



HAL
open science

Experimental investigation of the physical foaming of tannin-based thermoset foams

Z. Marie, V. Nicolas, A. Celzard, V. Fierro

► **To cite this version:**

Z. Marie, V. Nicolas, A. Celzard, V. Fierro. Experimental investigation of the physical foaming of tannin-based thermoset foams. *Industrial Crops and Products*, 2019, 138, pp.111424. 10.1016/j.indcrop.2019.05.073 . hal-02357731

HAL Id: hal-02357731

<https://hal.science/hal-02357731>

Submitted on 17 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Experimental investigation of the physical foaming of tannin-based thermoset foams

Z. Marie, V. Nicolas*, A. Celzard, V. Fierro

Université de Lorraine, CNRS, IJL, F-88000 Epinal, France

Abstract

The physical foaming of thermosetting biosourced formulations, mainly based on tannin extracts and furfuryl alcohol, was investigated in-depth with a specially designed setup. Mass loss, volume expansion, and temperature measured at the bottom, in the middle and at the top of foams were continuously monitored during their preparation, from the first moment after the liquid formulation was poured into a mould until the final foams hardened and dried. Correlations were found between the observed phenomena. Thus, successive foaming mechanisms involving: (i) phase change of the blowing agent at 55°C, (ii) pore opening at a critical inner pressure, which induced 4% mass loss, and (iii) surface evaporation, could be elucidated and were discussed. The effects of the amounts of blowing agent on the one hand, which increases foam expansion, and of polymerisation catalyst on the other hand, which reduces the induction time, were also investigated, leading to some shifts in the aforementioned phenomena. The present results are certainly relevant to other self-foaming formulations based on thermosetting polymers such as traditional polyurethanes expanded by physical foaming with pentane.

Keywords: Thermoset foams; Physical foaming; Tannin; Data acquisition; Heat and mass transfers; biosourced formulation

* Corresponding author. Tel: + 33 372 74 96 54. Fax: + 33 372 74 96 38. E-mail address : vincent.nicolas@univ-lorraine.fr (V. Nicolas)

22 **1 Introduction**

23 Rigid foams are mature products that are abundantly used in various sectors, such as
24 construction, transport, and industry in general (Landrock, 1995). Among them, phenolic
25 foams are of special interest because of their low cost, low density, good mechanical and
26 insulating properties, and excellent retardance to fire associated with low smoke emission and
27 no dripping of molten plastic (Denslow and Rickle, 1989; Haberstroh and Schlumm, 2011;
28 Mendelsohn et al., 1979b, 1979a; Rangari et al., 2007; Shen and Nutt, 2003; Shutov, 1984).
29 However, they are produced from toxic and non-renewable raw materials, hence the need of
30 finding cheap, abundant, ecological but still effective substitutes.

31 Many trials were successfully carried out for replacing phenol by poorly or non-toxic
32 natural phenolic molecules, either partly for instance by lignin (Carvalho et al., 2003), by
33 cardanol (Bo et al., 2016, 2018) or by hydrolysable tannins (Lagel et al., 2014), or even
34 completely by condensed tannins of various natures (Lacoste et al., 2013, 2014; Martinez de
35 Yuso et al., 2014; Tondi et al., 2009a). The latter materials were the most promising ones,
36 since many formulations were developed, leading to acid-free (Basso et al., 2014a), solvent-
37 free (Basso et al., 2013a), and even formaldehyde-free (Basso et al., 2011, 2015) foams, all
38 having relevant physical properties for most of the traditional uses of phenolic foams
39 (packaging, cushioning, insulation, building materials, automobiles, aircrafts and marine
40 structures, electronics and flame retardance).

41 Although continuous preparation processes have been suggested (Basso et al., 2014b),
42 tannin-based foams are mainly produced in batch until now. The problem with such
43 preparation method is the impact of the experimental conditions on the structure, and hence
44 on the properties, of the resultant foam. Indeed, most tannin-based formulations are self-
45 foaming, i.e., based on the heat induced by polymerisation reactions and by which gases are
46 produced, thereby leading to a dramatic increase of volume. It is then easy to understand that,

47 for instance, changing the nature and/or the size of the mould for a given amount of
48 formulation poured into it leads to different results since part of the heat is absorbed by the
49 walls of the mould. Therefore, the higher is the contact area with the mould, and/or the higher
50 is the thermal effusivity of the mould, the lower will be the temperature inside the foam and
51 the lower will be its expansion. As a result, foams with higher density will be obtained,
52 having smaller cells, higher mechanical properties but lower insulating character, and so forth
53 (Letellier et al., 2017a).

54 In a similar way, introducing higher amounts of formulation in a given mould will produce
55 more heat upon polymerisation, thus a higher expansion, larger cells, lower mechanical
56 strength, etc. (Letellier et al., 2017a). Beyond a critical quantity of reagents, and whereas all
57 proportions are kept constant, a potentially dangerous auto-acceleration of the polymerisation
58 reactions (Trommsdorff effect) may even occur. For avoiding reconsidering completely the
59 formulations each time some experimental conditions are changed (amounts of reactants, air
60 temperature, moulds, etc.), less empiricism is thus necessary.

61 In the recent past, first attempts for streamlining the batch production of thermoset foams
62 have been carried out and applied to polyurethane (Bikard et al., 2005, 2007; Bouayad et al.,
63 2008, 2009; Ireka et al., 2015; Karimi and Marchisio, 2015) and tannin-based (Basso et al.,
64 2013d, 2013b, 2013c) foams. In the latter case, a special commercial device initially
65 developed for investigating the preparation of polyurethane foams, called FOAMAT®
66 (Messtechnik, Germany), was used. The FOAMAT® 285 Foam Qualification System allows
67 measuring at the same time the changes of several parameters during foam growth, such as
68 temperature (at a fixed position), foam height, pressure exerted on the bottom of the mould,
69 and dielectric polarisation (related to the extent of polymerisation reactions). With such
70 system, temperature and expansion are the most commonly measured quantities, and are
71 generally measured only at the beginning or until the three-quarters of the foaming process.

72 In the present work, further advances in the characterisation and in the understanding of
73 the foaming process of thermosetting tannin-based formulations are proposed. After a
74 foaming model was developed in a former paper (Marie et al., 2019), a new experimental
75 setup is offered herein for the ultimate purpose of refining the mechanisms of expansion of
76 such formulations, and better taking into account the effect of some ingredients on the final
77 foams properties. Compared to previous experiments carried out with the FOAMAT®, the
78 present system allows temperature measurements for very long times, i.e., including foam
79 cooling, and at three different positions within the material instead of a single one.
80 Additionally, the mass changes were measured continuously, which had never been done so
81 far for this kind of formulations. Based on the corresponding results, and especially by
82 examining the extent and the synchronisation of the observed changes, new information about
83 foaming mechanisms and about the impact of selected ingredients could be obtained.

84 **2 Materials and Methods**

85 **2.1. Preparation of tannin-based foams**

86 In the present work, the formulation abundantly described elsewhere and referred to as the
87 “standard” one for tannin-based foams (see for instance (Delgado-Sánchez et al., 2018a;
88 Tondi et al., 2009a, 2009b; Zhao et al., 2010) and refs. therein) was used. It is based on
89 mimosa tannin extract, commercially available under the name FINTAN-OP and kindly
90 provided by the company SilvaChimica (St. Michele Mondovi, Italy). It typically comprises
91 80% of flavonoid compounds (i.e., condensed tannins of prorobinetinidin type (Braghiroli et
92 al., 2012)), which are soluble in water and can easily react with both furfuryl alcohol and
93 formaldehyde in order to lead to crosslinked phenolic-furanic resins (Basso et al., 2014b;
94 Delgado-Sánchez et al., 2018b; Li et al., 2012a; Pizzi et al., 2008). The latter are prone to
95 foam spontaneously as soon as a low-boiling point solvent is present in the formulation, for

96 instance diethyl ether (Celzard et al., 2013), pentane (Celzard et al., 2015) or a mixture of
97 both (Li et al., 2013).

98 Herein, tannin extract and furfuryl alcohol were first dissolved in water by mechanical
99 stirring, and then formaldehyde (37% in water) and diethyl ether were added. After
100 homogenisation of the mixture, the resultant viscous resin was poured into a cylindrical
101 container of diameter 63 mm and height 103 mm. Then, para-toluenesulphonic acid (pTSA,
102 65% in water) was introduced and the blend was intimately mixed again for a few seconds.
103 pTSA catalysed the very exothermic polymerisation reactions, so that diethyl ether started to
104 boil, and hence to produce a dramatic expansion of the material. At the same time, the heat
105 that was generated helped hardening the as-produced foam so that it never collapsed and
106 continued growing from the surface of the still liquid resin. Table 1 gathers the nature, the
107 role and the amount of each ingredient used in the formulation.

