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2 **Estimation of the reaction kinetic parameters of a mimosa**
3 **tannin-based thermoset resin with a simulation approach**

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16

17 **Abstract**

18 This study presents the estimation of the parameters of the polymerization kinetics of a
19 mimosa tannin-based thermosetting resin. A dual approach, experimental and numerical, was
20 used. The numerical approach consisted in solving a time-dependent 0D numerical model of
21 the polymerization kinetics and the heat equation. Thus, the parameters were estimated by
22 minimizing the difference between the measured and the simulation values for four different
23 polymerization kinetics. During the mixing phase, the temperature was recorded in order to
24 observe the impact of the mixer and the introduction of the polymerization catalyst on the
25 temperature. The modeling showed that the reaction starts directly with the introduction of the
26 catalyst and that this data should not be neglected in order to achieve the minimization. A
27 numerical study on the effect of the simulation time showed a very limited impact on the
28 estimation of the parameters. A simulation time of 350 s was chosen in order to better take
29 into account heat losses. The four polymerization kinetics were consistent with the
30 experimental data and the fit improved from kinetics #1 to kinetics #4 as the number of fitting
31 parameters increased, but the results were of the same order of magnitude. In conclusion, this
32 work presents a simple method from an experimental point of view but very effective for
33 estimating the reaction kinetic parameters of a thermosetting resin based on mimosa tannin.
34 The method can probably be adapted to other polymer systems.

35

36

37 **Keywords:** Bio-based materials; simulation; reaction kinetics parameters; estimation
38 parameters; tannin

39

40 **Highlights**

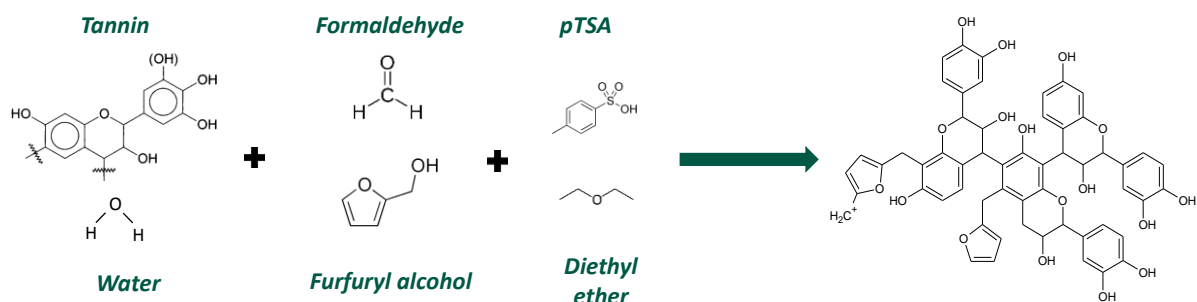
- 41 • The polymerization kinetics of a mimosa tannin-based resin were determined
- 42 • A dual approach, experimental and numerical, was used to find the kinetics parameters
- 43 • The simulation must start as soon as the catalyst is introduced
- 44 • All four polymerization kinetics provided results consistent with the experimental data
- 45 • The polymerization kinetics having 8 parameters best fits the experimental data

46

47 1. INTRODUCTION

48 Rigid polymeric foams are used in a variety of applications, from the automotive field to
49 buildings or appliance insulation. Until recently, these foams were mainly based on phenolic
50 or polyurethane resins, or on polyolefin or PVC thermoplastics. However, foams of biological
51 origin, derived from tannins, could offer an interesting and realistic alternative to
52 petrochemical foams. Tannins are phenolic constituents that can be found in different parts of
53 plants such as leaves, fruits, shells and in particular in the wood and bark of trees (Sjöström,
54 1993). Condensed tannins are the most studied tannins and can be extracted from different
55 trees such as mimosa (*Acacia mearnsii*), spruce (*Picea abies*), pine (*Pinus radiata* and *Pinus*
56 *pinaster*), quebracho (*Schinopsis balansae* and *Schinopsi lorentzii*), and larch (*Larix gmelinii*)
57 (Basso et al., 2013; Čop et al., 2014; Lacoste et al., 2015, 2014; Li et al., 2019; Zhou et al.,
58 2019). These tannins are mainly extracted from crushed bark and heartwood using a solvent,
59 generally hot water with a little sodium bisulfate added, in an autoclave. The resultant liquid
60 is then filtered and evaporated by spray drying to finally obtain a fine brown powder. The low
61 manufacturing costs, availability and non-toxicity of these natural resources have increased
62 the use of tannins to develop new materials that can compete with synthetic foams of
63 petrochemical origin.

64 The exothermic nature of the polymerization reaction between tannin, formaldehyde,
65 furfuryl alcohol and *para*-toluenesulfonic acid (pTSA) produces a foam by boiling and
66 vaporization of a blowing agent (Marie et al., 2019), such as diethyl ether (DEE) (Figure 1).



68 **Figure 1:** Reaction scheme of thermoset foams based on mimosa tannin. The polymerized
69 structure shown is only one representative example among a large number of other
70 possibilities.

71 Such a way of preparation is known as physical foaming. The generation of gas inside the
72 tannin-based thermoset resin thus produces its expansion. In parallel, as the polymerization
73 progresses, the viscosity of the reaction medium increases sharply until the resin hardens and
74 sets the final porosity. The reader can easily imagine that this process is similar to baking a
75 cake where the baking time must be carefully chosen to avoid its collapse during cooling
76 (Tondi et al., 2009). Back to the laboratory bench, it can be concluded that the
77 characterization and perfect control of the polymerization phenomenon is essential to control
78 the production of tannin-derived foams. Indeed, if the polymerization starts too early, the
79 porosity cannot be developed; if the polymerization is too late, the porous structure cannot be
80 stabilized and collapses before becoming rigid (Basso et al., 2013a; Basso et al., 2013b; Basso
81 et al., 2013c; Basso et al., 2015).

