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1 Comparative curing kinetics study of high char yield 2 formaldehyde- and terephthalaldehyde-phenolic thermosets

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8 Abstract

9 Phenol-Formaldehyde (PF) resoles exhibit excellent thermal properties, high temperature
10 degradation and high char yield. The formaldehyde can be replaced by terephthalaldehyde
11 (TPA), a non-toxic aromatic dialdehyde. The thermal performances of phenol-TPA (PTPA)
12 resole are very interesting for further development and industrialization. The present
13 investigation presents for the first time a thermo-kinetics study of curing of PTPA, in
14 comparison with a commercial PF resole. Non-isothermal, at constant heating rates DSC
15 experiments are performed on both resoles. PF shows one single exothermic peak, whereas
16 PTPA exhibits two DSC peaks, suggesting a two-step curing mechanism which appears to be
17 conversion-dependent. In addition, isoconversional analysis is used to elucidate the activation
18 energies as a function of the degree of curing. Differential Friedman and integral Vyazovkin
19 methods are considered for computations, giving equivalent results. Furthermore, the whole
20 kinetic triplets (E , A , f) is elucidated for both resoles with Sestak-Berggren model fitting.
21 Finally, isothermal isoconversional predictions are compared to experimental data.

22 Highlights

- 23 • The curing kinetics of a new formaldehyde-free resole is compared to PF resole
- 24 • Isoconversional analyses are employed to determine activation energy values
- 25 • Sestak-Berggren model is used to fit the data, elucidating the kinetic triplet
- 26 • Isothermal predictions are consistent with experimental data

27 Graphical Abstract

28 **Insert Graphical Abstract**

29 **Key-words**

30 Resoles; Phenol; Terephthalaldehyde; Curing kinetics; DSC; Isoconversional analysis.

31 **Introduction**

32 Phenolic thermosets are extensively used as binders in composites in many fields of
33 applications such as microelectronics, wood industry, aerospace *etc.* [1,2]. These phenolic
34 networks (PF) are crosslinked polymers obtained by reaction between phenol and
35 formaldehyde. The mechanisms of synthesis of those PF, which involves two successive
36 steps, are perfectly described in the literature [3–14]. The first reaction consists in the addition
37 of formaldehyde onto phenol (pre-polymerization). Then, during curing, the crosslinking is
38 achieved by condensation of methylol moieties, releasing water. Two main routes are used to
39 produce high crosslinking density (Fig. 1). Novolacs are synthesized in acidic catalytic
40 conditions, whereas resoles are obtained under alkaline conditions. Moreover, the resoles
41 could reach high crosslinking and aromatic density without adding further crosslinking agent.
42 Such high aromatic densities are required to achieve the excellent thermal resistance of
43 resoles (high char yields) [15–19].

44 **Insert Fig 1 (see captions in the end of the manuscript)**

45 However, phenol and formaldehyde are rather toxic and classified as carcinogenic, mutagenic
46 and reprotoxic (CMR) substances. Especially formaldehyde is highly volatile and is classified
47 CMR 1B by the European Chemical Agency. Therefore there is sufficient evidence to
48 demonstrate its carcinogenicity on mammals and as a consequence, to presume
49 carcinogenicity for humans [20]. Thus, efforts have been focused on the substitution of the
50 formaldehyde in phenolic resins. Several challenging issues were reported, such as (i) poor
51 reactivity of higher molar mass aldehyde compounds [21], (ii) enolisable aldehydes are prone
52 to side-reactions [22] and (iii) aliphatic aldehydes significantly reduce aromatic density and
53 thus the thermal properties [23].

54 In a previous study, the reactivity of several bio-based, non-toxic and non-CMR dialdehydes
55 with phenol was evaluated [24]. Among them, terephthalaldehyde showed the best reactivity,
56 which could be explained by the presence of the second aldehyde in para-position. Indeed, the
57 second aldehyde acts as an electron-withdrawing group and thus enhances the reactivity with
58 phenol.

