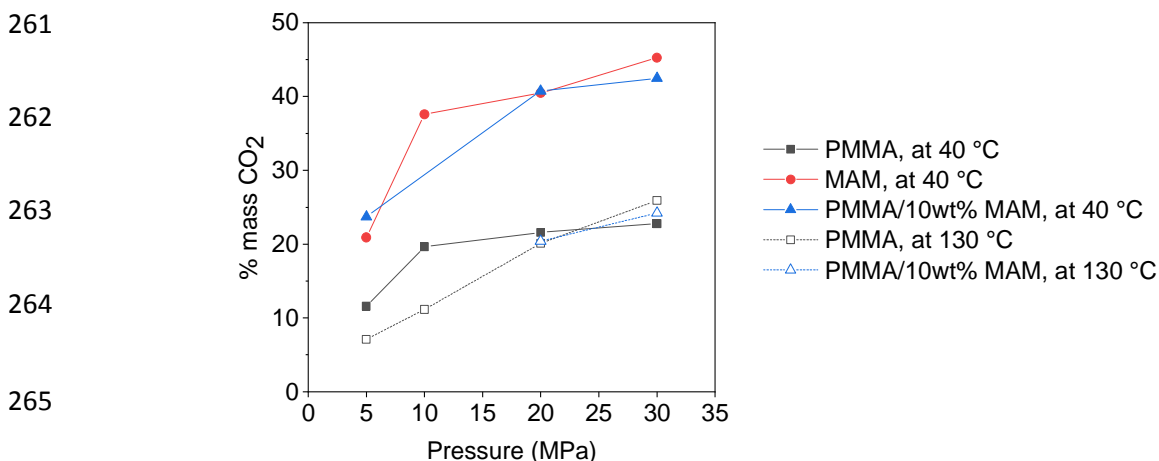


Figure 6: CO₂ mass uptake as function of pressure in PMMA, MAM and PMMA/10 wt% MAM at T = 40 °C and at T = 130 °C

266 In neat PMMA, the CO₂ concentration in the polymer sample increases with the pressure, no matter
 267 the temperature. At 40 °C and 30 MPa the PMMA sample contains 22 wt% CO₂ while at 130 °C and
 268 30 MPa it contains 26 wt% CO₂. These results are quite consistent with values measured by
 269 gravimetric methods, as shown in Figure 7 [12],[17].

270 In neat MAM copolymer at 40 °C, the measured CO₂ sorption values follow the same increasing trend
 271 as in PMMA but reaches a much higher value, close to 45 wt% e.g. at 40 °C and 30 MPa. It was
 272 impossible to measure the CO₂ sorption at 130°C in MAM using our experimental set-up because of
 273 the polymer flow, as previously stated.

274 Neat MAM or the PMMA/10 wt% MAM blend have a higher CO₂ sorption than neat PMMA in all
 275 pressure-temperature conditions because the PBA (central block of the MAM triblock copolymer)
 276 have a much higher CO₂ sorption than PMMA (PMMA chains either as homopolymer in the PMMA
 277 matrix or as lateral blocks in MAM).

278 Therefore, the dispersion of MAM as micelles can act as “CO₂-reservoirs” in a PMMA matrix [3][29],
279 and will increase the cell density of our foams. In fact, the 90/10 blend has advantageously a highly
280 nonlinear behavior, i.e. the resulting sorption is not a linear combination of the two polymers
281 sorption. For example, swelling of the PMMA/10 wt% MAM blend may reach values close to those of
282 100 % MAM at low pressure. Also, the CO₂ sorption of the PMMA matrix is multiplied by 2 as soon as
283 10 wt% MAM is added.

284 In the blend (PMMA/10 wt% MAM), at a chosen temperature (40 or 130 °C), the CO₂ mass uptake
285 logically increases with pressure, but in two different trends, one seemingly close to that of neat
286 MAM at 40 °C, and one seemingly close to that of PMMA at 130 °C.