82 The foaming of tannin-based thermoset resins has been modelled by a numerical
83 approach in order to optimize their formulations and manufacturing process (Marie et al.,
84 2020). However, to allow the modelling of phenolic resins foaming, the latter study showed a
85 lack of input data concerning the evolution of viscosity and the extent of polymerization. A
86 first-order kinetics was proposed for the polymerization reaction and was introduced into a
87 general foaming model. Thus, the trends in temperature changes and foam deformation were
88 adequately predicted, but there was an overestimation of the final expansion and an
89 underestimation of the heat generated by the exothermic reactions that govern the foaming
90 mechanisms. These differences between the modelling and the experiment highlighted the
91 need to better define the polymerization kinetics and the resulting heat release. As we were

92 convinced that it was possible to do better, the aim of this new work was to improve our
93 predictions by determining the reaction kinetics.

94 The determination of the polymerization kinetics as well as the value of the enthalpy of
95 reaction is often carried out by differential scanning calorimetry (DSC) (Guigo et al., 2007).
96 However, DSC is not suitable for tannin-derived thermoset resins due to their rapid
97 polymerization reaction. When the reacting mixture is prepared, exothermic reactions start
98 suddenly and some heat is released before the mixture is poured into the crucible of the
99 instrument, and hence before data acquisition begins. To overcome these difficulties, at least
100 partially, a measurement protocol was established here to monitor temperature changes and
101 determine the polymerization kinetics by fitting the temperature evolution with a numerical
102 model. The final objective was to find the parameters of the polymerization kinetics in order
103 to minimize the difference between predicted and experimental laws.

104 This protocol included the measurement of the temperature in the bulk of the thermoset
105 resin in the absence of blowing agent. We therefore assumed that the blowing agent is a
106 chemically inert component, which does not participate in polymerization reactions. This is
107 actually the case as we here deal with a physical foaming. In parallel, a 0D numerical model
108 was developed to simulate the temperature and the progress of the reaction using the four laws
109 of polymerization presented in the next section.

110 **2. MATERIALS AND METHODS**

111 **2.1. Formulation and temperature acquisition**

112 The device used to follow the evolution of the temperature of the tannin-based thermoset
113 resin over time is now described. A "standard"-type, tannin-based, resin containing all the
114 reagents with the exception of the blowing agent (Basso et al., 2013a; Marie et al., 2020) was
115 used here, and its composition is presented in Table 1.

116 First, the tannin was dissolved in water with furfuryl alcohol and formaldehyde by
 117 mechanical stirring. The stirring speed was set at about 400 rpm for 150 s in a first beaker.
 118 The pTSA was then added and incorporated for 30 s under vigorous stirring at more than
 119 1000 rpm before being rapidly poured into the reaction cell of the experimental device. Thus,
 120 the reaction process was carried out in two stages, a "mixing" stage (in a beaker of height 4
 121 cm and diameter 3 cm) and a "reaction and cooling" stage (in a beaker of height 10 cm and
 122 diameter 6 cm), in order to get as close as possible to the protocol used in the manufacture of
 123 the foam.

124

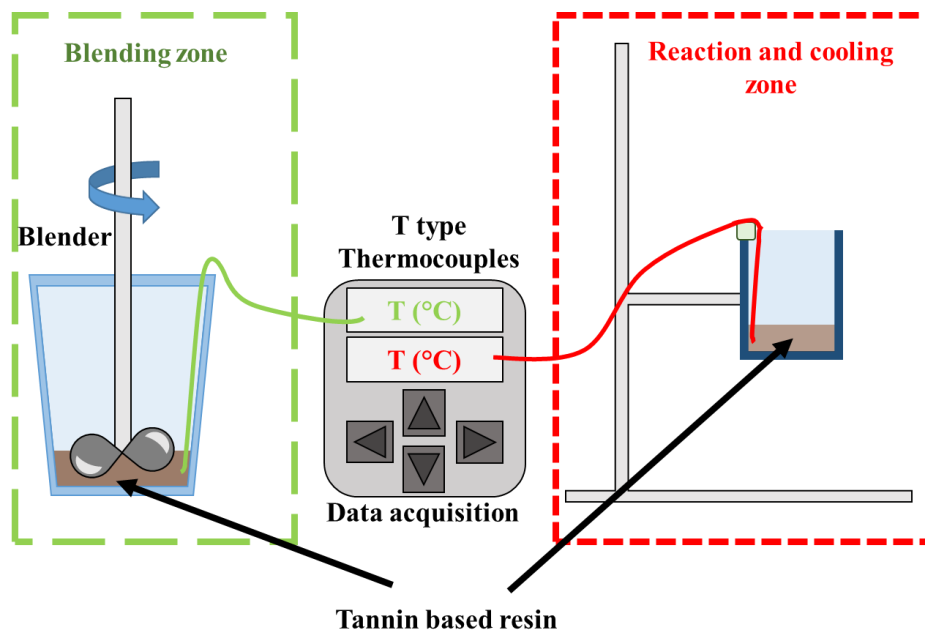
125 **Table 1** : “Standard” formulation used for the polymerization tests

Constituents	Mass (g)
Mimosa extract tannin (base of the resin)	12
Water (solvent)	2.4
Furfuryl alcohol (co-monomer and heat generator upon polymerization)	4.2
Formaldehyde (37% in water, crosslinker)	2.96
<i>para</i> -toluenesulfonic acid (pTSA, 65% in water, catalyst)	4.4