108 **2.2. Investigation methods**

109 An experimental setup was specially designed for the present work, enabling the
110 continuous measurements of temperature, deformation and mass (Figure 1). The temperature
111 was recorded at three different positions of the foam during its different steps of growth,
112 stabilisation/hardening and cooling. Two K-type thermocouples were installed at fixed points,
113 one being located at 1.2 cm from the bottom of an HDPE beaker in which the foam was
114 grown, and the other at 6 cm from the bottom. For avoiding as much as possible any
115 disturbance of the foam rise due to the presence of these thermocouples, the latter were
116 introduced from below into the beaker, through well-adjusted pinholes, and oriented along its
117 revolution axis. The beaker was itself installed on a heavy wooden support throughout which
118 the thermocouples were inserted. The whole was installed on an electronic balance
119 (ENTRIS623I-1S 620G X) with resolution of 0.001 g. Thanks to this special design, the wires

120 of the thermocouples produced a negligible friction on the rising foam and did not interfere
121 either with the weight measurements (Figure 2a).

122 The third measurement point was the upper surface of the foam, whose temperature was
123 monitored using an infrared camera (OPTRIS PI 640 O33 T900) placed above the balance
124 with a tripod (**Figure 1b**).

125 A camera (Logitech C925 1920x1080 Webcam Full HD Webcam) was also placed just in
126 front of the electronic balance, at beaker level. After processing, the images were binarised so
127 that the material appeared black and the background appeared white, as clearly shown in
128 Figure 2b. Based on such binarised images, the projected area of the foam at every moment
129 could be accurately determined. Then, a relative area was determined by calculating the ratio
130 of the foam projected area at each time step ($t > 0$) to its initial area ($t = 0$). Finally, the mass
131 of the foam was measured as a function of time thanks to the aforementioned balance
132 connected to an acquisition unit.

133 The webcam and the balance were connected to a computer. The thermocouples were
134 plugged into a NI 9211 thermocouple input module, itself connected to the same computer
135 through a cDAQ-9174 chassis. The triggering of the recording and the acquisition were
136 simultaneously carried out by the LabView software at a frequency of 3 measurements per
137 second. During the expansion of the foam, the top of the foam cracked, letting appear part of
138 the still hot material beneath the surface, which therefore was not representative of the actual
139 surface temperature. The relevant zone for evaluating the correct temperature of the top
140 surface of the foam was then chosen as a large crack-free area identified after viewing the
141 video from the infrared camera (see "Area" in Figure 3).

142 **3 Results and discussion**

143 The results concerning the "standard" formulation are first given below. Then, the effects
144 of changing the amounts of diethyl ether on the one hand, and of pTSA on the other hand, are
145 discussed.

146 **3.1 Studies of the standard formulation**

147 *3.1.1 Temperature variation as a function of time*

148 As explained in the previous section, the temperatures were measured at three different
149 positions: at the top surface with the infrared camera (here referred to as "Top"), and at two
150 fixed positions with thermocouples at 1.2 cm and 6 cm from the bottom of the beaker (here
151 referred to as "Bottom" and "Middle", respectively). Generally speaking, these 3 temperatures
152 changed with time as described below.

153 A first stage was observed with a rapid increase of temperature during the first seconds of
154 the experiment, until a maximum was reached after around 60 s. Then, cooling was observed
155 until the return to the outside temperature (Figure 4a). The stage of temperature rise is
156 obviously due to the exothermic polymerisation reactions occurring in the resin, since the
157 very same process is exploited for producing the foam, as already detailed in subsection 2.1.
158 Once these reactions are completed, the only remaining phenomenon is the convective and
159 radiative heat exchange with the atmosphere, which induces the cooling of the material. At
160 the maximum of temperature, it can be seen that "middle" temperature is the highest,
161 followed by "bottom" and finally "top" temperature. As "bottom" and "top" temperatures are
162 measured near the surface, they are submitted to a higher cooling heat flux than in the
163 "middle" of the foam, because the atmosphere temperature was close to 20°C. If the "bottom"
164 of the foam had been insulated, the temperature measured there would have been the highest,
165 followed by the "middle" temperature, and the "top" temperature would have been the lowest.

166 Regarding the bottom probe, the first recorded temperature was 30°C because the reaction
167 already started before the resin was completely poured into the beaker, 30 s of mixing being
168 necessary after the addition of the catalyst (pTSA). As clearly shown in Figure 4b, the
169 increase of temperature is not linear. Acceleration can be observed between 0 and 35 s,
170 followed first by a pseudo-plateau until 50 s at a temperature close to 55 °C and then by
171 another fast increase until the temperature saturates at its maximum value.

172 The plateau observed at 55°C was confirmed by plotting the derivative of the temperature
173 with respect to time as a function of temperature (Figure 5), evidencing two inflection points
174 and, between them, a minimum corresponding to the intermediary plateau. This finding
175 suggests that some phenomenon absorbs energy, offsets the exothermic reaction, and hence
176 delays and reduces the increase of temperature.

177 The temperature in the middle of the foam increased sharply because of the fixed position
178 of the sensor which was not in contact with the material at the beginning of the measurements
179 (see again Figure 4). Once the foam expanded enough (within 30 s), it touched the
180 thermocouple, thus explaining the sudden rise of temperature. Once buried inside the foam,
181 the middle probe logically experienced the highest temperature (about 90°C).

182 Interestingly, this maximum is synchronised in time (about 60 s, see Figure 4a) with that of
183 the bottom temperature. Moreover, the decrease of temperature beyond the maximum
184 followed the same regime for both bottom and middle points (Figure 4a), which suggests that
185 heat exchanges (both radiative and convective) with the exterior prevail. Here, no phase
186 change such as condensation of diethyl ether vapours was observed.

187 The way the surface temperature changed with time was different from that of the two
188 other positions. Not only the maximum was reached faster, i.e., at shorter time than the others
189 (see again Figure 4b), but the temperature also dropped quite fast and reached values as low
190 as 16°C, i.e., below room temperature (which was 20°C during all the experiments). The latter

191 finding is clearly seen on the infrared picture at 858 s, see Figure 6. It is likely that the
192 different behaviour of the surface temperature is due to the evaporation of the blowing agent
193 (diethyl ether), which necessarily occurs at the surface of the material. Such evaporation was
194 confirmed by the continuous mass loss observed in Figure 8 (see below). Evaporation is a
195 phase change and therefore induces a significant absorption of heat, leading to the faster
196 decrease of the surface temperature. As the latter is in thermal equilibrium with ambient air,
197 the heat extraction related to evaporation imposes a temperature lower than that of the
198 atmosphere.

199 By observing the images of the infrared camera (Figure 6), it can be seen that, within a
200 range of a few seconds, the surface temperature is rather homogeneous from one area to
201 another, except where cracks appeared on the skin of the foam. These images support that the
202 area selected in Figure 3 was relevant for describing the overall behaviour of the surface
203 temperature.

204 *3.1.2 Expansion as a function of time*

205 As explained in subsection 2.1, the relative changes of volume were not directly measured,
206 but are expected to be proportional to the changes of projected area determined after
207 binarisation of the foam images caught by the webcam (Figure 2b). Foam expansion occurred
208 in three distinct phases, see Figure 7, and especially Figure 7b. In the first phase, i.e., at the
209 very beginning of the foaming process, the volume remained constant for 25 s. The expansion
210 could indeed not start as long as diethyl ether did not reach its phase change temperature
211 (34°C if pure). After such induction time, diethyl ether turned from liquid to vapour and
212 hence expansion occurred. The production of vapour, along with the increase of temperature,
213 creates a mechanical balance between the inner pressure (within the pores) and the skin of the
214 material. As the polymer matrix is poorly viscous at the beginning of the process, the inner

215 pressure prevails and outweighs the surface energy, and hence the volume increases. The
216 observed expansion lasted for about 20 s.

217 Figure 7c shows the change of relative expansion as a function of bottom temperature, and
218 its corresponding derivative. The bottom temperature was chosen instead of that of the middle
219 because the thermocouple is continuously immersed in the mixture. Unlike what was
220 conjectured above, the expansion did not only occur at 34°C. While the phenomenon indeed
221 (slowly) began at the expected phase change temperature of pure diethyl ether, it continued in
222 a range of higher temperatures and was even the fastest at 55°C. It is quite possible that
223 blending diethyl ether with other solutes (water solutions of formaldehyde and pTSA, both
224 present in the formulation, as well as impurities coming from the tannin extract and dissolved
225 in water, such as alkali) produced an increase of boiling point, which is a classic colligative
226 property that one may expect (Raoult's law). Moreover, the highest expansion rate occurring
227 at 55°C coincides with the pseudo-plateau of bottom temperature already observed in Figure
228 4b, and therefore further supports the assumption of phase change of a mixture of diethyl
229 ether and aqueous solution instead of pure blowing agent.