287 Generally speaking, as observed in various polymers [7],[11],[19], the sorption curves may have
288 different behaviors upon pressure rise. Either the pressure curve is first linear and then it is levelling
289 off (existence of a plateau) or it exhibits a purely linear regime. Indeed Tomasko et al. [7] have shown
290 that depending on the pressure range, the CO₂ sorption is not always proportional to CO₂ pressure.
291 This is due to the variations of the Henry’s coefficient (k_H) in Henry’s law (Equation 9):

$$C_{CO_2} = k_H \times P_{CO_2} \#(9)$$

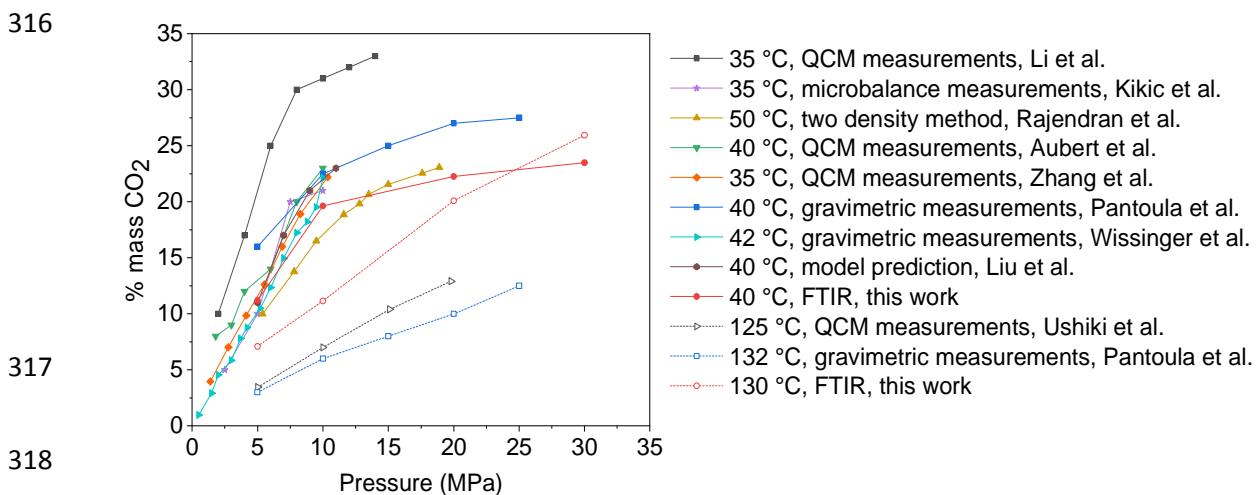
292 with C_{CO_2} the concentration of CO₂ sorbed into the polymer sample (in g.cm⁻³), k_H the Henry’s
293 coefficient (in g.cm⁻³.MPa⁻¹) and P_{CO_2} the pressure of the CO₂ (in MPa).

294 Indeed, at low pressure, k_H is often dependent on temperature and polymer state, and at high
295 pressure, k_H may not be constant and becomes dependent on the CO₂ sorption.

296 In our case, linearity of CO₂ mass uptake (vs pressure) is observed when PMMA/CO₂ mixture is in the
297 rubbery state (130 °C) and therefore a pseudo-Henry’s law is obeyed. Even if the intercept is not 0 at
298 0 MPa, a Henry’s coefficient is evaluated from the slope of the $C_{CO_2} = f(P)$ curve (Figure 6). For
299 PMMA at 130°C, $k_H = 5.9 \cdot 10^{-9} \text{ Pa}^{-1} = 1.4 \cdot 10^{-5} \text{ mol.g}^{-1}.\text{bar}^{-1}$. Our work seems to be the first evaluation of
300 Henry’s constant by a FTIR method.

301 This value is in very good agreement with literature values for other molten polymer/CO₂ solutions.
 302 Polymer/CO₂ systems were already studied as C_{CO_2} pressure dependency [33],[34],[35]. Chen et al.
 303 [34] found a very similar order of magnitude ($6 \cdot 10^{-9} \text{ Pa}^{-1}$) for melted polypropylene in CO₂, at 200 °C
 304 (same pressure range). Rahman et al. [35] found Henry's coefficients between 2 and $5 \cdot 10^{-5} \text{ mol.g}^{-1} \cdot \text{bar}^{-1}$
 305 in two melt CO₂-philic diblock copolymers based on poly(ethylene glycol terephthalate) (PEGT)
 306 and poly(butylene terephthalate) (PBT), also consistent with our FTIR-determined value of k_H .

