Prediction of Curing Kinetics of Resorcinol-Added Resole Phenolic Resins using DSC for the Fabrication of C/C Composites

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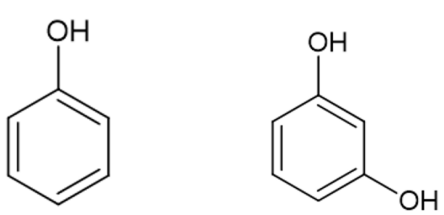
Phenolic resins are commonly used as carbon precursors for the fabrication of Carbon/Carbon composites due to their high carbon yield and aromatic nature. To decrease curing times, acid catalysts are generally used, but the addition of resorcinol was found to have a similar effect while being incorporated into the resin matrix with no contamination or corrosion issues. In this work, the curing kinetics of pure, 10, 20 and 30 wt% resorcinol-added phenolic resins were investigated through differential scanning calorimetry. Heating rates of 0.5, 1, 2.5 and 5 °C min^{-1} were used with several curing models to predict isothermal curing. Averaged MAE (mean absolute error) for the isoconversional mathematical approaches namely Kissinger-Akahira-Sunose (MAE = 12.9 min), Flynn-Wall-Ozawa (15.8 min) and Vyazovkin (14 min) show that these methods provide the best predictions, attributed to their adoption of an activation energy that depends on the extent of cure ($E_a(\alpha)$). The Kissinger method (MAE = 36 min), which depends only on peak temperature with a constant activation energy assumption, and the data noise sensitive Friedman model (MAE = 1144.7 min) provide the least accurate results. Thermogravimetric analysis revealed that resorcinol decreases the curing times by up to 71% without lowering carbon yield.

1 Introduction

Phenolic resins have a wide variety of applications, such as wood adhesives, aerospace components and composites. These thermoset resins can be cured by a number of methods, such as acid, base, or thermal action [1]. Phenolic resins provide high thermal conductivity and long term thermal and mechanical stability [2]. Formed from the reactions between phenol (Figure 1(a)) and formaldehyde, the ratio of reactants is one of the factors that determines curing properties of phenolic resins into two distinct categories: resoles and novolaks. Resoles are cured using an excess of formaldehyde under acidic, basic or thermal conditions, while novalaks use excess phenol and are manufactured under acidic conditions.



(a) Phenol (b) Resorcinol

Figure 1: Comparison of phenol and resorcinol molecules.

Due to their high carbon yield and aromatic nature, phenolic resins are commonly used as a carbon matrix precursor for the fabrication of Carbon/Carbon (C/C) composites. These composites are made of carbon fibers reinforced with a continuous carbonaceous matrix. Due to the high strength and thermal conductivity combined with low thermal expansion coefficients and densities, C/C composites are typically used in space and aerospace industries, such as heat shields for re-entry of space vehicles and disk brakes on airplanes [3, 4]. The thermal and mechanical performance of C/C composites is directly correlated to

the type of carbon matrix precursor used and its carbon yield [5]. Additionally, a carbon precursor with an aromatic nature can facilitate the formation of a graphitized carbon matrix, which favors heat transfer and improves mechanical properties of C/C composites [3, 6, 7]. The precursors that best fit these criteria are pitch, mesophase pitch [8, 9], and phenolic resins [10]. Phenolic resins have a distinct advantage over pitch due to their ease of use that allows for carbon fibers to be impregnated at room temperature, while providing a high carbon yield [8].

For phenolic resins, curing is divided into three distinct stages: A, B and C. A-stage curing is characterized by the beginning of condensation reactions of the monomers, including the reaction between phenol and formaldehyde. These pre-polymers are generally dissolved in solvents to facilitate handling and impregnation and have no evidence of cross-linking [1]. B-stage curing is identified by a great increase in the viscosity of the mixture, with some cross-linking occurring. The transition between A-stage and B-stage curing is commonly known as the gel time (gelling), determined by the increase in viscosity due to rapid increase in molecular weight. The bulk of polymer cross-linking happens during C-stage curing, resulting in a 3D cross-linked network. The reduction of curing times through the addition of catalysts is a common approach that allows for cure at lower temperatures, thus reducing processing costs [11]. For resoles, the addition of a strong acid catalyst greatly increases reaction rate, resulting in a highly exothermic reaction. This, in turn, leaves very little time for appropriate composite processing [1]. The addition of phosphoric acid [12], however, has been shown to reduce curing times in a more controlled manner, producing materials with low void content. Through a different mechanism, basic catalysts, such as potassium and sodium hydroxide, can also accelerate the curing rate [13]. The use of acid and basic catalysts is known to cause corrosion issues to process equipment, thus increasing costs due to need of using corrosive resistant materials [1, 2]. These catalyst components remain in the cured resin matrix and may affect the final mechanical properties of the composite [12]. In addition, when it comes to the production of C/C composites, the use of catalysts may decrease carbon yield, which is a major factor that impacts the mechanical and thermal properties of the finalized composite [14].

Due to its higher reactivity, resorcinol has been used as a modifier in phenolic resins, decreasing curing times and temperatures [1, 2, 15, 16] without the addition of contaminants. Resorcinol has a similar structure to phenol: the presence of two hydroxyl functional groups attached to an aromatic benzene ring (Figure 1(b)) makes it more reactive than phenol (Figure 1(a)). One of the most popular applications is in wood adhesives, allowing for phenolic resins to cure even at room temperature [1, 17, 18, 19, 20, 21]. Although the curing kinetics of the resorcinol resin counterpart (resorcinol-formaldehyde resin) have been recently investigated [22], resorcinol-added phenolic resins is yet to be effectively explored. Two limited characterization studies have been performed on this class of resin system, earlier by S. Chow (1977) [15] and later by J. Lisperguer et al (2005). [23]. There is, however, limited experimental data to accurately predict resorcinol-added resin cure behavior, and no supporting cure modelling study has been attempted, which this work aims to cover. The current study will use DSC (differential scanning calorimetry) not only to investigate the curing kinetics of resorcinol-added phenolic resins, but also to evaluate the accuracy of different curing models that are based on constant DSC heating rate experiments.