230 The end of the expansion can be explained by two simultaneous phenomena. The first one
231 corresponds to the hardening of the polymer matrix, which prevents any further deformation
232 after a given time controlled by the polymerisation kinetics. The second phenomenon is
233 related to the opening of the porosity by rupture of cell walls, resulting in a balance between
234 internal and ambient pressures and thus stopping the expansion (see below the discussion
235 about weight loss). Finally, a very low shrinkage can be observed at high time in Figure 7b,
236 due to both cooling and to the relatively fast expansion rate but low crosslinking rate of the
237 polymer matrix.

238 3.1.3 Mass variation as a function of time

239 The relative changes of mass are shown in Figure 8, and three successive steps can be
240 observed over time. The first one is a linear but very low mass decrease during the first 25 s
241 of the experiment. Then, a sudden and exponential decrease of mass occurs. Finally, a slow
242 and roughly linear mass loss is seen, expected to tend towards a constant value after quite a
243 long time. The transition between 1st and 2nd steps corresponds to the onset of foam
244 expansion, while that between 2nd and 3rd steps seems to be related to the moment at which
245 both bottom and middle temperatures start to decrease, as seen in Figure 4b. Such moment
246 coincides with the depletion of the reagents present in the system. The observed phenomena
247 can be detailed further and are discussed as follows.

248 In step 1, the mass loss is very low and most probably corresponds to the surface
249 evaporation of the liquid resin, driven by the difference of vapour pressure of either diethyl
250 ether or water, or both, between the material surface and the atmosphere. For instance, since
251 water is in liquid phase before foaming, the surface can be considered as saturated and, at
252 20°C, the saturation pressure is equal to 2300 Pa. If in the atmosphere, the relative humidity is
253 50% and the temperature is again 20°C, the vapour pressure becomes equal to 1150 Pa, and
254 therefore evaporation mass flow should exist at the surface of the resin. The evaporation mass
255 flow, F_m (kg s⁻¹), indeed reads:

$$256 \quad F_m = - \int_0^S k_m \frac{M_v}{R} \left(\frac{P_{v,a}}{T_a} - \frac{P_v}{T} \right) dS \quad (1)$$

257 where k_m (m s⁻¹) is the convective mass transfer coefficient, S (m²) is the exchange area, T_a
258 and T (K) are the temperatures of air and material surface, respectively, $P_{v,a}$ and P_v (Pa) are the
259 vapour pressures in air and at the surface of the material, respectively, M_v (kg mol⁻¹) is the
260 molecular weight of the vapour, and R (J mol⁻¹ K⁻¹) is the ideal gas constant. Thus, taking
261 into account the aforementioned values of saturation pressure and vapour pressure, the

262 difference of p_v/T ratios in Eq. (1) between the atmosphere and the surface becomes positive
263 (3.92 Pa K⁻¹), which indeed induces a negative mass flux and therefore a loss of mass.

264 This assumption also applies to diethyl ether as well as to any other volatile constituent of
265 the formulation, such as formaldehyde. The amount of diethyl ether in the beaker induces a
266 vapour pressure at the surface of the liquid resin, which is always higher than the vapour
267 pressure in air, assumed to be close to zero.

268 The 2nd step, corresponding to a steep loss of mass of a few %, occurred during the
269 expansion of the material. It was observed that the foam, once stabilised, contains open
270 porosity. The transition from closed to open porosity allows explaining such abrupt mass loss.
271 Indeed, during foam growth, the total pressure which is generated, and which is initially
272 trapped as bubbles in the viscous resin, increases with the amount of diethyl ether undergoing
273 phase change from liquid state to vapour. After a critical volume increase, pore opening
274 occurs, driven by the difference of pressure between the core of the foam and the atmosphere,
275 and thus creating a continuity of the gas phase with the exterior. Darcy's law may explain gas
276 transfers in a porous matrix submitted to a pressure gradient, established at the moment at
277 which the pores open: it states that the gas velocity, v (m s⁻¹), is proportional to the pressure
278 gradient and to the permeability of the medium, according to:

$$279 \quad \frac{r}{v} = -\frac{k}{\mu} \nabla P \quad (2)$$

280 where k (m²) is the gas permeability of the foam, μ (Pa s) is the gas dynamic viscosity, and
281 ∇P (Pa) is the gas pressure gradient.

282 Thus, the pressure gradient produced at the onset of pore opening leads to a sudden flow of
283 gas expelled from the material. For instance, if an (arbitrarily chosen but still realistic)
284 overpressure of 1000 Pa is considered between the core of the material and its upper surface,

285 let $P(x = 0) = 1000 + P_{atm}$ and $P(x = L) = P_{atm}$, where L is the distance between the middle
286 part of the foam and its upper surface (average of 7.5 cm) and P_{atm} is the atmospheric
287 pressure. Thus, the pressure gradient is $-1000 / 0.075 = -13333.3 \text{ Pa m}^{-1}$. Considering a gas
288 permeability of 10^{-11} m^2 and a viscosity of 0.224 mPa s, a speed of $5.95 \cdot 10^{-4} \text{ m s}^{-1}$ is
289 calculated. This calculated flux is positive, so a transfer of gas to the exterior can indeed exist.

290 This phenomenon can be observed with the infrared camera during the expansion of the
291 foam, as shown in Figure 9. A flux of gas expelled from the foam and hotter than the
292 surrounding atmosphere is indeed clearly seen in Figure 9b.

293 Finally, the last step of mass loss is slow and rather constant with time. Indeed, once the
294 total pressures inside and outside the foam are balanced, Darcy's flow vanishes, which marks
295 the end of the previous rapid mass loss (step #2). Observing the fresh foam reveals that its
296 porous structure is wet, and the final mass loss step thus corresponds to drying. The surface
297 evaporation observed here is explained by the same phenomenon as in step #1, i.e., by a
298 difference of vapour pressure between the material surface and the atmosphere. Another hint
299 that can explain this phenomenon is related to the temperature at the surface. Indeed, it was
300 observed that the latter was lower than the external temperature at the end of the experiment
301 (see again Figure 4a). This is a very usual finding when it comes to drying in air, because the
302 energy required to evaporate the liquid decreases the temperature of the wet material surface.

303 **3.2 Impact of the amount of diethyl ether**

304 The previous section was dedicated to foaming studies of the standard formulation
305 described in Table 1, i.e., using 3g of diethyl ether. Herein, the same formulation was
306 investigated but using two different amounts of blowing agent: 1g or 5g of diethyl ether.
307 Figure 10 clearly shows the dramatic impact of this ingredient on the expansion of the foam,
308 already demonstrated (Celzard et al., 2010, 2012, 2015; Li et al., 2013; Tondi et al., 2009b)

309 and quantitatively established (Amaral-Labat et al., 2013; Letellier et al., 2017b, 2017a; Li et
310 al., 2012b; Zhao et al., 2010) in former works from our group.

311 The curves presented in Figure 11a, 11b, 11c and 11d show that the lower was the amount
312 of blowing agent, the higher was the maximum temperature obtained and the faster it was
313 reached. This finding is readily explained by considering the sensible heat transfer from the
314 exothermic reaction to the diethyl ether: more energy must indeed be brought for increasing
315 the temperature of the liquid blowing agent until it reaches its phase change temperature, thus
316 slowing down the rise of the overall material temperature. But the phase change of a higher
317 amount of diethyl ether also requires more energy, and such impact of the latent heat transfer
318 can be seen in Figure 11b, showing a longer pseudo-plateau of temperature related to phase
319 change, thereby delaying further the increase of overall temperature.

320 In contrast, a larger amount of blowing agent led to faster cooling. This phenomenon is not
321 only explained by the correspondingly lower temperatures discussed above, since the change
322 of temperature with time is faster. As the volume of the foam increases sharply with the
323 amount of diethyl ether (see Figure 10 and 11e), the exchange surface area increases
324 accordingly. And since the convective heat flux, ϕ_{cv} (W), increases with the exchange area
325 (see Eq. (3)), it is thus logical to observe a faster temperature decrease:

$$326 \quad \phi_{cv} = \int_0^S h(T_a - T)dS \quad (3)$$

327 In Eq. (3), h ($\text{W m}^{-2} \text{K}^{-1}$) is the convective heat transfer coefficient, S (m^2) is the exchange
328 area, and T_a and T (K) are the temperatures of air and material surface, respectively.

329 As expected, the relative deformation increased with the amount of diethyl ether (Figure 10
330 and 11e) since more liquid was converted into vapour. Regarding mass changes, the sudden
331 loss of mass due to pore opening varied accordingly, so that higher mass losses were obtained

332 with more blowing agent in the formulation. The evaporation mass flow was also higher
333 because, as suggested by Eq. (1), it depends on the exchange area with the exterior, which
334 was higher with foams produced with more diethyl ether.