307 On another side, Figure 7, plotting a comparison of CO₂ sorptions in PMMA measured by various
 308 methods, shows that FTIR CO₂-sorptions are in good agreement with values obtained following other
 309 methods. As an example, in a PMMA/MAM blend at the same (P,T) conditions, Pinto et al. [13]
 310 measured a CO₂ uptake of 30 wt% by gravimetry (weighting the sample after batch saturation) at 40
 311 °C and 30 MPa. However, this is a rather low-value, in comparison with our FTIR-measured value of
 312 42 wt%. In our case, we measured the CO₂ sorption in the cell during the saturation whereas they
 313 measured it after a possible desorption, once the CO₂ vessel is opened. This difference can principally
 314 explain the gap between their value and the one we measured. Another source of difference is the
 315 sample geometry and volume.



319

Figure 7 : CO₂ mass uptake in PMMA as a function of pressure, comparison of results obtained following various methods such as quartz crystal microbalance (QCM) [13],[14],[15],[16], microbalance [34], gravimetry [11], two density method (in which both swelling and CO₂-sorption are simultaneously measured) [17] or FTIR (this work, [35]).

3.2. CO₂ sorption through FTIR spectra recovery

While measuring the *in situ* CO₂ sorption, swelling was evaluated at, respectively, 40 °C and 130 °C under a pressure ranging from 5 to 30 MPa. Swelling of PMMA, MAM and PMMA/10 wt% MAM was calculated with Equation 5, analyzing the polymer peak, and plotted as a function of pressure in Figure 8. Generally speaking, the swelling ratio (S) follows globally a similar trend as solubility with increasing CO₂ pressure.

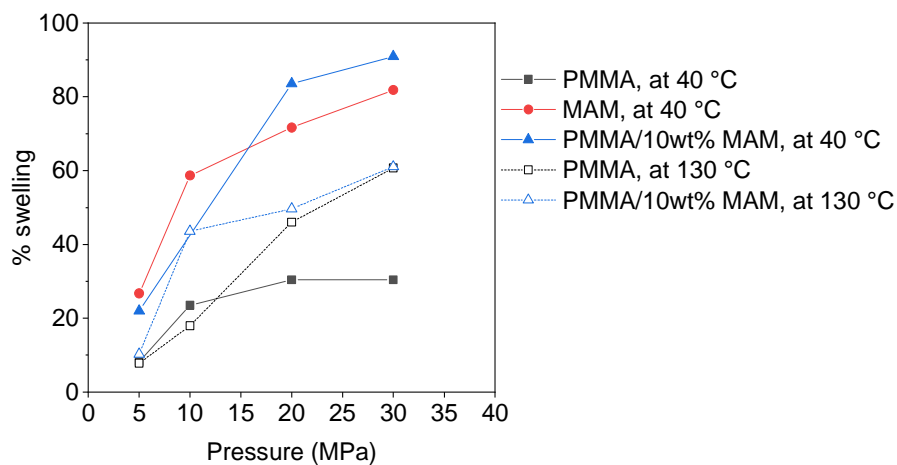


Figure 8 : Percentage of swelling of PMMA, MAM and PMMA/10 wt% MAM blend at 40 °C and 130 °C

For neat PMMA at 40 °C, a swelling plateau value is reached above 20 MPa with a well-defined swelling maximum of roughly 30 %. It shows that the “best” conditions before foaming are attained at a rather low pressure, i.e. there is no need to reach 30 MPa.

The situation is somehow different for PMMA at 130 °C where the state is definitely well above the plasticized T_g of the polymer/CO₂ system, so that the system is able to flow, and swelling is constantly increasing.

In a similar manner, for neat MAM and a blend containing MAM, i.e. a PBA block, no matter the temperature, swelling increases constantly with the pressure and does not reach a plateau value in these conditions. This phenomenon is due to the increase in the free volume where the CO₂ can enter thanks to the mobility of the chains and their disentanglement.

3.3. Correlation between swelling and sorption

In order to evaluate a direct correlation (i.e. a linear proportional relation) between CO₂ solubility and swelling, swelling is plotted as a function of CO₂ mass uptake in Figure 9.