By using the DSC methodology described in Section 3.3, a relationship between the peak temperature, heating rate, and extent of cure was obtained and used with a variety of different mathematical methods [24, 25, 26, 27, 28, 29]. The most widely used method, which is also evaluated in this work is the Kissinger model [30], which is based on an assumption that with a constant heating rate, the maximum rate of reaction coincides with the point of maximum heat transfer [31]. Thus, for a given heating rate, a corresponding peak temperature can be used to obtain the derived activation energy and pre-exponential factor in an Arrhenius model of curing rate. Other methods are also used here to evaluate kinetic data including the Kissinger-Akahira-Sunose (KAS) [32], Flynn-Wall-Ozawa (FWO) [33, 24, 34], Friedman (FR) [35, 26], and Vyazovkin (VO) methods [36, 37]. These models allow the time-dependent extent of cure to be calculated at isothermal conditions. Furthermore, the use of isothermal DSC data presented in this work is used to evaluate the accuracy of these models [31]. For the first time, a commercially available resole phenolic resin (Georgia-Pacific Chemicals LLC / GP® 5236H) with added resorcinol is investigated in this work. The resin has a high carbon yield (62.3%), making it attractive for the fabrication of aviation and space

materials, such as C/C composites. The effect of resorcinol addition on carbon yield is also investigated using TGA (thermogravimetric analysis).

2 Theory

The curing of thermosetting resins involves the irreversible conversion of relatively small monomers to solid materials. The extent of cure, or degree of conversion (α), is defined as the process of changing the properties of the resin by increasing viscosity, gelation, and hardening. For thermosetting resins, cure is the formation of the polymer network, and cross-linking is usually promoted by a heat treatment. The heat released during the reaction is generally assumed to be proportional to the extent of cure (α), which is defined by Equation 1 [38]:

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{t\to\infty}} \tag{1}$$

where $\Delta H(t)$ is the partial heat of reaction up to time (t) and $\Delta H_{t\to\infty}$ is the total heat of reaction. By using this relation, models have been developed with the aim of predicting the extent of cure given an isothermal condition, which in turn can be used to model and optimize curing processes that involve pure and resorcinol-added phenolic resins. Thus, by using the Arrhenius relation, the extent of cure can be correlated with the activation energy (E_a) and the pre-exponential factor (A), as shown in Equation 2:

$$\frac{d\alpha}{dt} = A\exp\Big(-\frac{E_a}{RT}\Big)f(\alpha) \tag{2}$$

where R is the gas constant, T is the absolute temperature, and $f(\alpha)$ is a conversion factor particular to the reaction model used, which is also time dependent. For solid state reactions, such as the curing of resins, this relation of conversion with time and temperature is commonly used as a basis for the development of models [38]. For an nth order reaction, the model may be described with Equation 3:

$$f(\alpha) = k(1-\alpha)^n \tag{3}$$

where k is the kinetic constant, and n is the reaction order. When dealing with non-isothermal conditions at a constant heating rate ($\beta = dT/dt$), a new relation can be obtained from the Arrhenius equation, as shown in Equation 4.

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\,\beta = A\exp\Big(\frac{-E_a}{RT}\Big)f(\alpha) \tag{4}$$

The integral form of Equation 4, referred to as $g(\alpha)$, is also useful for multiple methods. The temperature integral seen below (Equation 5) cannot be algebraically solved, but multiple approximations have been developed, denoted by $p(x)$, where $x = E_a R^{-1}T^{-1}$.

$$\begin{aligned} g(\alpha) &= \frac{A}{\beta}\int_0^T \exp\left(\frac{-E_a}{RT}\right)dT \\ &= \int_0^\alpha \frac{1}{f(\alpha)}d\alpha \\ &= \frac{AE_a}{\beta R}p(x) \end{aligned} \tag{5}$$

Constant heating rate (β) DSC experiments can provide the extent of cure as a function of time (α from Equation 1) and temperature, which can be used in conjunction with mathematical methods to obtain activation energy values. First proposed by Vyazovkin (1996) [36], by assuming that the kinetic parameters are the same for a given conversion (α), Equation 5 can be equated to Equation 6 to obtain Equation 7.

$$g(\alpha) = A \int_0^t \exp\left(\frac{-E_a}{RT}\right) dt \tag{6}$$

$$t_\alpha = \frac{\int_0^T exp(-E_a(\alpha)/RT)dT}{\beta exp(-E_a(\alpha)/RT_0)} \tag{7}$$

Thus, with the activation energy calculated, the reaction time when curing has reached an arbitrary degree of conversion can be determined. Note that by using this approach, the calculation of the pre-exponential factor (A) for isothermal curing predictions is not necessary.

In the Kissinger model, the order (n) of the cure reaction needs to be known or assumed, which then describes the model function $f(\alpha)$ in the form of a reaction model [39]. The curing of resins involves a complex chain of reactions that is not easily described by a single reaction model. With this in mind, model-free kinetic methods have been developed by tying the activation energy to the conversion. The KAS, FWO, FR and VO models all use this approach, where the dependency of the activation energy on the conversion ($E_a(\alpha)$) have proved to provide more accurate predictions [36]. These methods are the most widely used in literature and are evaluated in this work by comparing with experimental data to assess their accuracy. A brief description with the equations used for each method is presented next.