335 **3.3 Impact of the amount of catalyst**

336 The present section is now dedicated to the effect of the amount of polymerisation catalyst
337 added to the standard formulation, using either 9 or 13g of pTSA, instead of 11g as formerly
338 presented in Table 1. As a general trend, and whereas all changes remained qualitatively the
339 same, decreasing the amount of pTSA delayed all phenomena, whether peak of temperature,
340 expansion, or mass loss (Figure 12). The effect was rather low with respect to what was
341 observed for the standard formulation when the amount of catalyst was increased, but the
342 foam expansion took typically two times longer by using 9g of pTSA instead of 11. The latter
343 finding is quite interesting in case one would like to delay the onset of foaming, for instance
344 for having enough time for pouring the liquid formulation into a mould.

345 **4 Conclusion**

346 An experimental setup was designed for continuously measuring the temperature at
347 different positions, the expansion, and the changes of mass of a phenolic/furanic foam all
348 along its growth from a self-foaming, tannin-based biosourced formulation. New phenomena
349 were observed:

- 350 • the energy absorbed by the phase change of the blowing agent (DEE) offset the exothermic
351 reaction and limited the increase of temperature at the resin – growing foam interface;
- 352 • the expansion did not only occur at the phase change temperature of pure DEE (34°C), but
353 took place in a range of higher temperatures and was even the fastest at 55°C;
- 354 • more blowing agent led to lower foaming temperature, explained by the enhanced latent
355 heat transfer, and to higher evaporation-induced mass flow, explained by the larger exchange
356 area, which also elucidated the faster cooling rate;

357 • more catalyst only accelerated the phenomena, which remained qualitatively the same.

358 The continuous measurement of mass loss, carried out for the first time in this context,
359 revealed a succession of three phases:

360 • a short drying one before expansion, explained by liquid evaporation at the surface;

361 • a sudden loss of mass during expansion, corresponding to a steep loss of mass of a few %
362 and observed with an infrared camera, induced by a pressure gradient driven by the onset of
363 pore opening at a critical inner pressure;

364 • an ongoing evaporation until complete drying of the as-produced thermoset foam. A
365 surface evaporation phenomenon was evidenced, resulting in a surface temperature that
366 decreased fast until below the atmospheric temperature during cooling.

367 The new phenomena highlighted in this study should allow developing new ways of foam
368 optimisation. Especially, the phenomenon of pore opening is crucial for the final quality of
369 the material. As for the phenomenon of drying, poorly studied so far, it shows that the foam
370 formation is not finished at the end of the expansion, but continues until final drying.

371

372 **Acknowledgements**

373 The authors gratefully acknowledge the financial support of the “Pôle M4” of University
374 of Lorraine and FEDER funds through the TALiSMAN project. Engineering students Eva
375 Dano and Michel Haubold are thanked for supplying the raw data from which the present
376 work could be successfully carried out.

377

378

379 **References**

- 380 Amaral-Labat, G., Gourdon, E., Fierro, V., Pizzi, A., and Celzard, A. (2013). Acoustic
381 properties of cellular vitreous carbon foams. *Carbon* 58, 76–86.
- 382 Basso, M.C., Li, X., Fierro, V., Pizzi, A., and Celzard, A. (2011). Green, formaldehyde-free,
383 foams for thermal insulation. *Adv. Mater. Lett.* 2, 378-382M.
- 384 Basso, M.C., Giovando, S., Pizzi, A., Celzard, A., and Fierro, V. (2013a). Tannin/furanic
385 foams without blowing agents and formaldehyde. *Ind. Crops Prod.* 49, 17–22.
- 386 Basso, M.C., Pizzi, A., and Celzard, A. (2013b). Dynamic Monitoring of Tannin-based Foam
387 Preparation: Effects of Surfactant. *BioResources* 8, 5807-5816–5816.
- 388 Basso, M.C., Pizzi, A., and Celzard, A. (2013c). Influence of formulation on the dynamics of
389 preparation of tannin-based foams. *Ind. Crops Prod.* 51, 396–400.
- 390 Basso, M.C., Pizzi, A., and Celzard, A. (2013d). Dynamic Foaming Behaviour of
391 Polyurethane vs Tannin/Furanic Foams. *J. Renew. Mater.* 1, 273–278.
- 392 Basso, M.C., Giovando, S., Pizzi, A., Lagel, M.-C., and Celzard, A. (2014a). Alkaline Tannin
393 Rigid Foams. *J. Renew. Mater.* 2, 182–185.
- 394 Basso, M.C., Delmotte, L., Al-Marzouki, F., Abdalla, S., and Celzard, A. (2014b). MALDI-
395 TOF and ¹³C NMR Analysis of Tannin–Furanic–Polyurethane Foams Adapted for Industrial
396 Continuous Lines Application. *Polymers* 6, 2985–3004.
- 397 Basso, M.C., Lagel, M.-C., Pizzi, A., Celzard, A., and Abdalla, S. (2015). First Tools for
398 Tannin-Furanic Foams Design. *BioResources* 10.
- 399 Bikard, J., Bruchon, J., Coupeuz, T., and Vergnes, B. (2005). Numerical prediction of the foam
400 structure of polymeric materials by direct 3D simulation of their expansion by chemical
401 reaction based on a multidomain method. *J. Mater. Sci.* 40, 5875–5881.
- 402 Bikard, J., Bruchon, J., Coupeuz, T., and Silva, L. (2007). Numerical simulation of 3D
403 polyurethane expansion during manufacturing process. *Colloids Surf. Physicochem. Eng.*
404 *Asp.* 309, 49–63.
- 405 Bo, C., Wei, S., Hu, L., Jia, P., Liang, B., Zhou, J., and Zhou, Y. (2016). Synthesis of a
406 cardanol-based phosphorus-containing polyurethane prepolymer and its application in
407 phenolic foams. *RSC Adv.* 6, 62999–63005.
- 408 Bo, C., Hu, L., Chen, Y., Yang, X., Zhang, M., and Zhou, Y. (2018). Synthesis of a novel
409 cardanol-based compound and environmentally sustainable production of phenolic foam. *J.*
410 *Mater. Sci.* 53, 10784–10797.
- 411 Bouayad, R., Bikard, J., and Agassant, J.F. (2008). Injection of thermoset foam: comparison
412 between simulation and experiment. *Int. J. Mater. Form.* 1, 683–686.
- 413 Bouayad, R., Bikard, J., and Agassant, J.-F. (2009). Compressible flow in a plate/plate
414 rheometer: application to the experimental determination of reactive expansion's models
415 parameters for polyurethane foam. *Int. J. Mater. Form.* 2, 243.