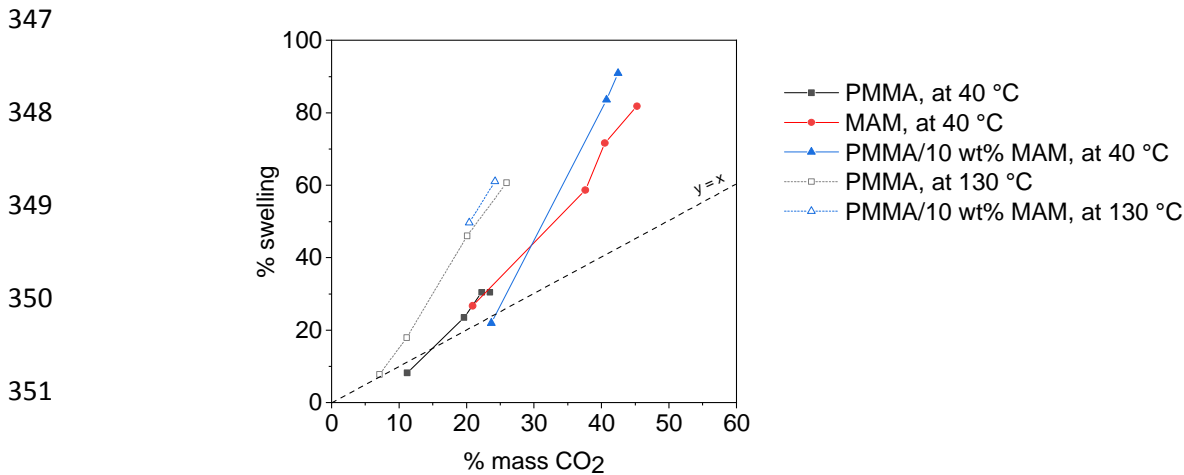


Figure 9: Swelling as a function of CO₂ mass uptake, in PMMA, MAM and PMMA/10 wt% MAM blend

Among studies dealing with several CO₂/amorphous neat polymer homogeneous systems (PS, PMMA, PC,...), studied by any method, a global (not necessarily linear) correlation between swelling and sorption is always observed [18],[36],[37],[38],[39],[40],[41],[42] : a concomitant increase in swelling and sorption in isothermal conditions and a concomitant decrease with temperature in isobaric conditions were observed. Figure 9 also shows this trend in our results.

However, looking at pressure dependencies (e.g. Figure 6, Figure 7, Figure 8) or at swelling-solubility evolution (Figure 9 which is a “pressure-abstracted” dependence), the tendencies are not linear and exhibit several regimes. Figure 7 represents the pressure evolution for several polymers in literature and temperatures, compared to our systems.

and Figure 8 represent only our systems. Plateau pressures, that we name $p^{\text{plateau onset}}$, were evidenced between 8 to 10 MPa [36] for neat PC at 35 °C; between 8 to 10 MPa for neat PMMA at 33 °C; or between 7 to 8 MPa for neat PMMA at 30 to 35 °C [39]. The plateau is lost above 40 °C, where only linear trends take place for both swelling and mass uptake.

Two regimes observed in the case of pressure dependencies (“isothermal pressure regimes”) were defined by Wissinger et al. [36].

369 Interestingly the two regimes are eligible on all the curves ($S = f(P)$ "dilatation curve", $\%CO_2 = f(P)$,
370 "solubility curve", $S = f(\%CO_2)$ "correlation curve").

371 Vitoux et al. [19] observed a similar pressure-swelling correlation trend for other non amorphous
372 polymers (hydroxypoly(butadiene), poly(ethylene glycol), polysiloxane). These polymers are either
373 liquid (HPBD, PDMS) or semi crystalline (PEG). Their behavior is the following: upon CO_2 uptake,
374 swelling is first proportional to solubility; then swelling is much "higher" than solubility.

375 In regime I, isothermal swelling and sorption increase first linearly up to $P^{plateau\ onset}$, above which
376 solubility and swelling level off. Regime I can occur at a temperature ($T^{experiment}$) for which the
377 CO_2 /polymer system is (or may become) glassy.

378 For example, such a case may occur when T_g of polymers (bearing polar functions or atoms) is
379 decreased by the CO_2 interactions [38] leading to a glass transition temperature named T_g^{plasti} (the so
380 called plasticization effect) lower than the experiment saturation temperature.

