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

Lérys Granado, Romain Tavernier, Gabriel Foyer, Ghislain David, Sylvain Caillol

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

Lérys Granado[1], Romain Tavernier[1], Gabriel Foyer[2], Ghislain David[1], Sylvain Caillol[1*]

[1] *Institut Charles Gerhardt UMR 5253, CNRS, Université de Montpellier, ENSCM, 240, Avenue Professeur Emile Jeanbrau, 34296 Montpellier, France*

[2]*ArianeGroup, Rue de Touban, 33185 Le Haillan, France.*

**Corresponding author:* sylvain.caillol@enscm.fr

Abstract

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

Highlights

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

Graphical Abstract

Insert Graphical Abstract

Key-words

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

Introduction

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

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

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

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

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

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

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

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

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

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

Insert Fig 2

Insert Table 1

Experimental Section

1. Materials

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

2. Pre-polymerization synthesis

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

3. DSC

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

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

4. Implementation of computations

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

Theoretical background

1. Conversion calculation

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

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

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 curing temperature T, as time integral of the instantaneous heat flow ($\dot{q}(t,T)$), and ΔH_{TOTAL} is the total enthalpy of the reaction determined non-isothermally (average of 5 measurements). The zero degree of curing (α = 0) corresponds to the pre-polymer.

2. Principles of isoconversional analyses

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

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

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

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

where $d\alpha/dt$ is the reaction rate, k is the rate constant and f is a function of the conversion (representing of the reaction mechanisms). The rate constant is assumed to be described by the Arrhenius equation:

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

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

The isoconversional principle leads to the following equation:

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

Because $f(\alpha)$ is constant (α = constant), this equation leads to the fundamental expression of isoconversional analysis:

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

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

3. Friedman method

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

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

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

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

4. Vyazovkin method

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

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

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

Considering the principle of isoconversional analysis, it follows:

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

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

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

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

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

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

Results and Discussions

1. DSC thermograms

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

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

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

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

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

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

Insert Table 2

2. Non-isothermal curing kinetic profiles

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

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

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

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

3. Activation energy of curing

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

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

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

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

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

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

Insert Fig 5

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

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

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

$$f(\alpha) = (1-\alpha)^n \cdot \alpha^m \tag{11}$$

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

$$\frac{d\alpha}{dt} = A\, e^{-\frac{E}{RT(t)}} \cdot (1-\alpha)^n \alpha^m \tag{12}$$

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

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

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

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

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

Insert Table 3

5. Isothermal predictions using isoconversional analysis

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

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

$$t_{\alpha,\mathrm{T0}} = \sum_{\alpha} \frac{\hat{J}(E_\alpha,T)}{exp\left(-\frac{E_\alpha}{RT_0}\right)} \quad (13)$$

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

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

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

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

Insert Fig 8

Conclusions

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

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

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

References

[1] Hirano K, Asami M. Phenolic resins-100 years of progress and their future. React Funct Polym 2013;73:256–69. doi:10.1016/j.reactfunctpolym.2012.07.003.

[2] Takeichi T, Furukawa N. Epoxy Resins and Phenol-Formaldehyde Resins. Polym. Sci. A Compr. Ref., Elsevier; 2012, p. 723–51. doi:10.1016/B978-0-444-53349-4.00157-6.

[3] Pizzi A, Stephanou A. On the chemistry, behavior, and cure acceleration of phenol–formaldehyde resins under very alkaline conditions. J Appl Polym Sci 1993;49:2157–70. doi:10.1002/app.1993.070491212.

[4] Pizzi A, Garcia R, Wang S. On the networking mechanisms of additives-accelerated phenol - Formaldehyde polycondensates. J Appl Polym Sci 1997;66:255–66.

[5] Holopainen T, Alvila L, Rainio J, Pakkanen TT. Phenol- formaldehyde resol resins studied by 13C- NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. J Appl Polym Sci 1997;66:1183–93. doi:10.1002/(SICI)1097-4628(19971107)66:6<1183::AID-APP18>3.3.CO;2-4.

[6] Park B-D, Riedl B, Bae H-J, Kim YS. Differential scanning calorimetry of phenol-formaldehyde (PF) adhesives. J Wood Chem Technol 1999;19:2279–89. doi:10.1080/02773819909349612.

[7] Pilato L. Phenolic resins: 100Years and still going strong. React Funct Polym 2013;73:270–7. doi:10.1016/j.reactfunctpolym.2012.07.008.

[8] Pizzi A, Horak RM, Ferreira D, Roux DG. Condensates of phenol, resorcinol, phloroglucinol, and pyrogallol as model compounds of flavonoid A- and B- rings with formaldehyde. J Appl Polym Sci 1979;24:1571–8. doi:10.1002/app.1979.070240618.