- 416 Braghiroli, F.L., Fierro, V., Izquierdo, M.T., Parmentier, J., Pizzi, A., and Celzard, A. (2012).
417 Nitrogen-doped carbon materials produced from hydrothermally treated tannin. *Carbon* 50,
418 5411–5420.
- 419 Carvalho, G. de, Pimenta, J.A., Santos, W.N. dos, and Frollini, E. (2003). Phenolic and
420 Lignophenolic Closed Cells Foams: Thermal Conductivity and Other Properties. *Polym.-*
421 *Plast. Technol. Eng.* 42, 605–626.
- 422 Celzard, A., Zhao, W., Pizzi, A., and Fierro, V. (2010). Mechanical properties of tannin-based
423 rigid foams undergoing compression. *Mater. Sci. Eng. A* 527, 4438–4446.
- 424 Celzard, A., Tondi, G., Lacroix, D., Jeandel, G., Monod, B., Fierro, V., and Pizzi, A. (2012).
425 Radiative properties of tannin-based, glasslike, carbon foams. *Carbon* 50, 4102–4113.
- 426 Celzard, A., Fierro, V., Pizzi, A., and Zhao, W. (2013). Multifunctional porous solids derived
427 from tannins. *J. Phys. Conf. Ser.* 416, 012023.
- 428 Celzard, A., Szczurek, A., Jana, P., Fierro, V., Basso, M.-C., Bourbigot, S., Stauber, M., and
429 Pizzi, A. (2015). Latest progresses in the preparation of tannin-based cellular solids. *J. Cell.*
430 *Plast.* 51, 89–102.
- 431 Delgado-Sánchez, C., Sarazin, J., Santiago-Medina, F.J., Fierro, V., Pizzi, A., Bourbigot, S.,
432 and Celzard, A. (2018a). Impact of the formulation of biosourced phenolic foams on their fire
433 properties. *Polym. Degrad. Stab.* 153, 1–14.
- 434 Delgado-Sánchez, C., Santiago-Medina, F., Fierro, V., Pizzi, A., and Celzard, A. (2018b).
435 Optimisation of “green” tannin-furanic foams for thermal insulation by experimental design.
436 *Mater. Des.* 139, 7–15.
- 437 Denslow, K.R., and Rickle, G.K. (1989). Surfactant Effects in Phenolic Foam Resins. *J. Cell.*
438 *Plast.* 25, 31–42.
- 439 Haberstroh, E., and Schlumm, M. (2011). Properties and Manufacturing of Sandwich Parts
440 with Phenolic Foam Cores. *J. Polym. Eng.* 26, 213–226.
- 441 Ireka, I.E., Niedziela, D., Schäfer, K., Tröltzsch, J., Steiner, K., Helbig, F., Chinyoka, T., and
442 Kroll, L. (2015). Computational modelling of the complex dynamics of chemically blown
443 polyurethane foam. *Phys. Fluids* 1994-Present 27, 113102.
- 444 Karimi, M., and Marchisio, D.L. (2015). A Baseline Model for the Simulation of
445 Polyurethane Foams via the Population Balance Equation: A Baseline Model for the
446 Simulation of Polyurethane.... *Macromol. Theory Simul.* 24, 291–300.
- 447 Lacoste, C., Basso, M.C., Pizzi, A., Laborie, M.-P., Celzard, A., and Fierro, V. (2013). Pine
448 tannin-based rigid foams: Mechanical and thermal properties. *Ind. Crops Prod.* 43, 245–250.
- 449 Lacoste, C., Pizzi, A., Basso, M.-C., Laborie, M.-P., and Celzard, A. (2014). Pinus pinaster
450 tannin/furanic foams: PART I. Formulation. *Ind. Crops Prod.* 52, 450–456.
- 451 Lagel, M.-C., Pizzi, A., Giovando, S., and Celzard, A. (2014). Development and
452 Characterisation of Phenolic Foams with Phenol-Formaldehyde-Chestnut Tannins Resin. *J.*
453 *Renew. Mater.* 2, 220–229.

- 454 Landrock, A.H. (1995). Handbook of Plastic Foams: Types, Properties, Manufacture and
455 Applications (Noyes Publications, Park Ridge, New Jersey, USA).
- 456 Letellier, M., Szczurek, A., Basso, M.-C., Pizzi, A., Fierro, V., Ferry, O., and Celzard, A.
457 (2017a). Preparation and structural characterisation of model cellular vitreous carbon foams.
458 Carbon *112*, 208–218.
- 459 Letellier, M., Macutkevic, J., Bychanok, D., Kuzhir, P., Delgado-Sanchez, C., Naguib, H.,
460 Mosanenzadeh, S.G., Fierro, V., and Celzard, A. (2017b). Modelling the physical properties
461 of glasslike carbon foams. J. Phys. Conf. Ser. *879*, 012014.
- 462 Li, X., Basso, M.C., Fierro, V., Pizzi, A., and Celzard, A. (2012a). Chemical modification of
463 tannin/furanic rigid foams by isocyanates and polyurethanes. Maderas Cienc. Tecnol. *14*,
464 257–265.
- 465 Li, X., Basso, M.C., Braghiroli, F.L., Fierro, V., Pizzi, A., and Celzard, A. (2012b). Tailoring
466 the structure of cellular vitreous carbon foams. Carbon *50*, 2026–2036.
- 467 Li, X., Pizzi, A., Lacoste, C., Fierro, V., and Celzard, A. (2013). Physical Properties of
468 Tannin/Furanic Resin Foamed With Different Blowing Agents. BioResources *8*, 743-752–
469 752.
- 470 Marie, Z., Nicolas, V., Celzard, A., and Fierro, V. (2019). First approach for modelling the
471 physical foaming of tannin-based thermoset foams. Int. J. Therm. Sci. (*submitted to*).
- 472 Martinez de Yuso, A., Lagel, M.C., Pizzi, A., Fierro, V., and Celzard, A. (2014). Structure
473 and properties of rigid foams derived from quebracho tannin. Mater. Des. *63*, 208–212.
- 474 Mendelsohn, M.A., Meier, J.F., Rudd, G.E., and Rosenblatt, G.B. (1979a). Effects of density
475 and structure on load bearing and permeability characteristics of a family of shock mitigating
476 phenolic foams. J. Appl. Polym. Sci. *23*, 333–339.
- 477 Mendelsohn, M.A., Meier, J.F., Rudd, G.E., and Rosenblatt, G.B. (1979b). Effects of
478 composition and processing conditions on the properties of a series of shock mitigating
479 phenolic foams. J. Appl. Polym. Sci. *23*, 341–351.
- 480 Pizzi, A., Tondi, G., Pasch, H., and Celzard, A. (2008). Matrix-assisted laser
481 desorption/ionization time-of-flight structure determination of complex thermoset networks:
482 Polyflavonoid tannin–furanic rigid foams. J. Appl. Polym. Sci. *110*, 1451–1456.
- 483 Rangari, V.K., Hassan, T.A., Zhou, Y., Mahfuz, H., Jeelani, S., and Prorok, B.C. (2007).
484 Cloisite clay-infused phenolic foam nanocomposites. J. Appl. Polym. Sci. *103*, 308–314.
- 485 Shen, H., and Nutt, S. (2003). Mechanical characterization of short fiber reinforced phenolic
486 foam. Compos. Part Appl. Sci. Manuf. *34*, 899–906.
- 487 Shutov, F.A. (1984). Phenolic foams in the USSR. Cell. Polym. *3*, 95–104.
- 488 Tondi, G., Zhao, W., Pizzi, A., Du, G., Fierro, V., and Celzard, A. (2009a). Tannin-based
489 rigid foams: a survey of chemical and physical properties. Bioresour. Technol. *100*, 5162–
490 5169.

491 Tondi, G., Blacher, S., Léonard, A., Pizzi, A., Fierro, V., Leban, J.M., and Celzard, A.
492 (2009b). X-Ray Microtomography Studies of Tannin-Derived Organic and Carbon Foams.
493 *Microsc. Microanal.* *15*, 384–394.

494 Zhao, W., Pizzi, A., Fierro, V., Du, G., and Celzard, A. (2010). Effect of composition and
495 processing parameters on the characteristics of tannin-based rigid foams. Part I: Cell structure.
496 *Mater. Chem. Phys.* *122*, 175–182.

497

498

499

500 **Table 1:** Standard formulation of tannin-based foam

Ingredients and roles in the formulation	Mass (g)
Mimosa tannin extract; base of the resin	30
para-toluenesulphonic acid (pTSA, 65% in water); catalyst	11
Furfuryl alcohol; co-reagent producing heat upon polymerisation	10.5
Formaldehyde (37% in water); crosslinker	7.4
Water; solvent	6
Diethyl ether (DEE); (physical) blowing agent	3

501

502

503 **Figure caption**

504 **Figure 1:** Specially designed system for the continuous and simultaneous measurements of
505 foam temperature, deformation and mass during growth, hardening and cooling: (a) schematic
506 view; (b) actual system installed in a fume hood.

507 **Figure 2:** (a) Zoom of the thermocouples passing through the beaker via a wooden support
508 placed on an electronic balance, and whose probes are located at two different positions from
509 the bottom; (b) real image of the foam caught by camera after growth, and its binarised
510 counterpart used to calculate the foam's relative area as a function of time.

511 **Figure 3:** Infrared image showing the area chosen for measuring the surface temperature.

512 **Figure 4:** Variation of temperature with time at three positions of the foam: bottom (green
513 continuous line), middle (red dashed line), top (blue dotted line): (a) whole curves; and (b)
514 zoom on the first 100 s.

515 **Figure 5:** Time derivative of the bottom temperature, as a function of temperature.

516 **Figure 6:** Infrared pictures of the growing foam as a function of time. The colour bar
517 corresponds to a temperature range from 16°C to 55°C.

518 **Figure 7:** Relative deformation of the foam as a function of time: (a) whole curve; (b) zoom
519 on the first 100 s; (c) Same as (b) but as a function of bottom temperature, and corresponding
520 derivative.

521 **Figure 8:** Relative mass change of the foam as a function of time.

522 **Figure 9:** Infrared pictures of the growing foam at two different times. The scale bar
523 corresponds to a temperature range from 16°C to 30°C, and is given in black and white
524 instead of colours as in Figure 6 for a better contrast.

525 **Figure 10:** Final morphology and volume of standard tannin-based foams produced with
526 increasing amounts of blowing agent; from left to right: 1, 3 and 5 g of diethyl ether.