126

127 During these two steps, temperature recording was made when the reaction started well
 128 before pouring the formulation into the reaction beaker. Indeed, it is very likely that the
 129 reaction begins with the incorporation of pTSA into the reaction mixture, which is followed
 130 by 30 seconds of stirring. Taking into account the time required to pour the formulation into
 131 the mold and the time to introduce the thermocouple in the solution, a recording time of
 132 between 30 and 50s is missing. During this time, data recording is not possible although the
 133 first moments of polymerization are crucial and rich in information to determine the

134 polymerization kinetics of the system. This is an important issue to overcome. For this reason,
135 during the “mixing stage”, a thermocouple type T was placed along the inner wall of the
136 beaker to record temperatures without being affected by stirring. Then, during the "reaction
137 and cooling" phase, another thermocouple type T was immersed in the resin to record the
138 temperature during polymerization and cooling (Figure 2).



139
140 **Figure 2:** Schematic representation of the continuous temperature measurement protocol
141 during the mixing and polymerization phase

142 2.2. Reaction modeling

143 This section focuses on the numerical model developed to determine the polymerization
144 kinetics of our reaction system. Indeed, the polymerization of tannin for foaming involves a
145 multitude of reactions, which are more or less favored by thermal conditions. The reaction of
146 tannins with formaldehyde is often the only reaction taken into account in the crosslinking of
147 tannin-based thermoset resins. However, the exothermic self-condensation reaction of furfuryl
148 alcohol in the presence of acid, which results in the production of furanic polymer chains, is
149 also important, together with the reaction of furfuryl alcohol with tannin oligomers. The
150 reaction mechanisms are therefore more complex and the approach proposed here aims to

151 define a general law encompassing all the phenomena in order to feed a numerical model. Our
152 reaction modelled was the so-called "standard" formulation (Table 1) but without blowing
153 agent (diethyl ether), which is inert.

154 For this, a 0D numerical model was developed with Comsol Multiphysics in order to
155 simulate the temperature and the progress of the polymerization reaction within the initially
156 liquid formulation. We aimed to determine, by minimizing the deviation from the
157 experimental temperature, the coefficients of a polymerization law and the associated
158 enthalpy of reaction. As the test mold was thin and the heat generated was large relative to the
159 volume of phenolic resin considered, it was assumed that during exothermic reactions, the
160 temperature was homogeneous inside the mold.

161 2.2.1. Equation of extent of reaction

162 During foaming, the matrix surrounding the gas bubbles polymerizes as it expands. This
163 polymer matrix is initially liquid and its viscosity gradually increases with the reaction and
164 finally becomes rigid.

165 Several approaches have been proposed to model the reaction phenomenon for different
166 foams (epoxy, polyurethane etc.). During the reaction of polyurethane foams, an approach
167 based on the conversion of polyol, X_p , and governed by an Arrhenius law, has been proposed
168 (Baser and Khakhar, 1994a, 1994b; Ferkl et al., 2016; Geier et al., 2009; Karimi et al., 2017,
169 2016; Seo and Youn, 2005). It reads:

$$170 \quad \frac{\partial X_p}{\partial t} = A_p \exp\left(-\frac{E_p}{RT}\right) (1 - X_p) (c_{c,0} - 2c_{w,0}X_w - c_{p,0}X_p) \quad (1)$$

171 where A_p (s^{-1}) is the pre-exponential factor, E_p ($J.mol^{-1}$) is the activation energy, R is the
172 universal gas constant ($8.314 J.mol^{-1}.K^{-1}$) and T (K) is the temperature. $c_{c,0}$, $c_{p,0}$ and $c_{w,0}$
173 ($mol.m^{-3}$) are the initial concentrations of isocyanate groups, polyol groups and water,

174 respectively. Finally, X_w is the conversion of water molecules, which react with isocyanate to
175 form a urea bond and carbon dioxide.

176 Most complete model approaches include a system of partial differential equations
177 describing the reactions taking place in the polymer to calculate the gelation rate (Al-Moameri
178 et al., 2015; Ghoreishi et al., 2014; Shen et al., 2014; Zhao et al., 2014, 2013; Zhao and
179 Suppes, 2015). However, a perfect knowledge of the existing reactions is required, such as:

$$180 \quad \frac{dc_{iso}}{dt} = -r_{gel} - r_{blow} \quad (2)$$

$$181 \quad \frac{dc_{OH,i}}{dt} = -r_{gel,i} \quad (3)$$

$$182 \quad \frac{dc_{water}}{dt} = -r_{blow} \quad (4)$$

$$183 \quad \frac{dc_{ure}}{dt} = r_{gel} \quad (5)$$

$$184 \quad \frac{dc_{CO_2}}{dt} = r_{blow} \quad (6)$$

185 where c_{iso} is the concentration of isocyanate, $c_{OH,i}$ the concentration of hydroxyl groups of
186 polyol i , c_{water} the concentration of water, c_{ure} the concentration of urethane, c_{CO_2} the
187 concentration of carbon dioxide, $r_{gel,i}$ the gel reaction rate of polyol i , r_{gel} the summation of gel
188 reaction rates of polyol mixtures, and r_{blow} the blowing reaction rate.

189 In the present study, which is only a first approach, this type of methodology cannot be
190 used since not all reactions are known in our system.

191 Other authors chose a more global approach to calculate the extent of polymerization
192 reaction, ξ (dimensionless).

193 Table 2 shows the different polymerization kinetics used to simulate the polymerization
 194 reactions, depending on the authors and the types of foam used (polyurethane or epoxy).