59 Terephthalaldehyde can be synthesized by the oxidation in vapor phase of para-xylene [25]
60 which is also the key intermediate to obtain terephthalic acid, mainly used for the production
61 of polyethylene terephthalate (PET). Bio-based routes to para-xylene have been developed in
62 order to access to fully bio-based PET, as a consequence, terephthalaldehyde is being
63 considered as a potentially bio-based building block [26].

64 In addition, the synthesized phenol-terephthalaldehyde (PTPA) resole showed a better thermal
65 resistance and char yield compared to conventional PF (Table 1). The PTPA thermosets show
66 highly crosslinked networks (networks totally insoluble in organic solvents with a low
67 swelling index). Furthermore, the rheological behavior of both PF and PTPA pre-polymers
68 are comparable. Such preliminary results are very promising for further development of
69 formaldehyde-free networks and composites, with an excellent thermal resistance and a high
70 char yield.

71 The manufacturing process of phenolic thermosets and composites is typically performed in
72 three steps: (i) synthesis of the pre-polymer (corresponding to the addition reaction in PF), (ii)
73 shaping (*i.e.* impregnation for composites) and pre-curing stage, within which partial
74 hardening of the matrix is achieved (*e.g.* pre-pregs) and (iii) post-curing stage which allows
75 complete crosslinking of the matrix. Noteworthy, the degree of curing drives all chemical and
76 physical parameters (*e.g.* rheological behavior, chemical resistance...). It is therefore of prime
77 importance to accurately control the curing kinetics all along the manufacturing process of
78 final piece.

79 The curing of phenolic thermosets is a thermally-activated process. Previous studies report on
80 the study of PF curing kinetics based on differential scanning calorimetry (DSC) experimental
81 data. In addition, several computation approaches have been studied to provide maximum
82 information on the kinetic parameters of PF curing such as model-free [27–32] and model
83 fitting kinetics [33]. Among them, the model-free kinetics approach, isoconversional analysis,
84 is known to offer accurate description of the kinetics from a short experimental dataset, with a
85 systematic and rather simple calculation process [34].

86 In the present paper, we suggest studying the curing kinetics of an innovative formaldehyde-
87 free and potentially bio-based phenolic thermoset with high char yield, *i.e.* phenol-
88 terephthalaldehyde resole, in comparison with a commercially available PF resole. Hence, the
89 curing kinetics data are provided from non-isothermal DSC experiments, at different linear
90 heating rates, following the recommendations found in literature [35]. In addition, kinetic

91 modellings are performed using isoconversional analysis. Hence, quantitative kinetic data of
92 phenol-terephthalaldehyde curing are presented. Finally, the predictability performances of
93 the kinetics parameters are evaluated.

94 **Insert Fig 2**

95 **Insert Table 1**

96 **Experimental Section**

97 **1. Materials**

98 The phenol was purchased from Alfa-Aesar. The terephthalaldehyde and the sodium
99 hydroxide were purchased from Sigma-Aldrich. PF resole was a commercially available pre-
100 polymer. The reactants and the solvent were 98-99% pure and used without further
101 purification. Pre-polymers were stored at -18 °C to avoid unwanted crosslinking.

102 **2. Pre-polymerization synthesis**

103 Phenol (1 eq.), sodium hydroxide (0.04 eq.) aqueous solution (50 wt.%) and ethanol
104 (14 wt.%) were introduced into a two-necked flask. A condenser, a magnetic stirrer and a
105 silicon oil bath were used. The temperature was set at 100 °C. When the mixture was on
106 temperature and homogeneous, terephthalaldehyde (0.4 eq.) was added (t_0). The reaction was
107 performed for 4 hours and monitored by ^1H nuclear magnetic resonance spectroscopy. The
108 color changed from orange to black between 1 and 2 h of reaction. It is important to stress
109 than after the pre-polymerization, only the first aldehyde functionality of TPA has reacted,
110 whereas the second aldehyde groups mostly remain unreacted.