2.1 Kissinger method

The Kissinger model [30] is a widely used method to calculate activation energy using DSC analysis with different constant heating rates (β). It starts from the assumption that for a given heating rate, there will be a point at which the rate of reaction will be at its maximum, defined as peak temperature (T_p). Furthermore, the mechanism to be modelled cannot involve multiple reactions, allowing for an increase in heating rate to be reflected into an increase in peak temperature. By taking the derivative of Equation 2 and equating it to zero, which corresponds to the point of maximum rate of cure, the relation shown in Equation 8 is obtained. The kinetics is then described by a reaction model of order n [39] for $f(\alpha)$.

$$E_a\beta(RT_p^2) = Af'(\alpha)exp\Big(\frac{-E_a}{RT_p}\Big) \tag{8}$$

The Kissinger model can be used to calculate activation energy and the pre-exponential factor by first assuming a first order reaction ($f(\alpha) = 1-\alpha$), and taking the logarithm of Equation 8 to obtain Equation 9:

$$-\ln\Big(\frac{\beta}{T_p^2}\Big) = -\ln\Big(\frac{AR}{E_a}\Big) + \Big(\frac{1}{T_p}\Big)\Big(\frac{E_a}{R}\Big) \tag{9}$$

Plots of $\ln\left(\beta T_p^{-2}\right)$ versus T_p^{-1} can then be used to calculate A and E_a. A major disadvantage of this method is the assumption that activation energy is to remain constant throughout the curing process, which is unlikely given the multiple reactions that are involved during the curing of phenolic resins. To calculate the extent of cure as a function of time, Equation 2 is solved for $\alpha(t)$. Assuming a first order reaction, Equation 10 is thus obtained, where k is the Arrhenius relation (Equation 11). In this approach, both activation energy and pre-exponential factor are necessary in order to calculate the extent of cure.

$$\alpha(t) = 1 - \exp(-k(T)t) \tag{10}$$

$$k(T) = A\exp\Big(-\frac{E_a}{RT}\Big) \tag{11}$$

2.2 Kissinger-Akahira-Sunose method (KAS)

The curing reactions of thermosetting resins are generally composed of several reactions between monomers, dimers and subsequent oligomers. Thus, the activation energy is not constant through the process. The KAS method [32], a derivation of the Kissinger method [30], calculates the activation energy as a function of the percentage cure. Being an isoconversional method, rather than using peak temperature, the KAS method uses the temperature corresponding to a given degree of conversion (T_α), which changes for different heating rates. This technique assumes that the activation energy is constant only within the conversion step ($\Delta\alpha$). Thus, the smaller the conversion step ($\Delta\alpha$), the more precise the results will be. The general equation for the KAS method is Equation 12, where the slope of the graph of $ln(\beta T_\alpha^{-2})$ versus T_α^{-1} gives the activation energy as a function of the extent of cure at each conversion step.

$$\ln\Big(\frac{\beta}{T_\alpha^2}\Big) = \frac{-E_a(\alpha)}{RT_\alpha} + \ln\Big(\frac{AR}{E_a(\alpha)}\Big) - \ln g(\alpha) \tag{12}$$

Note that it is not necessary to obtain the values for A and $g(\alpha)$ in order to calculate the activation energy. The KAS method uses the Doyle's Approximation [40] for temperature integral, as shown in Equation 13.

$$p(x) = \exp(-1.0518x - 5.330) \tag{13}$$

2.3 Flynn-Wall-Ozawa method (FWO)

The FWO method [34] is an improved version of a method originally developed by Ozawa [33]. It uses an isoconversional approach, as shown in Equation 14, where the activation energy can be determined from the slope of $\ln(\beta)$ vs T^{-1}. The FWO method uses the Coats and Redfern approximation (Equation 15 [41]) for the temperature integral. Similar to the KAS method, the time to cure is divided into steps of conversion ($\Delta\alpha$).

$$\ln(\beta) = \frac{-1.052E_a(\alpha)}{RT_\alpha} + \Big(\ln\Big(\frac{AE_a(\alpha)}{R}\Big) - \ln g(\alpha) - 5.331\Big) \tag{14}$$

$$p(x) = \frac{\exp(-x)}{x^2}\Big(1 - \frac{2}{x}\Big) \tag{15}$$

2.4 Friedman method (FR)

The FR approach [35] is a differential method that accounts for the extent of cure as a function of time to find the activation energy. By also considering the activation energy as a function of conversion, the main relation for the FR method is shown in Equation 16. A linear regression of $\ln(\beta d\alpha/dt)$ vs. T_α^{-1} is used to calculate the activation energy. The FR method also uses the Coats and Redfern approximation for the temperature integral (Equation 15).

$$\ln\Big(\beta\frac{d\alpha}{dt}\Big) = \frac{-E_a(\alpha)}{RT} + \big(\ln A + \ln f(\alpha)\big) \tag{16}$$

2.5 Vyazovkin method (VO)

Vyazovkin [36, 37] developed a new approach to calculate the activation energy and solve the temperature integral without the need of obtaining the pre-exponential factor (A), while still considering the dependency of the activation energy on the degree of conversion ($E_a(\alpha)$). From Equation 5, the method starts from the general assumption that the reaction kinetics is independent of the heating rate [36], and thus the temperature integral ($g(\alpha)$, Equation 17) can be taken as equal for a set of experiments, as demonstrated in Equation 18. The time integral ($J[E_a(\alpha), T]$ in Equation 19) can then be used to obtain an expression for the activation energy.

$$g(\alpha) = \frac{A}{\beta} I[E_a(\alpha), T] \tag{17}$$

$$\frac{A}{\beta_i} I[E_a(\alpha, T)]_i = \frac{A}{\beta_j} I[E_a(\alpha, T)]_j \tag{18}$$

$$g(\alpha) = AJ[E_a(\alpha), T] \tag{19}$$

By combining A from Equations 18 and 6, a set of equations (Equation 20) can be obtained, which can then be minimized using numerical methods to calculate the activation energy (E_a), where m is the number of available constant heating rates DSC experiments to be used for data fitting.

$$\sum_{i=1}^{m} \sum_{j \neq 1}^{m} \frac{J[E_a(\alpha), T]_i \beta_j}{J[E_a(\alpha), T] \beta_i} = m! \tag{20}$$

With the activation energy calculated for a given extent of cure (α), the temperature integral ($I[E_a(\alpha), T]$) is solved numerically, and is used to calculate the time to reach a given conversion using Equation 7. For the VO method, the commercially available software Wolfram Mathematica v12.0 ® was used to minimize Equation 20 and find activation energies.