195

196 **Table 2 :** Kinetic equations used to account for the extent of the polymerization reaction

Name	Equation	Type of foam and reference
Kinetics #1	$\frac{\partial \xi}{\partial t} = A_0 \xi^m (1 - \xi)^n$	<i>Polyurethane</i> (Abdessalam et al., 2015; Bikard et al., 2007, 2005; Dimier et al., 2002; Piloyan et al., 1966).
Kinetics #2	$\frac{\partial \xi}{\partial t} = A_0 \exp\left(-\frac{E_0}{RT}\right) \xi^m (1 - \xi)^n$	<i>Epoxy</i> (Bourdon et al., 2008; Rao et al., 2012); <i>Polyurethane</i> (Gupta and Khakhar, 1999; Marciano et al., 1986, 1982; Piloyan et al., 1966)
Kinetics #3	$\frac{\partial \xi}{\partial t} = \left(A_0 \exp\left(-\frac{E_0}{RT}\right) \right) (A_1 + \xi^m) (1 - \xi)^n$	<i>Polyurethane</i> (Rao et al., 2018, 2017)
Kinetics #4	$\frac{\partial \xi}{\partial t} = (k_1 + k_2 \xi^m) (1 - \xi)^n$	<i>Polyurethane</i> (Ireka et al., 2015)

197

198 These kinetic laws can be expressed by a more general equation introducing 8 parameters
 199 ($A_0, A_1, A_2, E_0, E_1, E_2, m$ and n) as follows:

200
$$\frac{\partial \xi}{\partial t} = k_0 (k_1 + k_2 \xi^m) (1 - \xi)^n \quad (7)$$

201 with, for $i = 0$ to 2 , $k_i = A_i \exp\left(\frac{-E_i}{RT}\right)$, where A_i , E_i , R and T have the same meaning as in Eq.

202 (1), and where m and n are constants varying from 0 to 3.

203

204 The studies cited in Table 2 highlighted that the polymerization laws depend on the
205 progress of the polymerization and on the temperature. In order to determine a specific law
206 corresponding to our reaction system, different equations have been tested as a function either
207 of the progress of the polymerization alone, or of the couple temperature - progress of the
208 polymerization. The general polymerization equation is written as follows:

$$209 \quad \frac{d\xi}{dt} = f(\xi, T) \quad (8)$$

210 *2.2.2. Equation of heat transfer*

211 The temperature was obtained by developing a simplified physical model taking into
212 account the polymerization reaction of the thermoset resin. For this, we have defined a 0D
213 numerical model that depends on the progress of polymerization ξ , temperature T (assumed
214 homogeneous within the mold), and time t .

215 The temperature variation during polymerization is due to the generation of heat by
216 exothermic reactions and to the heat exchange with the outside environment. Thus, for each of
217 the polymerization laws tested, the temperature variation was defined by the following
218 equation:

$$219 \quad \frac{dT}{dt} = -\frac{\Delta H_{pol}}{C_p} \frac{d\xi}{dt} + h_r \frac{(T_a - T)}{m_r C_p} \quad (9)$$

220 where h_T (W.K^{-1}) is the equivalent heat exchange coefficient, T_a (K) is the ambient air
221 temperature, m_r (kg) is the mass of thermoset resin, ΔH_{pol} (J.kg^{-1}) is the enthalpy of the
222 polymerization reaction, and C_p ($\text{J.kg}^{-1}.\text{K}^{-1}$) is the heat capacity of the thermoset resin.

223 2.2.3. Least squares optimization

224 The coefficients and enthalpy of polymerization of the chemical reaction were optimized
225 by the Comsol Multiphysics parameter estimation module, the convergence criterion being
226 the minimum difference between the simulated temperature and the experimental temperature
227 using the least squares method. Thus, the chosen polymerization law will be the one whose
228 objective function, Obj , is minimal. As indicated by Eq. (10), Obj is the quadratic sum of the
229 differences between simulated (T_{sim}) and experimental (T_{exp}) temperatures:

$$230 \quad Obj = \sum_{i=1}^N (T_{sim}(t_i) - T_{exp}(t_i))^2 \quad (10)$$

231 where N is the number of experimental points and t is the time.

232 The coefficients of the polymerization law were defined as parameters to be fitted by
233 applying a SNOPT-type algorithm that allows a function with several variables to be
234 minimized. SNOPT uses a sequential quadratic programming (SQP) algorithm that obtains
235 search directions from a sequence of quadratic programming sub-problems (Gill et al., 2002).
236 Each QP sub-problem minimizes a quadratic numerical model of a certain Lagrangian
237 function subject to a linearization of the constraints.

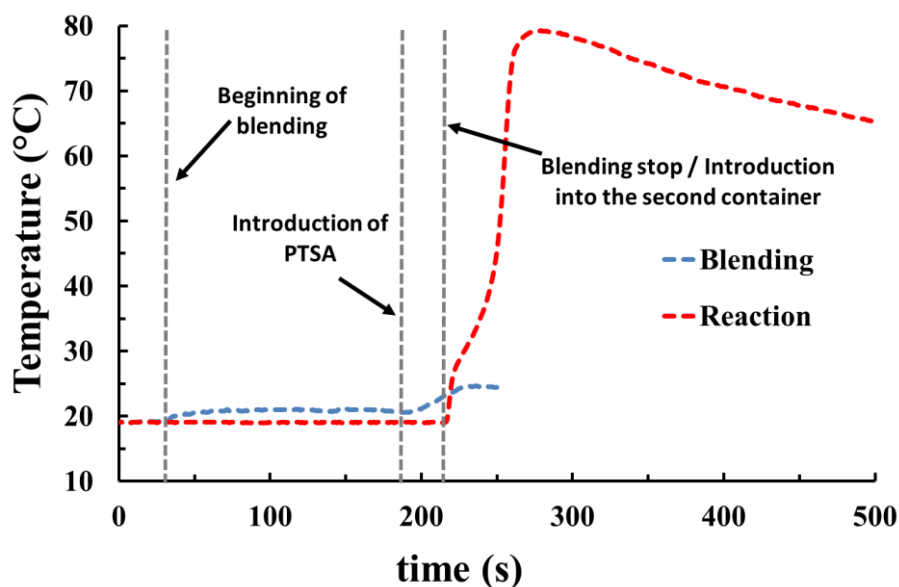
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239 3. RESULTS AND DISCUSSION