111 **3. DSC**

112 The DSC-3 F200 (Netzsch) equipped with an intra-cooler module is used to carry out the
113 calorimetric study, **with nitrogen atmosphere (at 50 mL/min)**. The temperature and sensibility
114 are calibrated with biphenyl, indium, bismuth and CsCl highly pure standards, at 10 °C/min.
115 To avoid interfering endothermic signal of solvent and water evaporations, high pressure
116 stainless steel pans and lids (Netzsch) are used (maximum pressure of 100 MPa). They are
117 sealed with golden seal at 3 N·cm. The samples are weighted on a 10^{-5} g precise analytical
118 balance (between 12.00 and 20.00 mg). The sample mass demonstrates no influence on the
119 total enthalpy of the reaction. Each pan + sample is weighed before and after analysis to be

120 sure that no evaporation has disturbed the measurement. In any case, the temperature
121 considered is the sample temperature. The curing reaction is monitored by DSC at the heating
122 rates: $\beta = 5, 7.5, 10, 12.5$ and 15 °C/min, for both PF and PTPA networks.

123 4. Implementation of computations

124 The Vyazovkin method code is implemented using Python software, using the modules Scipy
125 and Numpy. Integral functions are calculated using *scipy.integral.quad* built-in function, with
126 an increment of $\Delta\alpha = 0.01$. The Friedman method ($\Delta\alpha = 0.02$ as increment) and non-linear
127 model-fitting ($\Delta\alpha = 0.01$) are used with the help of Origin software, using damped least-
128 squares algorithm (Levenberg-Marquardt), with a convergence criterion of $\chi^2 < 10^{-9}$ and a
129 maximum iteration number of 400, without any weighing of the data. For the model-fitting
130 approach, multivariate (α, T) non-linear fitting is performed on reaction rate vs. degree of
131 curing curves. All heating rate curves associated to one reaction are simultaneously fitted
132 providing a maximum consistency (for this reason fitted curves may deviate from
133 experimental data at some points). All the presented computations are tested with simulated
134 data, giving consistent results.

135 Theoretical background

136 1. Conversion calculation

137 The degree of curing (α) is assumed to be directly proportional to the released heat, measured
138 in DSC:

$$139 \quad \alpha(t, T) = \frac{\Delta H_{t,T}}{\Delta H_{TOTAL}} \quad (1)$$

140 where $\Delta H_{t,T} = \int_0^t \dot{q}(t, T) dt$ is the cumulative released heat of reaction at the time t and
141 curing temperature T , as time integral of the instantaneous heat flow ($\dot{q}(t, T)$), and ΔH_{TOTAL} is
142 the total enthalpy of the reaction determined non-isothermally (average of 5 measurements).
143 The zero degree of curing ($\alpha = 0$) corresponds to the pre-polymer.

144 2. Principles of isoconversional analyses

145 The isoconversional analysis is focused in the determination of the activation energy of a
146 chemical conversion (i.e. crosslinking). Isoconversional analysis is a powerful tool to
147 determine the activation energy of a thermally activated reaction. This analysis does not

148 require identifying the reaction model and is therefore usually called model-free kinetic
149 method. This analysis relies on the isoconversional principle: “*the reaction rate at constant*
150 *extent of conversion is only a function of temperature*” [34]. In other word, the reaction
151 mechanisms are not affected by the temperature program.

152 It is based on the variable separation (conversion, α , and temperature, T), leading to the
153 general equation of the kinetics:

$$154 \quad \frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (2)$$

155 where da/dt is the reaction rate, k is the rate constant and f is a function of the conversion
156 (representing of the reaction mechanisms). The rate constant is assumed to be described by
157 the Arrhenius equation:

$$158 \quad k(T) = A \cdot e^{-\frac{E}{RT}} \quad (3)$$

159 where A is the pre-exponential factor, E the activation energy, R the gas constant and T the
160 temperature.