381 A plateau regime (regime I) cannot be considered as a true (linear) correlation between sorption and
382 swelling.

383 In regime II, at a chosen temperature, both sorption and swelling purely linearly increase with the
384 pressure, over a whole pressure range at a given temperature. Such a case may occur in the liquid
385 state of the CO_2 /polymer system. These regimes are sketched on Figure 10.

386

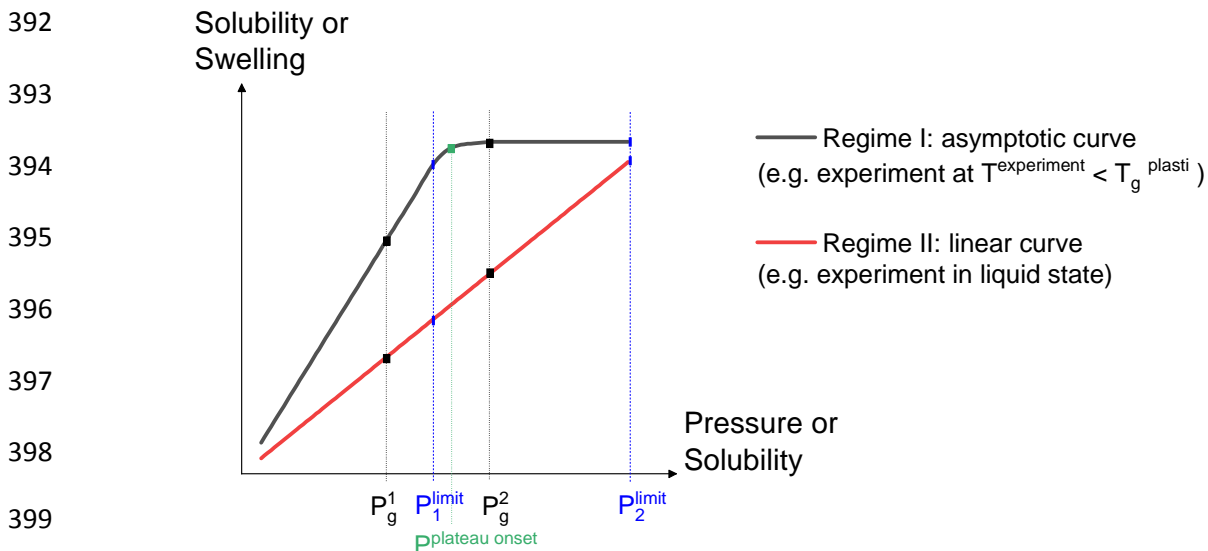
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400 *Figure 10: Schematic representation of the two regimes, represented as %CO₂/S = f(P) or S = f(%CO₂); with two examples of*
 401 *occurrence of regime I or II, and two cases of P_g (P_g¹, P_g²) and P^{limit} (P^{limit}₁, P^{limit}₂) (here experiments are carried out up to 30*
 402 *MPa, but often limited to ~ 8-10 MPa in literature)*

403 The existence of these different regimes is ruled by 4 main inputs: i) the polymer/CO₂ interactions, ii)
 404 the capacity of the CO₂ to move through the free volumes and iii) the physical state of a
 405 homogeneous or a heterogeneous mixture between polymer and CO₂ [43], iv) the pressure extent
 406 that can be investigated and the maximum pressure to which experiments are carried out.

407 Figure 10 is an attempt to represent schematically the two regimes, plotted as % CO₂/S = f(P) or S =
 408 f(% CO₂). In our work, the behavior at 40 °C lies in regime I while behavior at 130 °C lies in regime II.

409 Most studies found in literature [18],[36],[37],[38],[39],[40],[41],[42] are limited to 10 MPa or less,
 410 which does not allow to observe a broad pressure behavior, while our experimental set up allows to
 411 go up to 30 MPa (rather high pressure).

412 We define P^{limit} as the maximum pressure attained for one experiment. Parallely one can define P_g
 413 (called glass transition pressure, P_g), the ‘theoretical’ transition pressure at which the CO₂/polymer
 414 system becomes rubbery (or glassy). Most literature experiments are conducted to a low maximum
 415 pressure (e.g. P^{limit} < 5 to 6 MPa) so that P_g pressure is not always attained.