3 Methodology

3.1 Materials

Phenolic resin was supplied by Georgia-Pacific Chemicals LLC as a commercial resole resin (GP® 5236H). Resorcinol with a 99% concentration was obtained from BeanTown Chemical and acetone (99.5%) was acquired from VWR Chemicals. Nitrogen (N_2, 99.9%) used for the DSC analysis and TGA (see sections 3.3 and 3.4) was purchased from Linde.

3.2 Sample preparation

The phenolic resin with added resorcinol was prepared by first heating the pure resin at 40 °C for 24 hours in a convection oven to remove solvents. This temperature was chosen to prevent the cure reaction from starting, while also decreasing the viscosity to assist in mixing with a stir bar. The solvent-removed resin weight was then measured using a weighing balance with a precision of 0.0001 g, and used to determine the amount of resorcinol to be added to obtain the desired concentration. Resorcinol was pulverized and added to the resin after solubilizing with acetone. The resorcinol-resin mixture was then combined with constant stirring until a homogeneous solution was obtained. Next, the mixture was left at 40 °C for 24 hours to aid in removing the added acetone. Pure phenolic resin and 10, 20, and 30 weight percent (wt%) resorcinol-added phenolic resins were prepared and analyzed using DSC and TGA.

3.3 Differential scanning calorimetry analysis

DSC measures physical and chemical changes of a material in response to temperature. At a given heating rate, heat flux data as a function of temperature are obtained in a differential thermogram. DSC analysis were done using a TA Instruments DSC 2500 with Tzero hermetic aluminium pans. Tests were conducted at constant heating rates of 0.5, 1.0, 2.5 and 5.0 °C min^{-1} between 40-250 °C. Between 1-10 mg of resin were added to the aluminium pans, depending on the heating rate used. Smaller sample amounts were used at higher heating rates to prevent excessive vapor release, which can add endothermic peaks that mask the curing reaction.

Isothermal DSC tests were conducted for 8 hours at 130 °C. This temperature was chosen because it best balances clear peaks for analysis, while not requiring excessively long curing times. The analysis was done by ramping the temperature to 130 °C, taking between 2 to 5 minutes to stabilize. Although the

resin does start curing during this lag time, it is assumed to be insignificant when considering the total cure time. The isothermal DSC analysis was done in triplicates to ensure repeatability.

3.4 Thermogravimetric analysis (TGA)

To evaluate carbon yield of pure and resorcinol-added phenolic resins, TGA (TA Instruments TGA 5500 with alumina pans) was done under nitrogen atmosphere. Around 40 mg of sample was first heated to 250 °C with a hold time of 1 hour to promote curing, followed by heating to 1000 °C at a rate of 1 °C min^{-1}, leaving behind mostly carbon. Carbon yield is thus evaluated by comparing the initial weight of the cured resin with the final weight after the heat treatment at 1000 °C.

4 Results and discussion

4.1 Pure phenolic resin

Thermograms obtained using DSC were used to fit different methods to predict isothermal extent of cure with respect to time. Due to its exothermic nature, the degree of cure of the phenolic resin can be correlated to its thermal peak in the DSC thermogram, where extent of cure is calculated using Equation 1. To illustrate the typical DSC analysis data experimentally obtained, Figure 2 shows the thermograms for pure phenolic resin at 0.5, 1, 2.5 and 5 °C min^{-1}, with their corresponding peak temperatures. The slight endothermic behavior near 100 °C is attributed to water and solvent volatilization, which does not significantly affect the peaks related to the curing reaction. The start of resin curing is characterized by the increase of exothermic measurements, reaching a maximum rate at the peak temperature (T_p), and slowly decreasing as curing is finalized. Since the rate of curing will depend on both temperature and time, an increase in heating rate generally causes the peak of the exothermic curve to shift to a higher temperature for a given system [42]. This trend is observed for pure phenolic resins, but it is not always the case when multiple reactions are involved, as discussed in Section 4.2.

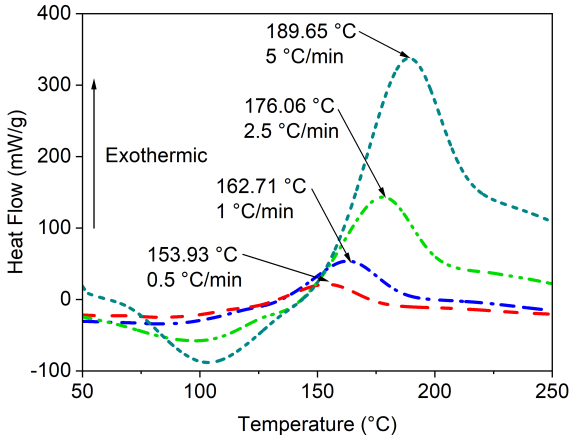


Figure 2: Comparison of DSC thermograms at different heating rates for pure phenolic resin.

4.2 Resorcinol addition

By adding the more reactive resorcinol to the commercial phenolic resin, a shift of the peaks to a lower temperature is expected, to indicate a faster curing rate. Table 1 shows peak temperatures for each concentration and heating rates evaluated. When comparing pure phenolic resin with the higher resorcinol concentrations (20 and 30 wt%), a decrease of around 24 °C in peak temperature is observed, which can be attributed to an increase in rate of curing. Although there is an overall decrease in peak temperature with resorcinol addition, there is a only a slight increase in peak temperature between 0 and 10 wt%, and little difference between 20 and 30 wt%. This may be seen as a contradiction to the faster rate of curing that

resorcinol gives but, an analysis of the DSC thermograms provides a better explanation of the mechanism responsible for these behaviors.

Table 1: Peak temperatures (°C) for different resorcinol concentrations.