161 The isoconversional principle leads to the following equation:

$$162 \quad \left[\frac{\partial \ln (d\alpha/dt)}{\partial T^{-1}} \right]_{\alpha} = \left[\frac{\partial \ln (k(T))}{\partial T^{-1}} \right]_{\alpha} + \left[\frac{\partial \ln (f(\alpha))}{\partial T^{-1}} \right]_{\alpha}. \quad (4)$$

163 Because $f(\alpha)$ is constant ($\alpha = \text{constant}$), this equation leads to the fundamental expression of
164 isoconversional analysis:

$$165 \quad \left[\frac{\partial \ln (d\alpha/dt)}{\partial T^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (5)$$

166 where E_{α} is the isoconversional value of the activation energy, *i.e.* the activation energy for a
167 given value of conversion degree, α . Hence, the activation energy is considered as a variable
168 along the transformation process [36].

169 **3. Friedman method**

170 The method of Friedman is the most common differential isoconversional method and is
171 applicable with its both differential and integral forms. The Friedman’s equations arise from
172 the previous analytical equations (2) and (3) without any approximation. Thus, this method is
173 therefore known as the reference [37].

174 The differential equation of Friedman is expressed as follows [37][37][37]:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}(t)} \quad (6)$$

175 where i represents the i^{th} temperature program and $T_{\alpha,i}$ is the temperature where the degree of
 176 curing, α , is reached under the i^{th} temperature program (depending on T in the case of non-
 177 isothermal conditions). The i index corresponds to an individual temperature for isothermal
 178 programs and to an individual heating rate for linear non-isothermal programs.

179 4. Vyazovkin method

180 Vyazovkin method (VA) is a numerical integral method [38,39]. It presents several
 181 advantages: it is applicable to both thermogravimetric and integrated DSC data, it takes into
 182 account the self-heating/cooling occurring during DSC (deviation of the sample temperature
 183 from the imposed $T = t \times \beta$, with β the heating rate value), it is applicable to any programs
 184 (cooling and multi-step programs) [34]. Moreover, integral method allows avoiding
 185 inaccuracies coming from noisy data, which are generally magnified with differential method.

186 To reach the best accuracy in determining the activation energy, small ranges of conversion
 187 degree, $\Delta\alpha$, are considered for the numerical integration. Introducing $g(\alpha)$, the integral form of
 188 $f(\alpha)$, we have:

$$189 \quad g(x) - g(\alpha - \Delta\alpha) = \int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{f(\alpha)} = A_\alpha \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} e^{-\frac{E_\alpha}{RT_{\alpha}(t)}} \cdot dt. \quad (7)$$

190 Considering the principle of isoconversional analysis, it follows:

$$191 \quad g(\alpha) - g(\alpha - \Delta\alpha) = A_\alpha \cdot J_1(E_\alpha, T_{\alpha,1}) = \dots = A_\alpha \cdot J_n(E_\alpha, T_{\alpha,n}) \quad (8)$$

192 where $J_i(E_\alpha, T_{\alpha,i})$ is the time integral of the i^{th} -temperature program $T_i(t)$:

$$193 \quad J_i(E_\alpha, T_{\alpha,i}) = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} e^{-\frac{E_\alpha}{RT_{\alpha,i}(t)}} \cdot dt. \quad (9)$$

194 In order to get free from the pre-exponential factor, the terms in equation (8) are normalized
 195 between each other, leading to a double-sum function to be minimized using the Vyazovkin
 196 method [39]:

$$197 \quad \Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i} \frac{J_i(E_\alpha, T_{\alpha,i})}{J_j(E_\alpha, T_{\alpha,j})} = n^2 - n \quad (10)$$

198 with an iterative process, E_α values are found being the solution of the minimum of Φ , the
 199 function for each isoconversion, α .

200 **Results and Discussions**

201 *1. DSC thermograms*

202 An exothermic signal is recovered during the curing reaction in all cases, as shown in DSC
203 thermograms after linear baseline correction (Fig. 3). As expected, the intensity of the
204 exothermic peak is higher at higher heating rates (as the energy amount released by the
205 reaction per unit of time is larger). Notably, we observed one single peak for PF (Fig.3PF)
206 whereas two peaks are observed for PTPA (Fig.3PTPA). In the latter case, the second peak
207 (towards higher temperature) is always a quarter less intense than the first one. The presence
208 of the two peaks in PTPA networks witnesses two successive steps during the crosslinking
209 mechanism, whereas one single step is observed in PF curing.