416 More generally, as far as pressure extent is concerned, two cases arise:

417 ▪ If $P^{\text{limit}} < P_g$, the system cannot reach P_g and the free volumes are “saturated or congested” by CO_2 .

418 At higher pressure or temperature, enough molecular mobility is triggered and one “gets rid” of free
419 volume effects.

420 ▪ If $P^{\text{limit}} > P_g$, one can overcome the CO_2 -penetration limit. Upon an isothermal pressure rise, one can
421 increase the penetration of CO_2 (linear regime). Besides, we can make the hypothesis that at still
422 higher pressures (if attainable, but not reached here), the effects of swelling and sorption would
423 counterbalance each other, i.e. the polymer chains would constrain due to isostatic pressure,
424 preventing CO_2 inlet (leading to loss of linearity).

425 On the contrary, when the system comes to a liquid or liquid-like state, e.g. 130 °C, the regime is
426 linear (CO_2 uptake follows a dissolution mode according to Henry’s law). In this regime (type II), there
427 is a true swelling-solubility correlation.

428 A thermodynamic theoretical analysis is provided by Liu et al. [39] through the calculation and fit of
429 an adjustable interaction parameter (named k_{ij}) and the application of the Sanchez-Lacombe equation
430 of state. They calculated the values of this specific interaction parameter for the CO_2 /PMMA solution.
431 They showed its inversely proportional dependency with temperature, and used this only parameter
432 to predict both solubility, swelling and T_g values. Also from their study, P_g is evaluated at ~ 7 MPa (33
433 °C, 20 wt % CO_2), and $P_g \sim 7.5$ MPa (42 °C, 18 wt% CO_2).

434 In comparison to our systems, $P^{\text{plateau onset}}$ values are estimated from the different swelling and
435 sorption curves, and are reported in Table 4. This table shows the existence of either a plateau
436 pressure or of linearity in the CO_2 /polymer systems, coherent with predictions of Liu et al. [39].

437 On the other side, introducing a heterogeneous component, such as MAM or PBA block in MAM, is
438 probably responsible for deviations from linearity in the swelling-sorption correlation (Figure 9) so
439 that a true correlation cannot be verified.

440 *Table 4: Existence (and pressures values) of either a plateau pressure or linearity in the sorption or swelling curves for the*
 441 *CO₂ systems, PMMA, MAM, PMMA/10 wt% MAM*

Curve	Neat PMMA		Neat MAM		PMMA/10 wt% MAM	
	Existence and value of $p^{\text{plateau onset}}$		Existence and value of $p^{\text{plateau onset}}$		Existence and value of $p^{\text{plateau onset}}$	
	Sorption=f(P)	Swelling=f(P)	Sorption=f(P)	Swelling=f(P)	Sorption=f(P)	Swelling=f(P)
At 40 °C	Yes at 10 MPa	Yes at 15 MPa	Yes at 10-12 MPa	Yes (poorly defined) at 10-15 MPa	Yes at 8-10 MPa	Yes at 20 MPa
At 130 °C	No	No	/	/	No	No

442

443 3.4. Role of heterogeneities

444 If regimes I or II apply for homogeneous systems, the situation is indeed different when the CO₂
 445 system contains a heterogeneous component, such as PBA in MAM or a MAM/PMMA blend. Here
 446 the pressure curves do not exhibit a straight forward behavior of type I or II, e.g. no plateau is well
 447 pronounced, or the onset of a plateau is not clear. Consequently, the changes in the pressure curves
 448 (swelling or sorption) are revealed as a change of slope or as a slow continuous increase.

449 More precisely, looking at Figure 9 (plot of swelling VS sorption), the first part of the curve (< 20-25
 450 wt% CO₂) coincides with a good sorption-swelling correlation. In fact, the CO₂-philic component (PBA,
 451 MAM) does not attract enough CO₂ to perturbate the correlation; whereas heterogeneities are
 452 responsible for perturbation at higher CO₂ solubility (> 20 %).