240 3.1. Experimental temperature evolution

241 Figure 3 shows the evolution of temperatures in the thermoset resin during mixing and
242 reaction, recorded as described above. Firstly, a slight temperature increase of about 2 °C was

243 recorded during the homogenization of the reagents (mixing phase), before the introduction of
244 pTSA. Since it is assumed that no reaction takes place without pTSA, this heating should
245 come from the energy supplied by the mechanical stirrer. This small temperature variation is
246 difficult to avoid with the current experimental system, which we wanted to keep as simple
247 and as functional as possible.



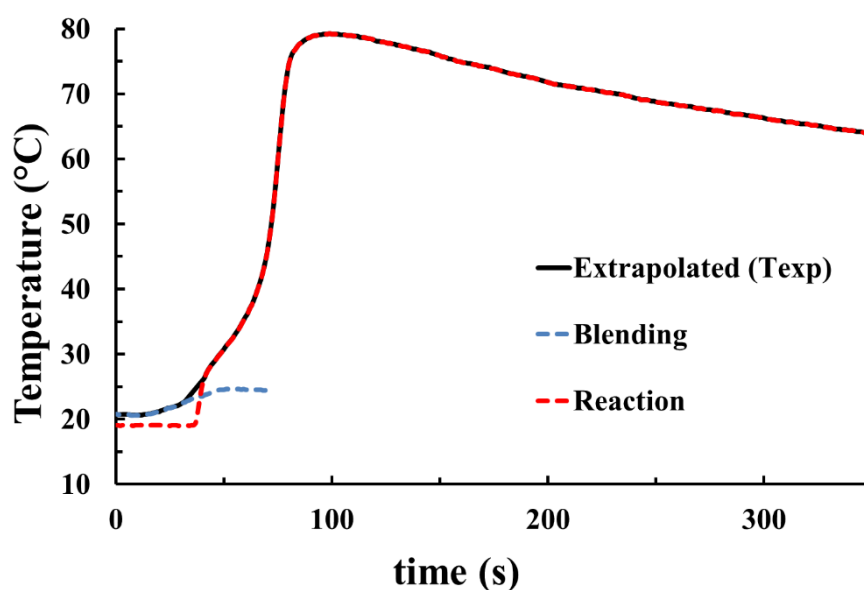
248
249 **Figure 3:** Evolution of the temperature as a function of time within the mixing container
250 (blue) and the reaction container (red).

251 Figure 3 also shows that the release of heat, due to exothermic reactions, begins a few
252 seconds after the addition of pTSA. The temperature increases exponentially as the
253 formulation is mixed until the resin is poured into the reaction container, where the curing
254 reaction continues. Recording the change in temperature over time in the mixing container has
255 provided a better understanding of what happened at the very beginning of the
256 polymerization. Thus, Figure 4 shows the addition of these two temperature curves (blending
257 and reaction), which has led to a better understanding of the polymerization kinetics.

258 The conclusions previously put forward for the evolution of foam temperatures can be
259 found. One can note a frank and rapid increase in temperature due to the release of heat by

260 exothermic reactions up to 80 °C at 90 s and a slow decrease, which seems to tend towards
261 room temperature when the polymer formed cools down. The latter point cannot be confirmed
262 since the experiments were stopped a few minutes after the end of the heat release because we
263 focused on the polymerization phenomenon. In Figure 4, a temperature of 65 °C was recorded
264 260 s after the maximum temperature.

265 This study also shows that, when the reaction mixture was poured, the polymerization
266 reactions were largely initiated, which necessitates the assumption of an initial temperature
267 above room temperature and a certain degree of polymerization progress, which is difficult to
268 measure. This is even truer as the polymerization reactions are rapid, especially when they are
269 catalyzed reactions, as it is the case here in the presence of pTSA.



270
271 **Figure 4 :** Definition of the extrapolated temperature (black line), obtained by adding the
272 temperature inside the mixing container (blue dashed line) and the temperature inside the
273 reaction container (red dashed line).

274 3.2. Determination of the parameters of the extent of reaction equations

275 In order to determine the kinetics parameters, specific to our reactions mechanism,
276 different polymerization kinetics were tested in a simple model that only calculated the

277 evolution of temperature and the extent of the thermoset resin reaction over time. The
 278 objective was to compare the experimental and the predicted temperature in order to select the
 279 best kinetics and then the corresponding kinetics parameters.

280 Table 3 shows the fixed parameters such as resin mass, specific heat capacity, atmosphere
 281 temperature, initial temperature at the introduction of the pTSA and initial extent of the
 282 reaction, which was set to zero.