527 **Figure 11:** Data related to foaming of standard formulations prepared with three amounts of
528 blowing agent (green: 1g of diethyl ether; red: 3g; and blue: 5g): (a) temperature changes at
529 three positions within the foam (continuous lines: bottom; dashed lines: middle; dotted lines:
530 top), and zooms on: (b) bottom, (c) top and (d) middle positions; (e) Relative deformation as a
531 function of time; (f) Relative mass loss as a function of time.

532 **Figure 12:** Data related to foaming of standard formulations prepared with three amounts of
533 catalyst (green: 9g of pTSA; red: 11g; and blue: 13g): (a) temperature changes at three
534 positions within the foam (continuous lines: bottom; dashed lines: middle; dotted lines: top);
535 and (b) zoom on the first 100 s; (c) Relative deformation as a function of time; (d) Relative
536 mass loss as a function of time.

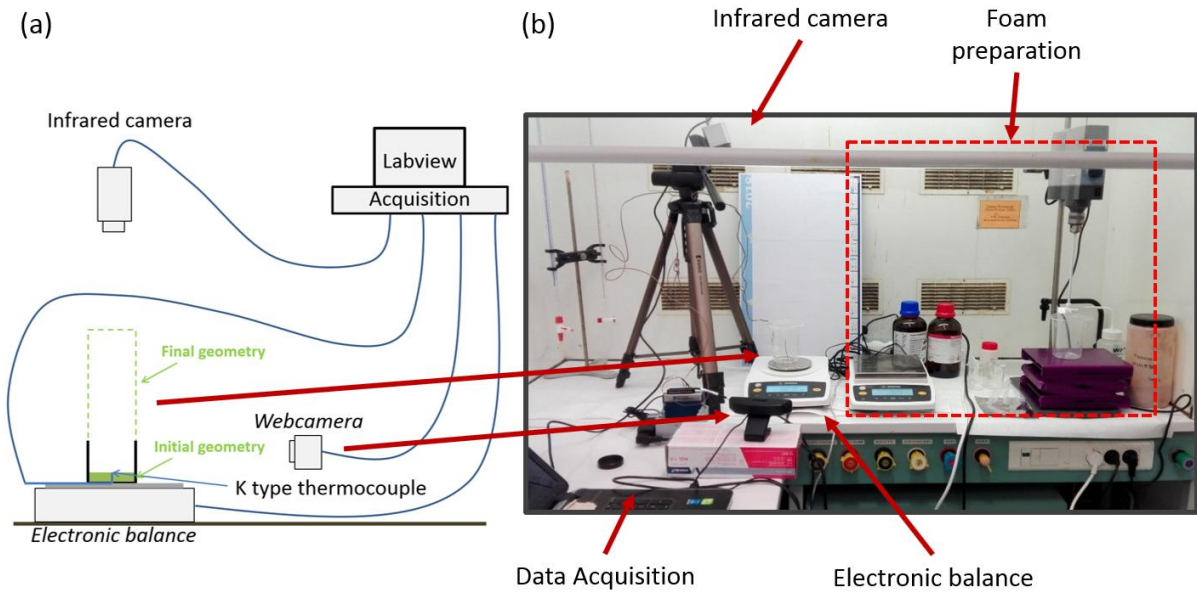
537

538

539

Figure 1

540



541

542

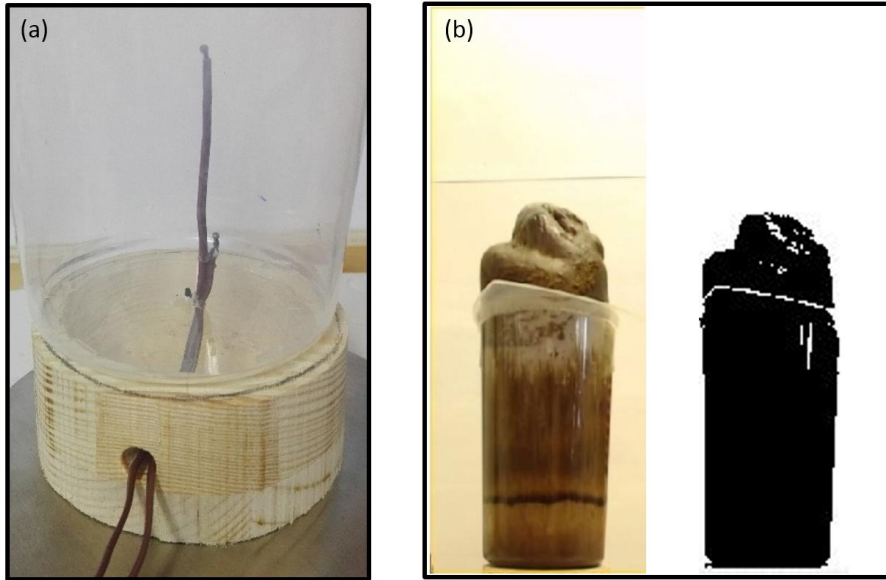
543

544

545

Figure 2

546



547

548

549

550

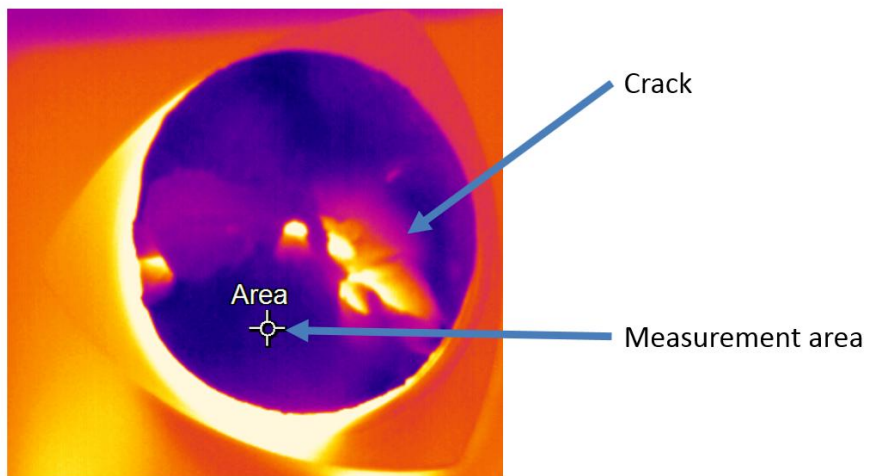
551

552

Figure 3

553

554



555

556

557

558

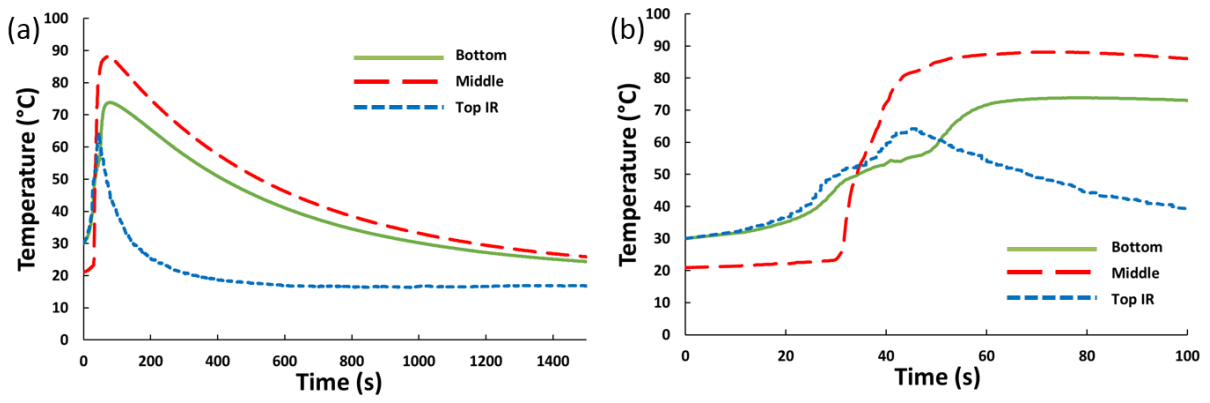
559

560

Figure 4

561

562



563

564

565

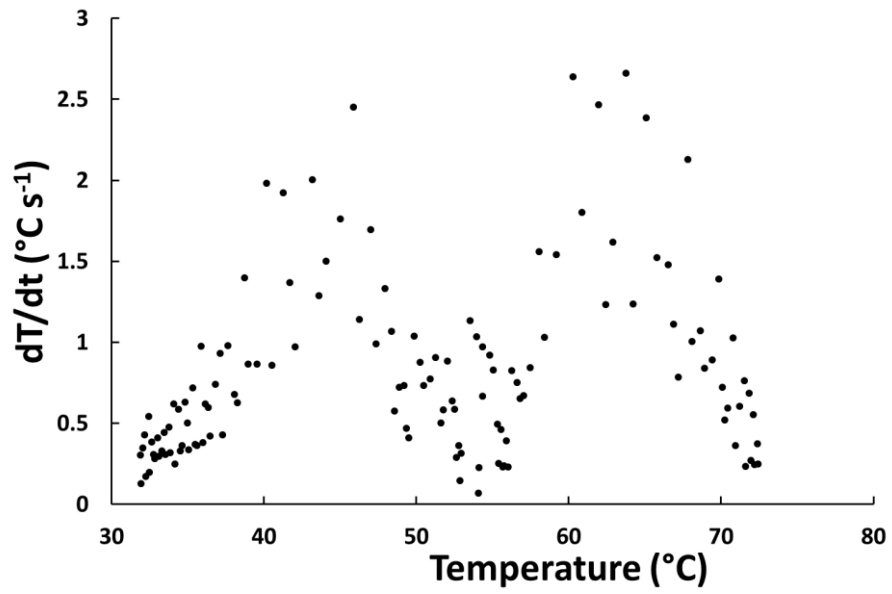