210 The maximum of first peak of PTPA is sensibly similar to the PF one (Table 2). The first peak
211 of PTPA crosslinking corresponds to the peak observed with PF. This suggests the same
212 reactivity and kinetics for the PF crosslinking and the reaction occurring during the 1st
213 exothermic peak of PTPA. Furthermore, the maximum of second peak of PTPA is
214 systematically 46 ± 3 °C above the first one.

215 The total enthalpy of the reaction is not dependent on heating rates for both formulations
216 (Table 2), suggesting that in both thermosets the temperature profile does not influence the
217 reaction mechanism. The total enthalpy values are respectively 349 J/g for PF and 204 J/g for
218 PTPA. The low relative standard deviation ($\leq 2\text{-}3\%$) over 5 measurements shows the good
219 reproducibility of the measurement method. The total enthalpy per gram is lower with PTPA,
220 but compared to molecular weight of typical entities, the total enthalpy gives rather similar
221 values: 68 kJ/mol for PF (with 200 g/mol, for two phenols and one methylene hinge) and 66
222 kJ/mol for PTPA (with 322 g/mol, for two phenols linked to one TPA).

223 Mechanistic information is readily provided from the thermograms. Hence, different
224 crosslinking mechanisms between PF and PTPA are observed, looking at the shape of the
225 exothermic signal. For PF, the single exothermic peak is assigned to the polycondensation of
226 the methylol groups. These moieties, which have been formed during the addition of
227 formaldehyde on phenolic rings (pre-polymerization stage), mostly condense on unreacted
228 phenolic groups. On the other hand, PTPA curing exhibits a two-step mechanism. The first
229 exothermic peak can be assigned to the condensation reaction of the secondary alcohol (which
230 has been formed during the pre-polymerization stage) onto phenol free positions (mainly

231 ortho and para, see reaction I in Fig. 2). The second peak is assigned to the addition of the
232 second aldehyde moiety onto phenol (see reaction II in Fig. 2).

233 **Insert Fig 3 PF (upper plot) and PTPA (lower plot)**

234 **Insert Table 2**

235 **2. Non-isothermal curing kinetic profiles**

236 The curing kinetic profiles of PF and PTPA are shown in Fig. 4. The degree of curing (α) is
237 plotted as a function of temperature, at different heating rates. Typical sigmoidal-shaped
238 curves are observed. The curves are shifted towards higher temperatures with higher heating
239 rates. Remarkably, the curing kinetics of PF and PTPA are quite similar for $\alpha < 0.55$. At $\alpha \sim$
240 0.55 , break-in-slopes are observed for PTPA and the curing kinetics start slower than PF. For
241 $\alpha > 0.55$, the curing kinetics of PTPA are slower than PF (*i.e.* toward higher temperatures).
242 This is explained by the two-step mechanism of PTPA curing observed by DSC.

243 The curing reaction rates are calculated as the ratio between the heat flow values and the total
244 reaction heat (ΔH_{TOTAL}). Reaction rates are plotted as a function of the curing degree (insets in
245 Fig. 4). As expected, the higher is the heating rates, the faster is the reaction, for both
246 formulations. However, the reaction curves of PTPA strongly differ from common PF. One
247 step is observed for PF curing, while two steps are obtained for PTPA.

248 Notably, the first step of PTPA curing is centered near a conversion of $\alpha \sim 0.3$, whereas the
249 second one is centered near $\alpha \sim 0.75$, independently of the temperature program. The two-
250 steps mechanism of PTPA curing is thus conversion-dependent. Because the temperature
251 program does not influence the reaction mechanism, the isoconversional principle is expected
252 to be valid.