Resorcinol	0.5°C min^{-1}	1.0°C min^{-1}	2.5°C min^{-1}	5.0°C min^{-1}
0	153.93	162.71	176.06	189.65
10%	156.70	165.43	180.84	191.86
20%	130.35	139.62	152.99	164.59
30%	130.74	139.98	154.60	166.46

Figure 3 shows a DSC data comparison between pure phenolic resin, 10, 20 and 30 wt% added resorcinol. It can be observed that with 10 wt% resorcinol, the curve displays two merged peaks, where the first is closer to the 20 and 30 wt% resorcinol systems, while the second and highest peak is very close to the peak temperature obtained for pure phenolic resin (Table 1). This highlights why the peak temperatures between pure phenolic resin and 10 wt% added resorcinol are similar, since the second peak is predominant. This behavior is consistent with results reported by Lisperguer et al. (2005) [23] for lower concentrations of resorcinol, where the authors have suggested that the first peak corresponds to the more reactive resorcinol, while the second peak relates to the phenol/formaldehyde reactions. This shows that resorcinol addition acts as a reagent modifier, decreasing curing times differently than catalysts. Rather than increasing rates of reaction through changes in activation energy, there is a change in the curing reactions themselves. Thus, a shift towards the resorcinol side of the reaction occurs which, due to its higher reactivity, results in the rate of curing to increase. From Figure 3, for the 20 and 30 wt% resorcinol systems, only one prominent peak is observed in the resorcinol side of the curve, showing that for the higher concentrations, the first peak dictates the curing behavior. Additionally, for these higher concentrations systems, the peak does not change significantly, but rather the area under the curve does. This demonstrates that relying only on peak temperature is insufficient to accurately predict curing.

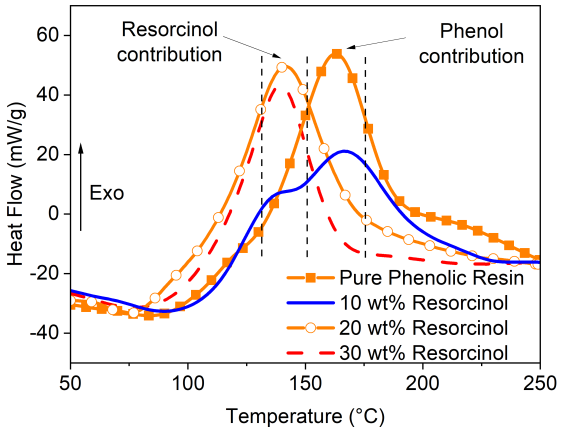


Figure 3: DSC thermogram for 10 wt% Resorcinol compared with pure, 20 and 30 wt% resorcinol-added phenolic resins at 1 °C min^{-1}.

4.3 Isothermal conversion

Isothermal DSC tests were conducted at a constant temperature of 130 °C, so that the corresponding exothermic peak can be used to obtain extent of cure over time with Equation 1. This temperature was chosen since it provides enough heat of reaction so that area under the curve can be measured and correlated to extent of cure over time ($\alpha(t)$), while also avoiding long curing times. For pure phenolic resin (Figure 4), all the methods with the exception of FR provided good predictions when compared to the experimental data, with a slight under prediction of the curing time. The FR method has been shown to be numerically unreliable due to its dependency on the rate of cure values ($d\alpha/dt$), which are slopes of

experimental data that are particularly sensitive to data noise [43, 44]. In addition, Sbirrazzuoli (2007) [45] has demonstrated that the FR method does not produce accurate results in systems where the heat of reaction changes with temperature (i.e. with heating rate). This is characteristic of complex resin curing systems, where multiple types of reactions can occur at different temperatures (like the case of resole phenolic resins in this study), where the author recommends the use of the VO method instead. The poor performance of the FR method continues for the resorcinol-added systems (see Figures 5 through 7). The similarity of the results between the Kissinger model and the more robust isoconversional methods (KAS, FWO and VO) show that, for systems that have a single DSC peak, such as the pure phenolic resin, the Kissinger model actually provides good estimates for isothermal curing.

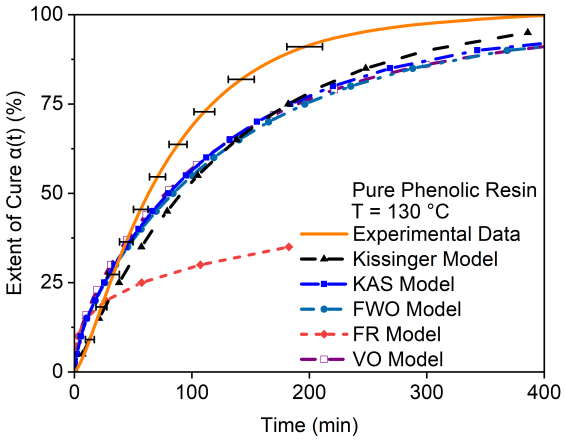


Figure 4: Isothermal extent of cure comparison between methods and experimental data for pure phenolic resin.

The most discrepancies between the methods can be observed with 10 wt% resorcinol-added phenolic resin (Figure 5). The KAS method slightly over-predicts the rate of curing to around $\alpha = 80\%$, while both VO and FWO methods are most accurate in that region. The Kissinger model greatly underpredicts curing times because of its reliance only on peak temperature. These results confirm what has been discussed in Section 4.2, that isoconversional methods (KAS, FWO, VO) have a distinct advantage in complex resin systems, such as the curing of resorcinol-added phenolic resins. The KAS, FWO and VO models are successfully able to account for the double peak behavior in the DSC thermograms that the 10 wt% resorcinol system displays (Figure 3), since activation energy is not assumed constant as in the Kissinger model, but rather as a function of conversion.

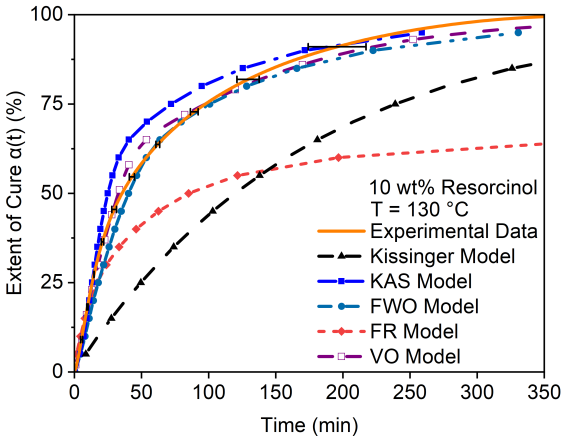


Figure 5: Isothermal extent of cure comparison between methods and experimental data for 10 wt% resorcinol-added phenolic resin.