[9] Astarloa-Aierbe G, Echeverría JM, Mondragon I. Kinetics of phenolic resol resin formation by HPLC. III: Zinc acetate. Polymer (Guildf) 1999;40:5873–8. doi:10.1016/S0032-3861(98)00816-7.

[10] Astarloa Aierbe G, Echeverría JM, Martin MD, Etxeberria AM, Mondragon I. Influence of the initial formaldehyde to phenol molar ratio (F/P) on the formation of a

411 phenolic resol resin catalyzed with amine. Polymer (Guildf) 2000;41:6797–802.
412 doi:10.1016/S0032-3861(00)00044-6.

413 [11] Astarloa-Aierbe G, Echeverría JM, Vázquez A, Mondragon I. Influence of the amount
414 of catalyst and initial pH on the phenolic resol resin formation. Polymer (Guildf)
415 2000;41:3311–5. doi:10.1016/S0032-3861(99)00519-4.

416 [12] Grenier-Loustalot MF, Larroque S, Grande D, Grenier P, Bedel D. Phenolic resins: 2.
417 Influence of catalyst type on reaction mechanisms and kinetics. Polymer (Guildf)
418 1996;37:1363–9. doi:10.1016/0032-3861(96)81133-5.

419 [13] Zamfirova G, Cherneva S, Gaydarov V, Djourelov N. Nanocomposites based on epoxy
420 resin. Simulation of microindentation process. Colloids Surfaces A Physicochem Eng
421 Asp 2014;460:254–64. doi:10.1016/j.colsurfa.2014.03.056.

422 [14] Gabilondo N, Martín MD, Mondragon I, Echeverría JM. Polymerization of
423 formaldehyde and phenol at different pressures. High Perform Polym 2002;14.

424 [15] Park BD, Wang XM. Thermokinetic behavior of powdered phenol-formaldehyde (PPF)
425 resins. Thermochim Acta 2005;433:88–92. doi:10.1016/j.tca.2005.02.016.

426 [16] Park BD, Kadla JF. Thermal degradation kinetics of resole phenol-formaldehyde
427 resin/multi-walled carbon nanotube/cellulose nanocomposite. Thermochim Acta
428 2012;540:107–15. doi:10.1016/j.tca.2012.04.021.

429 [17] Bessire BK, Minton TK. Decomposition of Phenolic Impregnated Carbon Ablator
430 (PICA) as a Function of Temperature and Heating Rate. ACS Appl Mater Interfaces
431 2017;9:21422–37. doi:10.1021/acsami.7b03919.

432 [18] Kershaw D, Still RH, Bashford VG. Thermal degradation of polymers. IX. Ablation
433 studies on composites: Comparison of laboratory test methods with tethered rocket
434 motor firings. J Appl Polym Sci 1975;19:983–98. doi:10.1002/app.1975.070190407.

435 [19] Natali M, Kenny JM, Torre L. Science and technology of polymeric ablative materials
436 for thermal protection systems and propulsion devices: A review. Prog Mater Sci
437 2016;84:192–275. doi:10.1016/j.pmatsci.2016.08.003.

438 [20] Agency EC. Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). 2015.

[21] Pilato L. Phenolic Resins: A Century of Progress. 2010.

[22] Smith M, March J. Advanced Organic Chemistry: Reactions, Mechanisms and structure. vol. 4.Ed. 1991.

[23] Pizzi A, Mittal KL. Handbook of Adhesive Technology. second ed. n.d.

[24] Foyer G, Chanfi BH, Virieux D, David G, Caillol S. Aromatic dialdehyde precursors from lignin derivatives for the synthesis of formaldehyde-free and high char yield phenolic resins. Eur Polym J 2016;77:65–74. doi:10.1016/j.eurpolymj.2016.02.018.

[25] Simmons KE, Williams JE. Oxidation of p-xylene to terephthalaldehyde. US4017547A, 1977.

[26] Boukis AC, Llevot A, Meier MAR. High Glass Transition Temperature Renewable Polymers via Biginelli Multicomponent Polymerization. Macromol Rapid Commun 2016;37:643–9. doi:10.1002/marc.201500717.

[27] Gabilondo N, López M, Ramos JA, Echeverría JM, Mondragon I. Curing kinetics of amine and sodium hydroxide catalyzed phenol-formaldehyde resins. J Therm Anal Calorim 2007;90:229–36. doi:10.1007/s10973-006-7747-3.