453 So in the high CO₂-concentration region (> 25 wt% CO₂), a severe deviation from linearization is
 454 obvious. In this region, a true sorption-swelling correlation cannot be possible because of several
 455 reasons: different CO₂-philicities, different mobility and dilatation states of phases. Those differences
 456 were also previously evidenced by Yang et al. [37] on several poly(alkyl acrylates) and in poly(butyl

457 acrylate) in a pressure scan, especially showing differences in the evolution of void fractions in these
458 polymers.

459 **4. Conclusion**

460 In this paper, the CO₂ uptake (solubility, % CO₂ in polymer) and the polymer swelling (volume change,
461 dilatation) in CO₂ of acrylic systems, namely poly(methyl methacrylate) homopolymer (PMMA), a
462 triblock CO₂-philic rubbery-core acrylic copolymer (MAM) and a PMMA/10 wt% MAM blend has been
463 determined simultaneously using a FTIR microscope combined to a high-pressure cell. Samples were
464 saturated with supercritical CO₂ (scCO₂) isothermally at either 40 °C or 130 °C up to high pressures
465 (namely 5 MPa, 10 MPa and 30 MPa), being typical saturation temperatures of a batch scCO₂ solid-
466 state foaming or a liquid-like state scCO₂ extrusion foaming. Pressures attained in the cell are high
467 compared to previous works.

468 FTIR reveals to be a robust method for *in situ* simultaneous measurement of CO₂ sorption and
469 polymer swelling. The measured values are in very good agreement with data determined by other
470 methods in literature. Besides we provide the first coherent value of a FTIR-determined Henry's
471 coefficient of PMMA in scCO₂. Furthermore, the addition of a MAM copolymer at 10 wt% in the
472 PMMA matrix (providing an advantageous heterogeneous system) led to a significant increase of CO₂
473 mass uptake, from 23 % CO₂ for a neat PMMA to 42 % CO₂ for the 10 wt% MAM blend at 40 °C and
474 30 MPa, and of swelling (from 20 % to 90 %). MAM is confirmed as a good additive that enhances
475 PMMA foaming in different processes (solid or liquid-like).

476 If both those CO₂ solubility and polymer swelling are increasing their behavior upon pressure
477 increase is indeed different at the two temperatures in the three systems. We highlighted a purely
478 linear increase or an increase followed by a plateau. Such a behavior corresponds to a specific regime
479 (regime I -asymptotic- or II -linear-, presented schematically on Figure 10). Experimentally we
480 observed either a linear correlation between swelling and sorption or a great deviation from linearity
481 (Figure 9). The existence (or not) of a direct linear correlation is ruled by several inputs: **i)** the

482 polymer/CO₂ interactions, **ii**) the capacity of the CO₂ to move through the free volumes and to
483 saturate those volumes, **iii**) the physical state of a homogeneous or a heterogeneous mixture
484 between polymer and CO₂ [43], **iv**) the pressure extent that is investigated and the maximum
485 pressure (P^{limit}) to which experiments are carried out.

486 For example, regime I happens if $P^{\text{limit}} < P_g$, the system cannot reach P_g and the free volumes are
487 “saturated or congested” by CO₂.

488 On the contrary, when the system comes to a liquid or liquid-like state, e.g. 130 °C, the regime is
489 linear (CO₂ uptake follows a dissolution mode according to Henry’s law). In this regime (II), there is a
490 true linear swelling-solubility correlation.

491 Such data are useful to find out the best routes towards low-density **and** (‘and’ en gras) nano porous
492 polymer foams, given that the material be should filled with as much as possible CO₂ (at the lower
493 possible pressure). Two chosen temperatures (40 or 130°C) are attempting to mimic a batch or an
494 extrusion process with scCO₂ as a foaming agent.

495

496 **5. Acknowledgments**

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499 **6. Data availability**

500 The raw/processed data required to reproduce these findings cannot be shared at this time due to
501 time limitations. However, the authors will try to answer questions by e-mails sent to them.