For 20 and 30 wt% resorcinol (Figures 6 and 7), the isoconversional methods, with the exception of FR,

provide good predictions of curing times. The Kissinger method slightly overpredicts curing times while the FR method continues to perform poorly. As discussed in Section 4.2, systems with 20 and 30 wt% resorcinol have one distinct peak, which explains the results of the Kissinger method. However, due to its reliance only on peak temperatures, the Kissinger model is not recommended for resorcinol-added phenolic resin systems, especially with low concentrations of resorcinol. In the case of the VO method, due to its friendly form for numerical algorithms, a very small conversion step ($\Delta\alpha$) of 0.1% helps to reduce errors from numerical approximations, providing the most accurate predictions.

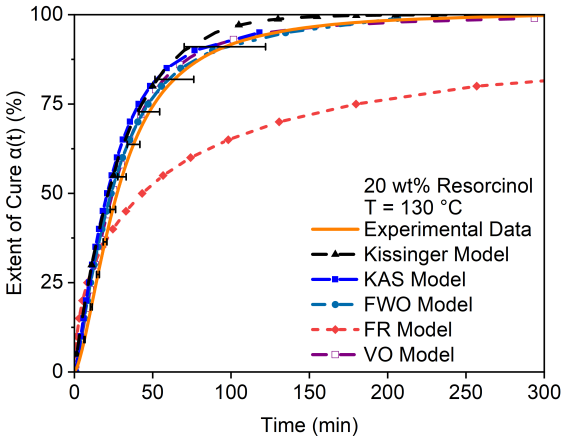


Figure 6: Isothermal extent of cure comparison between methods and experimental data for 20 wt% resorcinol-added phenolic resin.

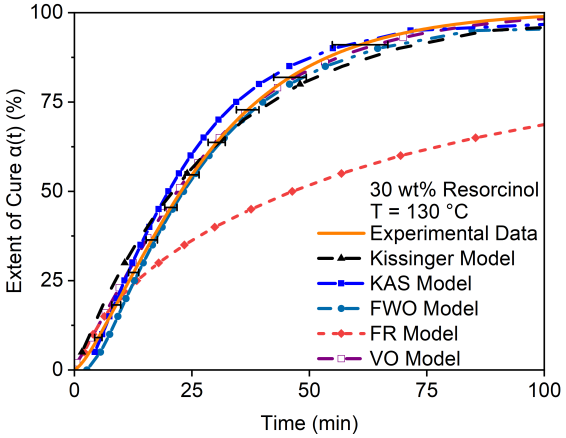


Figure 7: Isothermal extent of cure comparison between methods and experimental data for 30 wt% resorcinol-added phenolic resin.

In Figure 8, time to reach conversions of 50% and 90% are shown for the experimental data, the Kissinger model, and the VO method, to illustrate the decrease in curing times due to resorcinol addition. An endpoint of 90% was chosen to shorten the numerical modelling times. For the experimental data, it is clearly observed that adding resorcinol increases rates of cure, taking 65% and 71% less time to reach 50% and 90% extent of cure, respectively. Due to the reasons discussed (e.g. peak temperature shifts), the Kissinger model also results in a decrease in curing times between pure and 20/30 wt% resorcinol, but the model incorrectly predicts an increase in curing times for 10 wt%. Following the same trend as the experimental data, the VO method predicts a progressive decrease in curing times with higher concentrations of resorcinol.

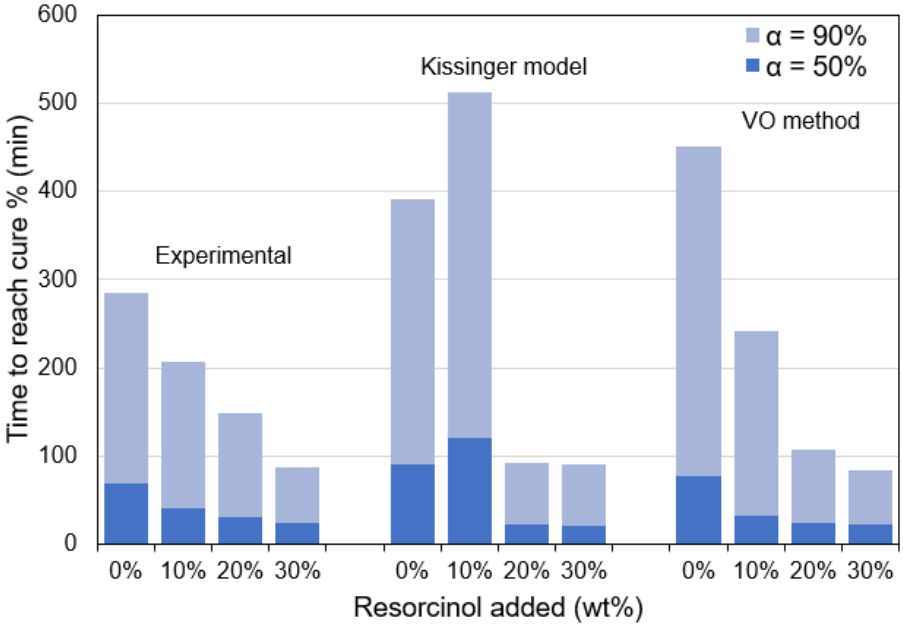


Figure 8: Time to reach 50% and 90% extent of cure (α) for each resorcinol concentration. Comparison between experimental data and results from the Kissinger and VO methods.

To evaluate the overall accuracy of the models, the mean absolute error (MAE) was calculated between predictions and experimental data, using Equation 21.

$$\mathrm{MAE} = \frac{1}{N}\sum_{i=1}^{N} |t_{model}(\alpha_i) - t_{experimental}(\alpha_i)| \tag{21}$$

where N is the number of evaluated extent of cure steps, t_{model} is the model's predicted time, and $t_{experimental}$ is the experimentally determined time. This calculation is performed with extent of cure steps of 5%, where the prediction time to reach a given extent of cure α_i is used. The detailed results of this comparison are available in the supplementary information, in Figures S1 and S2.