566

567

568

Figure 5

569



570

571

572

573

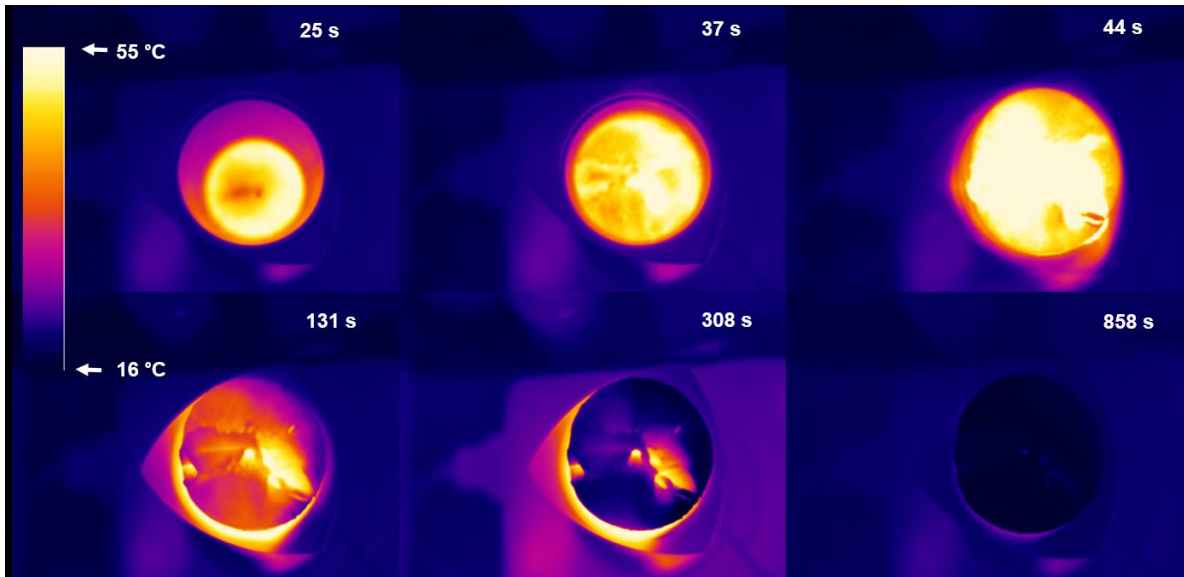
574

575

576

Figure 6

577



578

579

580

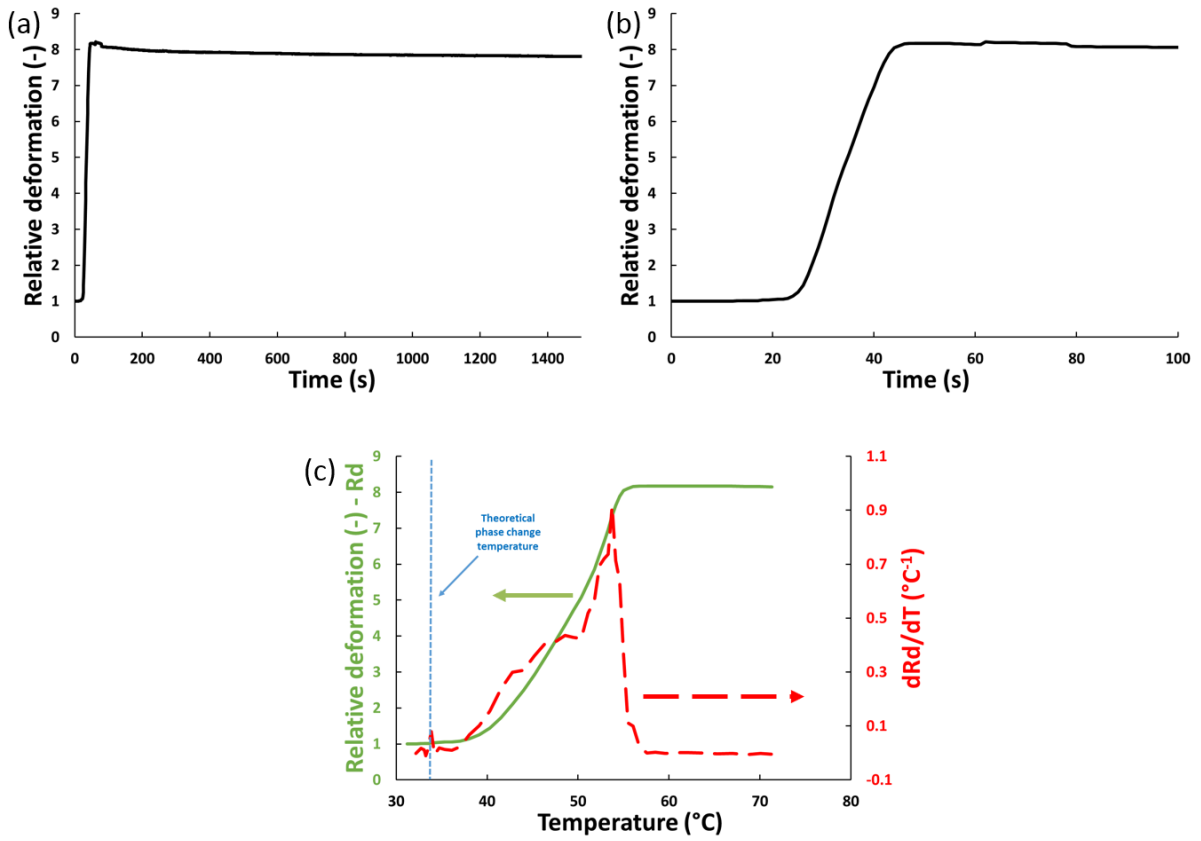
581

582

583

Figure 7

584



585

586

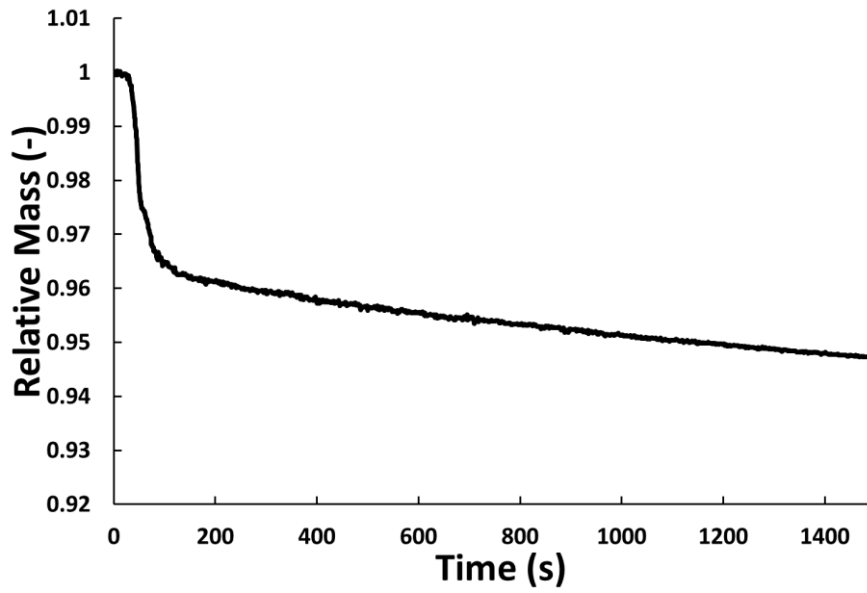
587

588

589

Figure 8

590



591

592

593

594

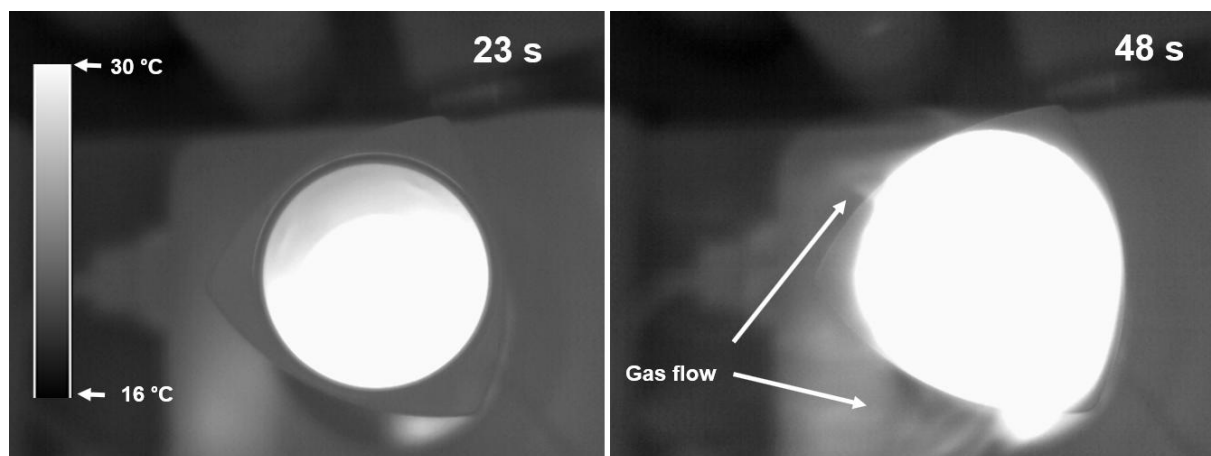
595

596

597

Figure 9

598



599

600

601

602

603

604

605

Figure 10

606



607

608

609

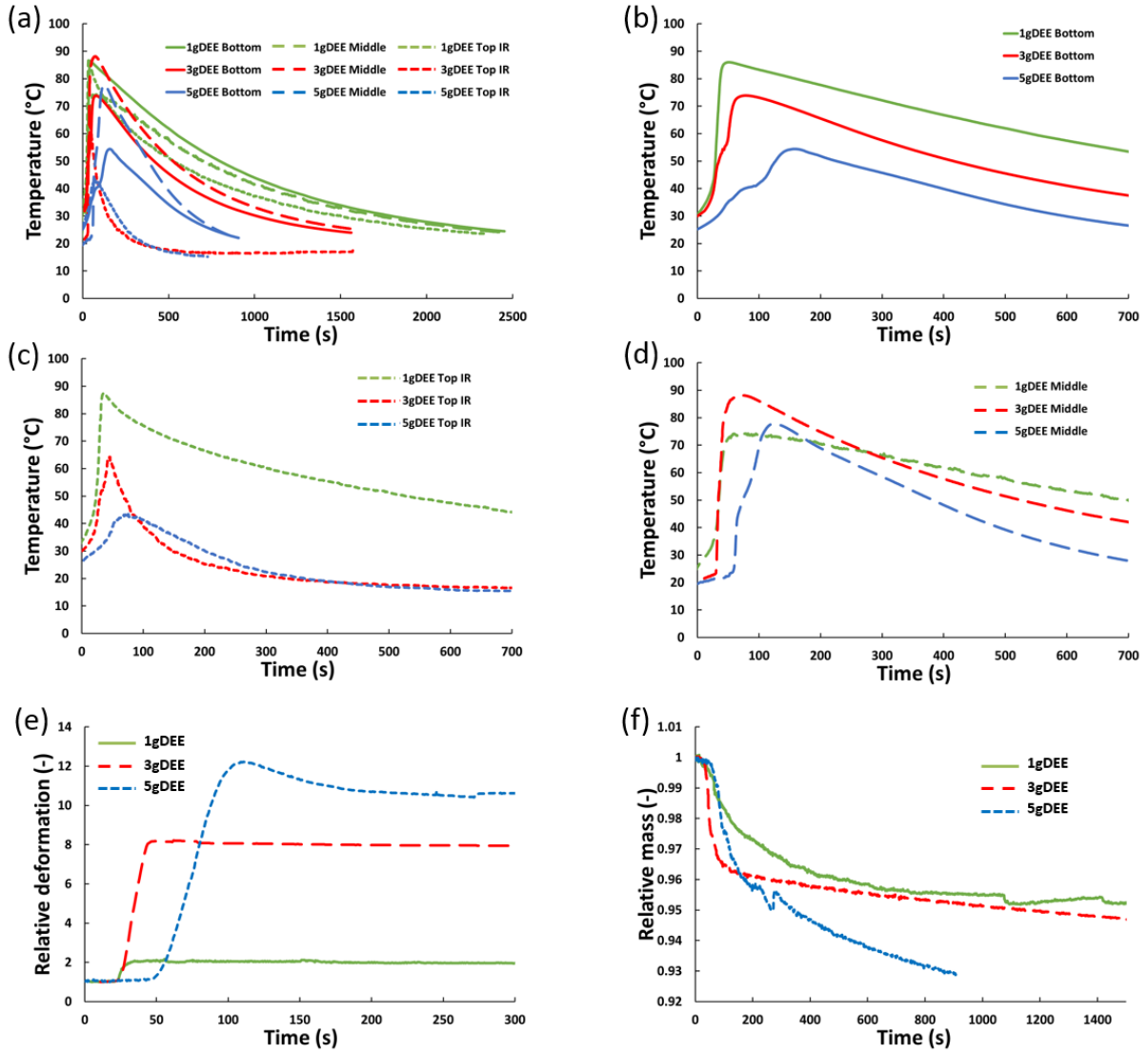
610

611

612

Figure 11

613



614

615

616

617

618

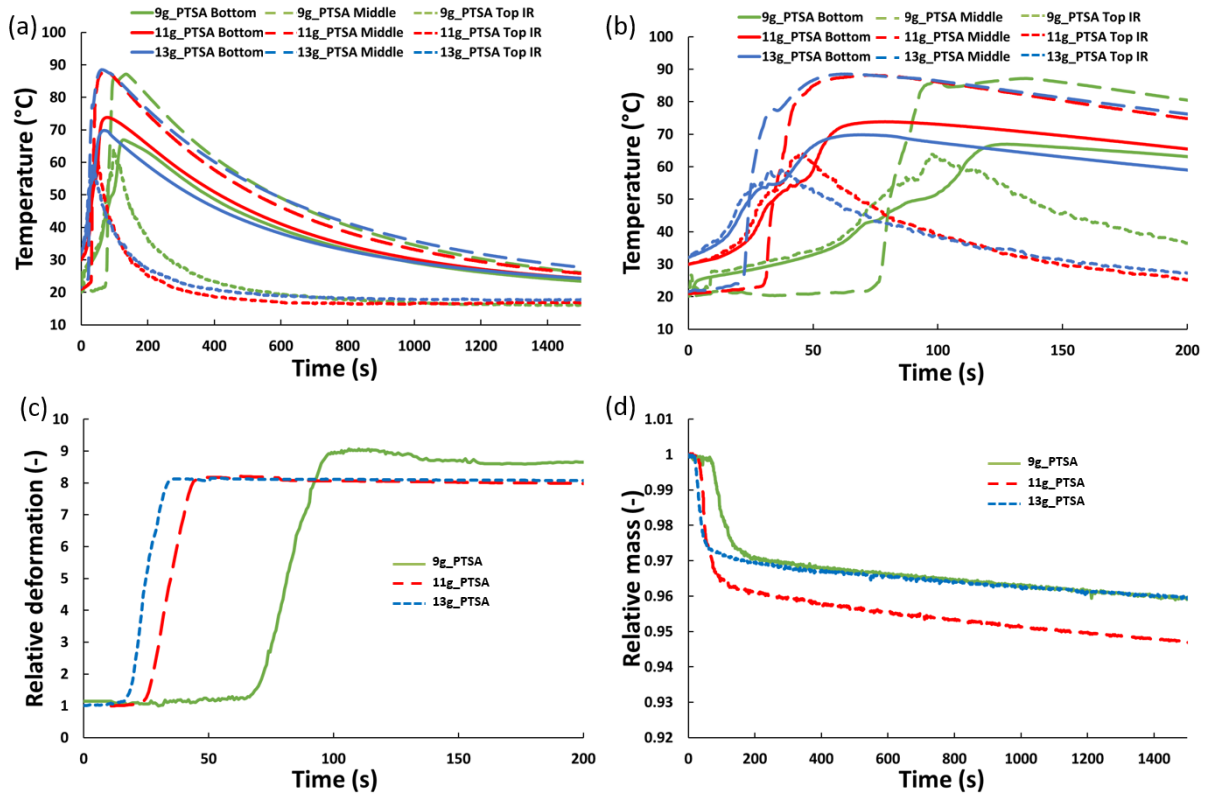
619

620

621

Figure 12

622



623

624

625