253 **Insert Fig 4 PF (upper plot) and PTPA (lower plot)**

254 **3. Activation energy of curing**

255 The activation energy calculated by isoconversional analysis for PF and PTPA resins is given
256 as a function of the curing degree in Fig. 5. The activation energy, E_α , for PF and PTPA is
257 ranged between 70 and 80 kJ/mol. The PF curve of activation energy does not exhibit strong
258 variations with the degree of curing. E_α increases from *ca.* 70 kJ/mol to reach a maximum of
259 80 kJ/mol near $\alpha \sim 0.75$, prior to slightly decrease in the later stage of curing. The PTPA
260 curve shows more variations. The activation energy is relatively constant at low degrees of

261 curing (78 kJ/mol for $\alpha < 0.3$), then linearly decreases down to 70 kJ/mol, for $0.3 < \alpha < 0.75$.
262 Finally, the activation energy starts increasing slightly for $\alpha > 0.75$, which is assigned to
263 increasing uncertainties (such errors probably arise from integration).

264 Two isoconversional methods are tested in parallel: the Vyazovkin (VA) and the Friedman
265 (FR). VA is an integral method – *i.e.* the activation energy is from integral kinetics profiles
266 (eq. 9-10, Fig. 4), whereas FR is a differential method – *i.e.* calculations are made from
267 differential curves (Fig. 4 insets). FR method provides elucidation of activation energy with
268 an analytical algebraic formula without any approximation. Arrhenius plots and linear
269 regressions of FR method are shown in Fig. 6. The coefficients of determination (inset in Fig.
270 6) are satisfying ($R^2 > 0.97$) in the complete range of curing degrees for PF and PTPA (for $\alpha <$
271 0.8). For the later, the coefficients of determination decrease down to 0.90 for $\alpha > 0.8$, which
272 results in higher uncertainties in activation energy values (represented by broader error-bars in
273 Fig. 5). Remarkably, VA and FR methods give consistent results. The excellent agreement
274 for both VA and FR allows concluding on the accuracy of the obtained results.

275 The evolution of the activation energy with the degree of curing is informative about the
276 crosslinking process. A rather monotonic shape of E_α for PF is observed due to the one-step
277 mechanism of crosslinking, *i.e.* the condensation of methylol group. The slight increase of E_α
278 is assigned to an increase of molecular motion restrictions due to the forming of a three-
279 dimensional crosslinked network. Hence, the apparent activation energy increases with the
280 degree of curing due to more intense diffusional potential barrier to overcome. Yet, because
281 this increase remains slight, diffusion phenomena are not expected to drastically slow down
282 the kinetics such as epoxy curing [40,41], for instance. During PF crosslinking, reactive
283 species (*i.e.* methylol group) are surrounded by free-position in phenol rings at any time,
284 unlike epoxy curing where reactive moieties are carried by dangling chains. In this latter case
285 such reactive moieties may be trapped into the polymer network, which drastically slows
286 down the curing kinetics (diffusion-controlled regime) [45].

287 On the other hand, the activation energy evolution with α of PTPA is more complex. The
288 experimentally observed two-steps curing can be observed on E_α curve, as well. The
289 activation energy plateau value, $E_\alpha = 78$ kJ/mol for $\alpha < 0.3$, is assigned to the condensation of
290 the secondary alcohol onto phenols (first reaction corresponding to first exothermic peak
291 observed in DSC thermograms). Then during the transient regime, the decrease of E_α for $0.3 <$
292 $\alpha < 0.75$ is associated to the shift in the curing process mechanism, from the first reaction to
293 the addition onto phenol of the second aldehyde function for the one-fold reacted TPA

294 (second reaction consistent with the second exothermic peak). The activation energy value
295 associated to the second reaction is determined at 70 kJ/mol, at $\alpha = 0.75$. The slight increase
296 of E_α during the later stage of curing is assigned to diffusional restrictions. In overall, the
297 activation energy values of PTPA are similar to the studied PF and other resole
298 [27,28,31,33,42].