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Supporting Information

646 *Table 5: Raw data recorded in FTIR for neat PMMA ($d = 1.19$); neat MAM ($d = 1.03$) and PMMA/10 wt% MAM ($d = 1.18$) at*
 647 *40 °C and 130 °C varying the baselines for the peak absorbance measurement and mean data calculated.*

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PMMA at 40°C

Baseline (6290.785-5496.217 cm ⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	74.39	0		
5	68.37	8.79		
10	60.45	23.05		
20	56.59	31.44		
30	56.60	31.41		
Baseline (6311.971-5496.217 cm ⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	72.01	0		
5	68.10	5.74		
10	58.15	23.85		
20	55.53	29.67		
30	55.93	28.76		
Baseline (6473.965-5496.217 cm ⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	73.72	0		
5	66.99	10.05		
10	59.63	23.62		
20	56.64	30.15		
30	56.24	31.08		
Mean				
Pressure (MPa)	Swelling (%)	Swelling	C_{CO_2} (g.cm ⁻³)	% mass CO ₂
5	8.20	0.08	0.14	11.21
10	23.51	0.24	0.24	19.63
20	30.42	0.30	0.26	22.25
30	30.41	0.30	0.28	23.48

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PMMA at 130°C

Baseline (4607.180-3787.569 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	241.41	0		
5	224.85	7.37		
10	203.91	18.39		
20	166.08	45.36		
30	152.45	58.35		
Baseline (4784.602-3787.569 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	246.39	0		
5	229.67	7.28		
10	209.99	17.33		
20	170.00	44.93		
30	155.06	58.90		
Baseline (4761.459-3770.212 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	234.22	0		
5	215.55	8.66		
10	198.23	18.15		
20	158.49	47.78		
30	142.04	64.89		
Mean				
Pressure (MPa)	Swelling (%)	Swelling	C_{CO_2} (g.cm ⁻³)	% mass CO ₂
5	8.01	0.08	0.08	7.10
10	18.27	0.18	0.13	11.15
20	46.57	0.47	0.20	20.09
30	61.62	0.62	0.26	25.93

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Baseline (4607.180-3810.710 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	221.56	0		
5	171.37	29.29		
10	138.93	59.48		
20	128.50	72.42		
30	121.75	81.99		
Baseline (4643.821-3804.925 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	202.17	0		
5	162.35	24.52		
10	128.82	56.94		
20	119.41	69.31		
30	111.81	80.82		
Baseline (4576.324-3804.925 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	211.15	0		
5	167.10	26.37		
10	132.24	59.67		
20	121.83	73.31		
30	115.54	82.75		
Mean				
Pressure (MPa)	Swelling (%)	Swelling	C_{CO_2} (g.cm ⁻³)	% mass CO ₂
5	26.73	0.27	0.22	20.97
10	58.70	0.59	0.39	37.69
20	71.68	0.72	0.41	40.58
30	81.85	0.82	0.47	45.36

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PMMA/10 wt% MAM (M53) at 40°C

Baseline (4607.180-3837.709 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	442.08	0		
5	364.42	21.31		
10	-	-		
20	243.68	81.42		
30	235.39	87.81		
Baseline (4763.388-3855.066 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	448.39	0		
5	374.64	19.69		
10	-	-		
20	251.48	78.30		
30	244.17	83.64		
Baseline (4607.180-3806.854 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	458.06	0		
5	366.49	24.99		
10	-	-		
20	239.85	90.98		
30	227.52	101.32		
Mean				
Pressure (MPa)	Swelling (%)	Swelling	C_{CO_2} (g.cm ⁻³)	% mass CO ₂
5	21.99	0.22	0.30	23.39
10	-	-	-	-
20	83.59	0.84	0.39	37.61
30	90.92	0.91	0.40	39.28

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PMMA/10 wt% MAM (M53) at 130°C

Baseline (4607.180-3787.569 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	315.01	0		
5	280.55	12.31		
10	216.25	45.71		
20	210.20	49.91		
30	195.07	61.53		
Baseline (4767.245-3787.569 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	319.19	0		
5	292.09	9.28		
10	-	-		
20	214.86	48.55		
30	200.00	59.60		
Baseline (4990.951-3787.569 cm⁻¹)				
Pressure (MPa)	Absorbance	Swelling (%)		
0.10	32..59	0		
5	295.55	9.15		
10	228.08	41.44		
20	214.40	50.47		
30	199.07	62.05		
Mean				
Pressure (MPa)	Swelling (%)	Swelling	C_{CO_2} (g.cm ⁻³)	% mass CO ₂
5	10.25	0.10		
10	43.57	0.44		
20	49.64	0.50	0.2	20.54
30	61.06	0.61	0.24	24.38