283 **Table 3** : Fixed properties and initial conditions

Properties and initial condition	Value or expression
C_p , heat capacity ($\text{J.kg}^{-1}.\text{K}^{-1}$)	$2500 - 820 \xi^*$
m_r , mass of the thermoset resin (g)	10.2
T_a , ambient temperature ($^{\circ}\text{C}$)	19.8
T_0 , initial temperature ($^{\circ}\text{C}$)	20.8
ξ_0 , initial extent of reaction ($^{\circ}\text{C}$)	0

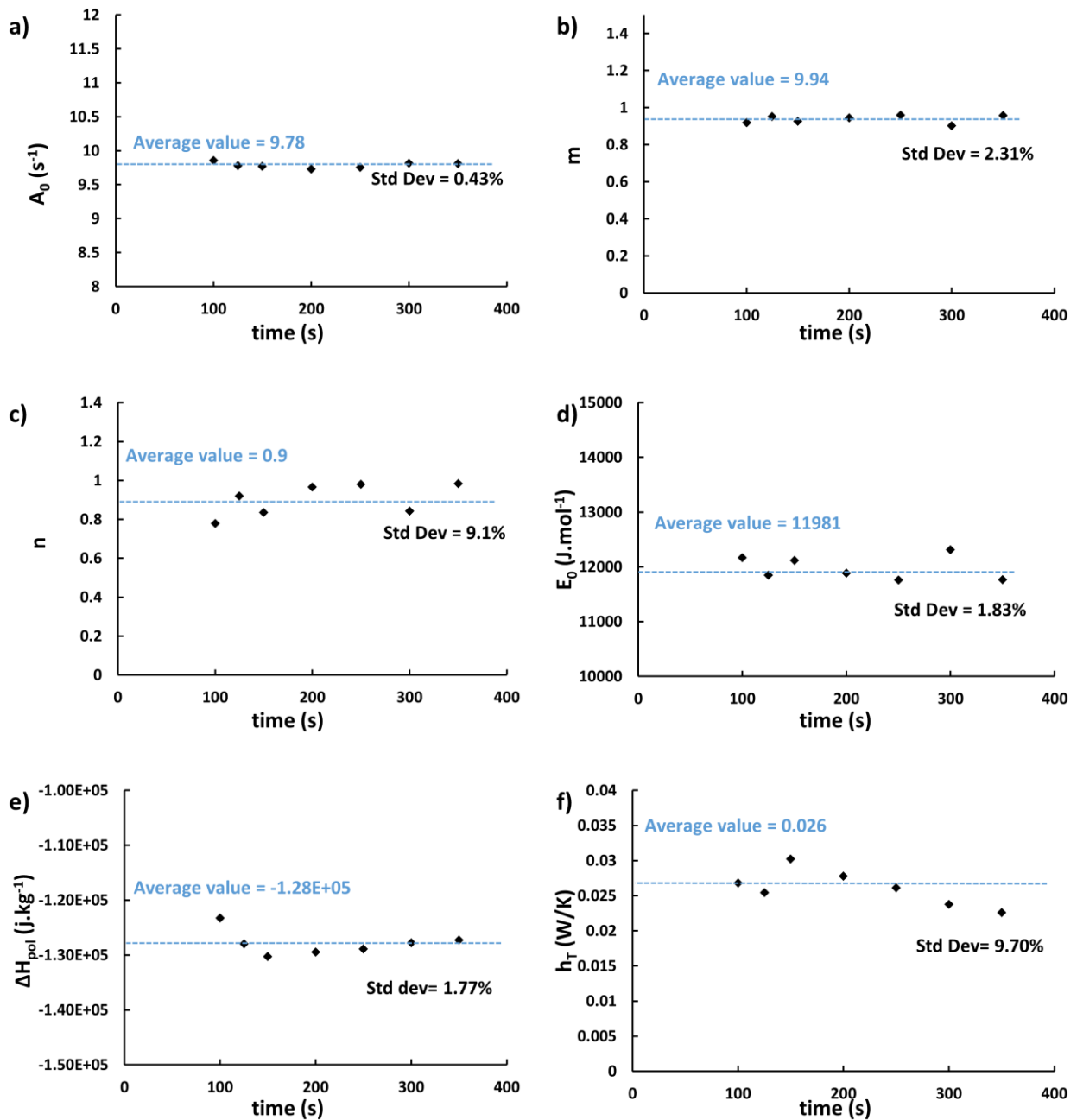
284 * estimated from a mixing rule based on DSC measurements carried out on more or less polymerized
 285 thermoset resins

286 3.2.1. Study of impact of the experimental time

287 First of all, a study was carried out to observe the impact of the experimental time
 288 considered for the simulation on the parameters set for Kinetics #2, which is the most widely
 289 used in the open literature and depends only on temperature and the progress of the reaction.
 290 Since the temperature reaches a maximum at 100 s but we recorded the temperature up to 350
 291 s, we used several values of experimental times between 100 s and 350 s (i.e., 100, 125, 150,
 292 200, 250, 300 and 350 s). The impact of the latter on the parameters of the polymerization law
 293 is shown in Figure 5.

294 This study shows a small impact of the experimental time considered on the majority of
295 the parameters (Figure 5). Indeed, for Kinetics #2, 4 parameters out of 6 have a relative
296 standard deviation of less than 2.4%. The parameters with the greatest variability are the
297 coefficients n and h_T , respectively 9.1 and 9.70%. Moreover, by observing the evolution of
298 these parameters with the experimental time, no obvious trend is observed except for h_T and n ,
299 which slightly decreased and increased, respectively, by increasing the duration taken into
300 account. For h_T , this tendency might indicate that heat losses are better taken into account in
301 our study. Concerning, ΔH_{pol} (Figure 5e), we can observe that it is approximately constant
302 after 150 s. Therefore, the other kinetics were applied to the entire recording time (350 s).