Table 2 summarizes the average MAE for all systems up to an extent of cure of 50% and 90%, showing that overall, the models are more accurate in the first half of cure. The isoconversional models KAS, FWO and VO are the most accurate, with the lowest average MAEs. The Kissinger model's simplicity is reflected in its higher average MAE of 16.3 (α =50%) and 36 minutes (α =90%). With an average MAE of 44.9 (α =50%) and 1144.7 minutes (α =90%), the FR model is confirmed to be the least accurate.

Table 2: Averaged MAE for the models in relation to experimental data. Values are given in minutes.

α	Kissinger	KAS	FWO	FR	VO
50%	16.3	3.6	4.4	44.9	3.1
90%	36	12.9	15.8	1144.7	14

4.4 Activation energy

For the Kissinger method, activation energy is assumed to be constant for a given system. Table 3 shows the activation energies and pre-exponential factors as calculated with the Kissinger method for each concentration. Since this model relies solely on peak temperature, curing times for different resorcinol concentrations are not consistent. For example, the slightly higher activation energy for 10 wt% resorcinol causes the model to predict a longer curing time under the same conditions, when compared with a pure phenolic resin system. However, as shown in the isothermal experimental results (Figures 4 through 7), the addition of resorcinol decreases curing times. These results demonstrate the limitations that model-dependent methods (such as the Kissinger method) have when dealing with complex reaction systems.

When comparing the activation energy values for pure phenolic resin with the higher concentrations of resorcinol (20 and 30 wt%), a decrease can be observed, which is a consequence of the shift in peak temperatures caused by the resorcinol addition.

Table 3: Activation energy E_a (kJ mol^{-1}) calculated with the Kissinger method.

Resorcinol (wt%)	Ea (kJ mol^{-1})	A (min^{-1})
0	97.13	4.17E+10
10	98.24	4.35E+10
20	85.91	2.74E+10
30	88.45	7.21E+09

For model-free isoconversional methods (FWO, KAS, FR and VO), activation energy is taken as a function of conversion ($E_a(\alpha)$). Due to their predictions relying on numerical solutions, the accuracy of these methods depend on the conversion step size ($\Delta\alpha$). A smaller $\Delta\alpha$ will provide more reliable results but with an increased computational cost. Because of its ease of use with computational tools, the VO model is used here to evaluate activation energy using a conversion step size of $\Delta\alpha = 0.1\%$. Figure 9 shows a plot of activation energy calculated with the VO method as a function of extent of cure, where resorcinol-added phenolic resins show a decreased activation energy overall.

For the concentration of 10 wt% resorcinol, a significant jump in activation energy is observed around 50% cure. Between 10 and 30% cure, the activation energy is relatively constant with an average value of 57.3 kJ mol^{-1}, which indicates that in this region the curing involves mostly a single reaction. At around 50 % cure, there is an increase in activation energy, which can be attributed to the transition between resorcinol and phenol reaction regions. As discussed in section 4.2 and referring to Figure 3, 10 wt% resorcinol has two reaction peaks due to the competition between resorcinol and phenol, especially at the beginning of curing. The increase in activation energy for the second half of the curve is a clear indication of the shift towards the less reactive phenol and the beginning of vitrification. When compared to the 20 and 30 wt% resorcinol systems, 10 wt% resorcinol has a lower activation energy, up to around 50%. As demonstrated by Vyazovkin et al. (2000)[46], the activation energy values obtained by using the isoconversional model-free methods are a consequence of the numerical approach used for solving the equations, with a confidence interval that can vary up to 26%. Thus, these values cannot be used to understand the curing mechanisms, but have been proven to be accurate in predicting isothermal curing times.

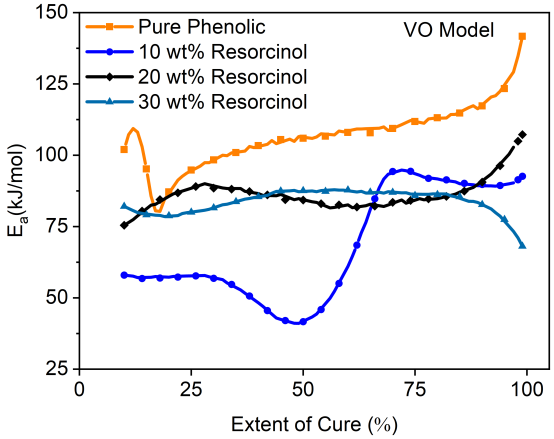


Figure 9: Plot of activation energy as a function of extent of cure calculated with the VO method for isothermal curing at 130 °C.

For reference, Tables 4 and 5 show the activation energies calculated with all methods, except Kissinger. For the KAS, FWO and FR methods, a conversion step ($\Delta\alpha$) of 5% was used. The calculations for the VO method were done with a step of 0.1% but, due to space constraints, the table only shows the activation energy at each 5%. It can clearly be seen that the FR method provides much higher values for activation

energy for all systems when compared to the other models. This reflects in its poor performance when predicting constant temperature curing. On the other hand, the similarity of the activation energy between KAS, FWO and VO models confirms that they are able to accurately predict curing of the phenolic resins evaluated in this work.

Table 4: Activation energy E_a (kJ mol^{-1}) for pure and 10 wt% resorcinol-added phenolic resin.