299 **Insert Fig 5**

300 **Insert Fig 6 PF (upper plot) and PTPA (lower plot)**

301 *4. Determination of the kinetic triplet using a model-fitting approach*

302 In order to provide a full description of the curing kinetics of both resoles (elucidation of the
303 kinetic triplet: A , E , $f(\alpha)$), we used the previous results of activation energy to reduce the
304 number of unknown in the model-fitting approach. To model the curing reaction of phenolic
305 resin [33], the truncated Sestak-Breggren (SB) model is used with the following expression
306 [43]:

$$307 \quad f(\alpha) = (1 - \alpha)^n \cdot \alpha^m \quad (11)$$

308 where n and m are the partial reaction orders. For PF resins, which presents one single step
309 mechanism, following fitting function was employed:

$$310 \quad \frac{d\alpha}{dt} = A e^{-\frac{E}{RT(\epsilon)}} \cdot (1 - \alpha)^n \alpha^m \quad (12)$$

311 with a fixed value of $E = 78$ kJ/mol, being the average activation energy value found with
312 previous isoconversional analysis. The fitted curves are displayed in the upper plot of Fig. 7.
313 Small deviations are observed due to simultaneous fitting. Nevertheless, the accordance
314 between fits and experimental data is good ($R^2 > 0.99$), leading to a good accuracy on the
315 fitting parameters (Table 3).

316 On the other hand, the PTPA curing must be analytically described by two successive steps
317 ($\frac{d\alpha}{dt} = \sum_i k_i f_i(\alpha)$, with $i = 1, 2$) [34]. Thus, reaction rate vs. degree of curing curves are first
318 deconvoluted with two Gaussian peak functions ($R^2 > 0.97$, global fits are shown in Fig. 7).
319 Then, the deconvoluted peaks are consecutively fitted with equation (12). The activation
320 energies are fixed at $E = 78$ and 72 kJ/mol, for the 1st and 2nd reaction, respectively. SB fits of
321 the deconvoluted curves are rather satisfying ($R^2 > 0.97$), as shown in the lower plot of Fig. 7.

322 The pre-exponential factor values vary significantly for PF and both reaction of PTPA (Table
323 3). Such large variations from resin to resin or along the curing process are noticed when
324 comparing literature values [30,44,45].

325 The partial reaction order m of PF is close to 0 (Table 3), concluding in a very low
326 autocatalytic behavior during the curing process. The reaction could therefore be described by
327 a simpler n^{th} order model (with a reaction order close to $n = 1.1$, which is in line with [33]). In
328 contrast, the m values of PTPA are higher. For the first reaction, the value $m = 0.87$ suggests a
329 higher autocatalytic behavior than PF. n of the second PTPA reaction is quite high due to the
330 shift in curing process from 1st to 2nd reaction. By symmetry, m order of second PTPA
331 reaction is also high (due to delayed starting of the 2nd reaction). It is important to stress that
332 these results must be taken carefully because of difficulties in mechanisms elucidation from
333 non-isothermal DSC data, and especially in multi-step mechanism reactions.

334 **Insert Fig 7 PF (upper plot) and PTPA (lower plot)**

335 **Insert Table 3**

336 **5. Isothermal predictions using isoconversional analysis**

337 One of the most industrially relevant applications of one kinetic analysis is the predictions at
338 both any time and temperature. Hence, one can easily tailor the curing stages (pre- and post-
339 curing) of the thermoset. Furthermore, predictions allow either confirming or infirming the
340 validity of the kinetics description when compared to experimental data.

341 The time needed to reach a certain α at the isothermal temperature T_0 , t_{α, T_0} , is calculated with
342 the following equation [46]:

$$343 \quad t_{\alpha, T_0} = \sum \alpha \frac{\hat{J}(E_{\alpha, T})}{\exp\left(-\frac{E_{\alpha}}{RT_0}\right)} \quad (13)$$

344 where $\hat{J}(E_{\alpha}, T_{\alpha})$ denotes the average of the J functions from all heating rates dataset (rather
345 than an arbitrary single one). Predictions are computed at each isoconversion ($\Delta\alpha = 0.01$
346 increments). Note that only the elucidation of J functions and E_{α} are necessary to compute
347 predictions. To evaluate the predictions accuracy, the simulated curves are compared to
348 experimental results. The isothermal temperature is selected at $T_0 = 160$ °C, being the working
349 temperature for curing the commercial PF.