303



305 **Figure 5** : Evolution of the parameters of Kinetics #2 as a function of the simulation time for
 306 the following parameters: (a) A_0 ; (b) m ; (c) n ; (d) E_0 ; (e) ΔH_{pol} ; and (f) h_T .

307 *3.2.2. Results for reaction kinetics.*

308

309 Table 4 shows m , n , H_{pol} and h_T for the four kinetics considered, and Figure 6 shows the
 310 experimental and predicted temperatures. It is evident that the fit improves from Kinetics #1

311 to Kinetics #4 as the number of fitting parameters increases, but the results are of the same
312 order of magnitude with a relative standard deviation equal to 13.0% for m , 5.4% for n , 1.3%
313 for H_{pol} and 6.3% for h_T . The reaction order, m , is equal to 1, which is higher than values
314 found in the literature for polyurethane: 0.2 (Rao et al., 2018), 0.3 (Bikard et al., 2005), 0.5
315 (Ireka et al., 2015), 0.8 (Abdessalam et al., 2015; Dimier et al., 2002), and for epoxy: 0 (Rao
316 et al., 2012). The reaction order, n , is about 0.9 – 1 in our study, which is somewhat lower
317 than what was found for polyurethane, between 1.2 and 2 (Abdessalam et al., 2015; Bikard et
318 al., 2005; Dimier et al., 2002; Ireka et al., 2015; Rao et al., 2018), or epoxy: 1.4 (Rao et al.,
319 2012). The h_T values seem consistent since it corresponds to a convective exchange
320 coefficient equal to $2.8 \text{ W.m}^{-2}.\text{K}^{-1}$, which is the order of magnitude for natural convection.

321

322 **Table 4** : Estimated parameters for the four kinetics tested

Name	A_0 (s^{-1})	A_1 (s^{-1})	A_2 (s^{-1})	E_0 (J.mol^{-1})	E_1 (J.mol^{-1})	E_2 (J.mol^{-1})	m	n	H_{pol} (J.kg^{-1})	h_T (W.K^{-1})	Obj
Kinetics #1	0.129	0	1	0	0	0	1.07	0.885	-1.26E+05	2.13E-2	408.35
Kinetics #2	9.811	0	1	11765	0	0	0.957	0.984	-1.27E+05	2.26E-2	299.81
Kinetics #3	11.185	0.001	1	11707	0	0	1.04	0.943	-1.25E+05	2.05E-2	277.92
Kinetics #4	1	6.961	9.978	0	22813	10879	1.29	1.001	-1.24E+05	1.95E-2	225.22

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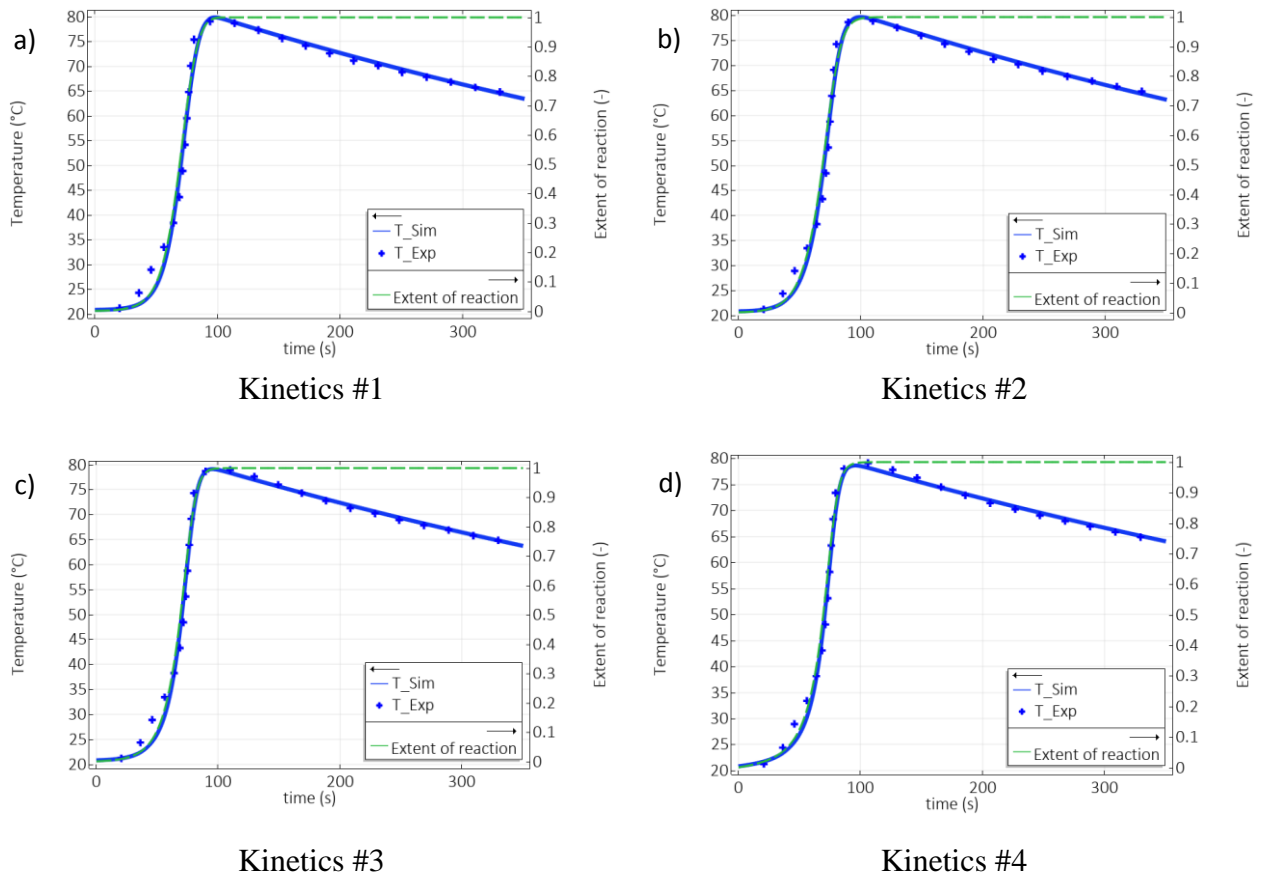
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330 **Figure 6** : Evolutions of simulated temperature (blue solid line) and extent of reaction (green
 331 dashed line), and of experimental temperature (blue plus sign) for: (a) Kinetics #1 (a); (b)
 332 Kinetics #2; (c) Kinetics #3; and (d) Kinetics #4.