[28] Wang J, Laborie MPG, Wolcott MP. Comparison of model-free kinetic methods for modeling the cure kinetics of commercial phenol-formaldehyde resins. Thermochim Acta 2005;439:68–73. doi:10.1016/j.tca.2005.09.001.

[29] Lee YK, Kim DJ, Kim HJ, Hwang TS, Rafailovich M, Sokolov J. Activation energy and curing behavior of resol- and novolac-type phenolic resins by differential scanning calorimetry and thermogravimetric analysis. J Appl Polym Sci 2003;89:2589–96. doi:10.1002/app.12340.

[30] He G, Riedl B, Aït-Kadi A. Model-free kinetics: Curing behavior of phenol formaldehyde resins by differential scanning calorimetry. J Appl Polym Sci 2003;87:433–40. doi:10.1002/app.11378.

[31] He G, Riedl B, Aït-Kadi A. Curing process of powdered phenol-formaldehyde resol resins and the role of water in the curing systems. J Appl Polym Sci 2003;89:1371–8. doi:10.1002/app.12417.

[32] Tejado A, Kortaberria G, Labidi J, Echeverria JM, Mondragon I. Isoconversional kinetic analysis of novolac-type lignophenolic resins cure. Thermochim Acta 2008;471:80–5. doi:10.1016/j.tca.2008.03.005.

[33] Lei Y, Wu Q. Cure kinetics of aqueous phenol-formaldehyde resins used for oriented strandboard manufacturing: Effect of wood flour. J Appl Polym Sci 2006;102:3774–81. doi:10.1002/app.24739.

[34] Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochim Acta 2011;520:1–19. doi:10.1016/j.tca.2011.03.034.

[35] Vyazovkin S, Chrissafis K, Di Lorenzo ML, Koga N, Pijolat M, Roduit B, et al. ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. Thermochim Acta 2014;590:1–23. doi:10.1016/j.tca.2014.05.036.

[36] Vyazovkin S. A time to search: finding the meaning of variable activation energy. Phys Chem Chem Phys 2016;18:18643–56. doi:10.1039/C6CP02491B.

[37] Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. J Polym Sci Part C Polym Symp 1964;6:183–95. doi:10.1002/polc.5070060121.

[38] Vyazovkin S. Model-free kinetics. J Therm Anal Calorim 2006;83:45–51. doi:10.1007/s10973-005-7044-6.

[39] Vyazovkin S, Dollimore D. Linear and Nonlinear Procedures in Isoconversional Computations of the Activation Energy of Nonisothermal Reactions in Solids. J Chem Inf Model 1996;36:42–5. doi:10.1021/ci950062m.

[40] Corezzi S, Fioretto D, Santucci G, Kenny JM. Modeling diffusion-control in the cure kinetics of epoxy-amine thermoset resins: An approach based on configurational entropy. Polymer (Guildf) 2010;51:5833–45. doi:10.1016/j.polymer.2010.09.073.

[41] Granado L, Kempa S, Bremmert S, Gregoriades LJ, Brüning F, Anglaret E, et al. Isothermal DSC Study of the Curing Kinetics of an Epoxy/Silica Composite for

Microelectronics. J Microelectron Electron Packag 2017;14:45–50. doi:10.4071/imaps.359903.

[42] Rivero G, Pettarin V, Vázquez A, Manfredi LB. Curing kinetics of a furan resin and its nanocomposites. Thermochim Acta 2011;516:79–87. doi:10.1016/j.tca.2011.01.022.

[43] Šesták J, Berggren G. Study of the kinetics of the mechanism of solid-state reactions at increasing temperatures. Thermochim Acta 1971;3:1–12. doi:10.1016/0040-6031(71)85051-7.

[44] Park B, Riedl B, Kim YSOO, So WONTEK. Effect of Synthesis Parameters on Thermal Behavior of Phenol – Formaldehyde Resol Resin 2001:1415–24. doi:10.1002/app.2302.

[45] Alonso M V., Oliet M, García J, Rodríguez F, Echeverría J. Gelation and isoconversional kinetic analysis of lignin-phenol-formaldehyde resol resins cure. Chem Eng J 2006;122:159–66. doi:10.1016/j.cej.2006.06.008.

[46] Samuelsson LN, Moriana R, Babler MU, Ek M, Engvall K. Model-free rate expression for thermal decomposition processes: The case of microcrystalline cellulose pyrolysis. Fuel 2015;143:438–47. doi:10.1016/J.FUEL.2014.11.079.

Fig. captions

Fig. 1 – The two main routes to synthetize PF thermosets: Novolac and Resole.

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

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

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

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

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

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

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

Table captions

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

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

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