350 Both predicted and experimental isothermal kinetic profiles of PF and PTPA are shown in
351 Fig. 6. Both PF and PTPA isothermal kinetic profiles exhibit a deceleratory shape, typical of

352 thermoset crosslinking. Notably the slopes at $\alpha = 0$ are similar for PF and PTPA. Then the PF
353 shows a faster isothermal kinetics that of PTPA. The completion is reached within 1 h for PF,
354 whereas the profile level off near $\alpha \sim 0.9$ for PTPA.

355 The accordance between experimental and predicted curves is excellent for both PF and
356 PTPA. Isoconversional analysis (VA method) provides accurate description of the curing
357 kinetics. Notably, the two-step mechanism of PTPA is well characterized by the variable
358 apparent activation energy along the curing process.

359 **Insert Fig 8**

360 **Conclusions**

361 The present investigation gave insights for the curing behavior of phenol-terephthalaldehyde
362 (PTPA) resoles, which was totally unknown. The curing kinetics of PTPA was compared to a
363 commercial PF resole. The thermosets were probed with non-isothermally DSC, at constant
364 heating rates. Furthermore, computational approaches were performed to get maximum
365 benefits from experimental data. Isoconversional analysis was computed using the differential
366 Friedman (FR) and integral Vyazovkin (VA) methods. The values of activation energy found
367 with both methods were in excellent accordance, allowing concluding on the high accuracy of
368 the presented kinetics data. Then, model-fitting approach was taken using Sestak-Berggren
369 model, to elucidate the kinetic triplet of each reaction.

370 Different curing behaviors were recorded between PF and PTPA. One single step was
371 observed for PF, which corresponded to the polycondensation of methylol moieties releasing
372 water. On the other hand, a two-step mechanism was observed for PTPA. The first was
373 assigned to the polycondensation of secondary alcohols (formed during the first addition of
374 TPA on phenol), whereas the second peak was assigned to the addition of the second
375 aldehyde moiety of TPA onto phenol. Further investigations are ongoing and will be reported
376 elsewhere.

377 In conclusion, despite different crosslinking mechanisms were observed for PF and PTPA, the
378 curing kinetic parameters showed rather similar values. Finally, isoconversional analysis
379 provided sufficient accurate description of the kinetics, as attested with the good correlation
380 between isothermal predictions and experimental data. The generated kinetics data will be of
381 a precious help for both future development and engineering of PTPA resins or completing
382 mechanistic elucidations of innovative resoles.

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514 **Fig. captions**

515 **Fig. 1** – The two main routes to synthesize PF thermosets: Novolac and Resole.

516 **Fig. 2** – Probable reactions of pre-polymerization and curing between phenol and
517 terephthalaldehyde.

518 **Fig. 3** – DSC thermograms after baseline corrections PF and PTPA.

519 **Fig. 4** – Non-isothermal kinetics profiles, inset: reaction rate as function of degree of curing.

520 **Fig. 5** – Activation energy of phenol-formaldehyde (PF) and phenol-terephthalaldehyde
521 (PTPA) as a function of the degree of curing as calculated with Vyazovkin (VA) and
522 Friedman (FR) isoconversional methods.

523 **Fig. 6** – Arrhenius plots of the Friedman method for PF and PTPA curing systems. Insets
524 display the determination coefficients of linear regressions, as a function of the degree of
525 curing.

526 **Fig. 7** – Model-fitting with SB model for PF and PTPA resins. For PTPA, SB model is fitted
527 on the deconvoluted peaks.

528 **Fig. 8** – Comparison of predicted and measured isothermal kinetic profiles, at 160 °C, of PF
529 ($R^2 > 0.99$) and PTPA ($R^2 > 0.98$) resin.

530 **Table captions**

531 **Table 1** – Comparison of properties between PF and PTPA networks [24].

532 **Table 2** – Total enthalpy and peak maximum as measured by DSC for PF and PTPA.

533 **Table 3** – Kinetic parameters of PF and PTPA as determined with the model-fitting approach
534 (with associated uncertainties of the fits).

535