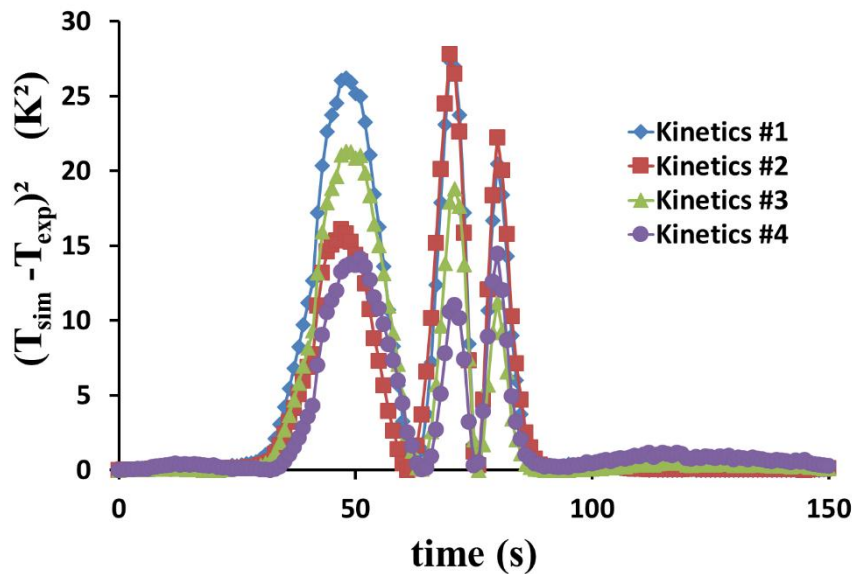
333 Figure 6 also shows that the four polymerization kinetics were able to predict temperature
 334 changes over time. Thus, the maximum temperature corresponds to complete polymerization
 335 (when the extent of reaction, ζ , reaches the value of 1), the heat released is therefore zero and
 336 the foam starts to cool from this moment.

337 Figure 7 shows the evolution of the objective function at each measurement and for each
 338 kinetics. In order to obtain a more in-depth overview of the different numerical models, the
 339 sum of the objective functions over the experimental time is also shown in .

340

341 **Table 4.**

342 The evolution of Obj over time shows that the kinetics deviated the most from the
343 experiment for times between 40 and 90 seconds, which corresponds to the stepwise increase
344 in temperature due to the polymerization reaction. It can be observed that Kinetics #4 shows
345 less variation than the other kinetics, which tends to confirm the better estimate of the
346 parameters with Kinetics #4.



347 **Figure 7 :** Objective function for each measurement point for Kinetics #1 (blue line with
348 diamonds), Kinetics #2 (red line with squares), Kinetics #3 (green line with triangles) and
349 Kinetics #4 (purple line with circles). Data are presented up to times of 150 s only for clarity
350 purposes, as there is no significant variation for longer times.

352 The four kinetics proposed for the polymerization law might be used in a future modeling
353 work, such as the simulation of the foaming kinetics of thermosetting tannin foams.
354 Obviously, if the objective is to maintain maximum accuracy, Kinetics #4 should be used as a
355 priority. However, in some cases where numerical problems may arise, a kinetics with fewer
356 parameters, such as Kinetics #2 and #3, would be of interest in order to simplify the
357 simulations. Finally, in case the simulation should be decoupled from the temperature,
358 Kinetics #1 might be used.

359

360 **4. CONCLUSION**

361 Simulation of resin thermosetting and foaming of tannin-based formulations is a relevant
362 challenge to pave the way for the paradigm shift in the chemical industry from petrochemicals
363 to biomass feedstocks. In order to find the parameters of the polymerization reaction of
364 tannin-based thermoset resins, a dual experimental and numerical approach was developed.
365 By minimizing the differences between the numerical model and the experimental evolution,
366 the parameters of several polymerization laws were found.

367 As expected, the experimental study showed that the reaction starts when pTSA is added,
368 which means that the numerical model, by which the kinetics parameters can be found, must
369 start the simulation at this moment and not at the time of pouring. A preliminary study on the
370 impact of the experimental time taken into account showed that the majority of the parameters
371 were practically unaffected. In order to use all the available data, the parameters have been
372 estimated with the longest calculation time (350 s).

373 Four kinetics describing the progression of the polymerization reaction were then tested,
374 Kinetics #1 being the law with the fewest parameters (5 parameters), and Kinetics #4 being
375 the model with the most parameters to be estimated (8 parameters). Kinetics #4 showed the
376 best results with a sum of the objective function divided by about half, compared to Kinetics
377 #1. It can be highlighted that the four models offer similar results, with a fitting close to the
378 experimental evolution. The kinetics parameters obtained in this study will be introduced into
379 a general model to simulate the expansion of tannin-based foams in a future study.

380

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