	Phenolic Resin					10 wt% Resorcinol			
α (%)	KAS	FWO	FR	VO	α (%)	KAS	FWO	FR	VO
5	123.0	129.5	240.9	131.1	5	82.3	88.8	160.4	74.5
10	114.9	121.6	228.4	101.9	10	75.3	81.9	139.6	58.0
15	108.7	115.5	213.6	96.1	15	71.2	77.9	135.3	56.1
20	104.3	111.2	209.4	88.3	20	68.1	74.9	127.7	57.6
25	103.2	110.2	209.8	95.9	25	64.6	71.4	117.4	58.5
30	103.0	110.0	211.5	96.5	30	61.1	68.0	113.6	56.2
35	103.2	110.3	213.1	103.0	35	59.0	65.9	116.0	53.7
40	103.6	110.7	214.9	101.4	40	58.0	65.0	119.3	48.5
45	104.1	111.3	217.0	101.7	45	57.5	64.6	122.1	42.4
50	104.6	111.8	218.3	108.5	50	57.4	64.5	124.9	41.2
55	105.0	112.3	219.3	110.3	55	57.7	64.9	130.3	47.6
60	105.5	112.8	220.6	107.5	60	59.0	66.2	141.0	60.2
65	105.9	113.3	221.7	107.9	65	62.2	69.4	158.7	80.0
70	106.4	113.7	223.0	108.8	70	67.6	74.9	172.5	93.8
75	106.9	114.3	224.5	113.4	75	72.7	80.1	177.9	93.8
80	107.5	115.0	226.4	111.8	80	76.8	84.2	182.0	91.9
85	108.3	115.8	228.7	112.2	85	80.4	87.9	185.7	90.7
90	109.4	116.9	231.3	115.9	90	83.8	91.3	189.7	88.6
95	111.0	118.6	235.0	124.8	95	87.4	95.0	194.7	90.0

Table 5: Activation energy E_a (kJ mol^{-1}) for 20 and 30 wt% resorcinol-added phenolic resin.

	20 wt% Resorcinol					30 wt% Resorcinol			
α (%)	KAS	FWO	FR	VO	α (%)	KAS	FWO	FR	VO
5	79.8	86.1	155.1	61.2	5	60.4	66.9	134.7	88.4
10	79.8	86.3	162.8	75.5	10	64.2	70.8	147.6	82.1
15	80.5	87.1	167.3	82.3	15	67.6	74.3	157.1	78.7
20	81.4	88.1	171.1	85.9	20	70.5	77.3	163.6	78.4
25	82.4	89.2	175.3	89.0	25	73.0	79.8	168.8	82.0
30	83.4	90.2	177.2	88.6	30	75.1	81.9	172.6	83.1
35	84.2	91.0	178.4	89.1	35	76.8	83.7	175.0	84.1
40	84.8	91.7	179.7	85.0	40	78.4	85.3	176.8	85.2
45	85.3	92.2	179.9	83.4	45	79.6	86.6	178.4	88.9
50	85.7	92.6	179.9	84.0	50	80.8	87.7	179.0	89.8
55	85.9	92.9	180.3	82.4	55	81.7	88.7	179.3	88.4
60	86.1	93.2	181.0	82.3	60	82.5	89.5	179.5	87.7
65	86.4	93.5	182.4	80.3	65	83.1	90.2	179.9	88.7
70	86.8	93.8	183.5	83.2	70	83.7	90.8	180.0	87.2
75	87.3	94.4	185.6	85.0	75	84.2	91.3	181.1	87.4
80	87.9	95.1	187.8	84.7	80	84.9	92.0	182.8	87.4
85	88.9	96.1	191.5	86.9	85	85.6	92.8	183.0	84.2
90	90.6	97.8	197.8	90.5	90	86.3	93.5	182.6	84.0
95	94.2	101.6	209.0	97.7	95	87.0	94.2	181.4	77.3

4.5 Carbon yield evaluation

To evaluate the impact on carbon yield, TGA of the phenolic resin with different concentrations of resorcinol was performed. The results are illustrated in Figure 10, where it can be observed that the resorcinol addition does not have a significant effect on carbon yield, maintaining around 62.3 wt% at 1000 °C under nitrogen

atmosphere. As high heat treatments are used to convert phenolic resins into a carbonaceous matrix in the fabrication of C/C composites, a high carbon yield is highly desirable. This characteristic improves mechanical and thermal properties and is directly correlated to the density of the final composite. In general, the higher the carbon yield of the resin used, the higher the density achieved during the fabrication of C/C composites. From these TGA results, it is shown that resorcinol addition does not reduce the high carbon yield of the phenolic resin while still being able to reduce curing times.

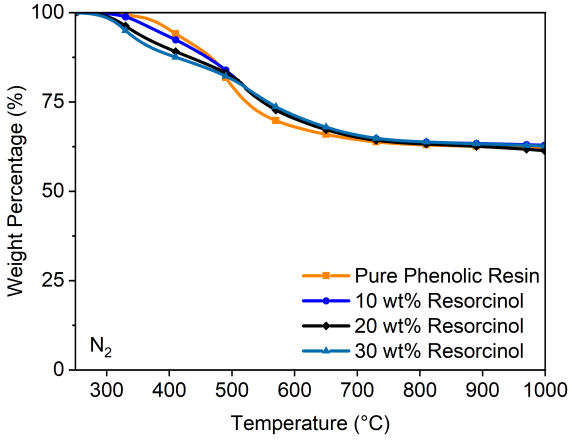


Figure 10: TGA results comparing different concentrations of resorcinol.

5 Conclusions

The curing kinetics of resorcinol-added phenolic resins cannot be reliably predicted simply through peak temperature measurements, such as the approach used by the original Kissinger model. Isoconversional model-free kinetic methods (KAS, FWO and VO) have the distinct advantage of considering an activation energy that varies with conversion, making them more appropriate to describe resorcinol-added phenolic resin systems. The methodology used for fitting models using constant heating rate DSC analysis was shown to be accurate for predicting isothermal curing times of resorcinol-added phenolic resins. The FR method, although based on an isoconversional approach, does not accurately predict the curing times for the concentrations evaluated in this work, with an average MAE of 1144.7 minutes. This behaviour is attributed to its sensibility to data noise and the assumption that the heat of reaction does not change with heating rate. The Kissinger method does well for cases where only one exothermic peak is present (pure, 20 and 30 wt% resorcinol),with an average MAE of 36 minutes. The isoconversional methods KAS, FWO and VO displayed the lowest errors, with average MAE of 12.9, 15.8 and 14 minutes respectively. These models were shown to accurately predict isothermal curing even in situations where two exothermic peaks are present, such as in the case of the 10 wt% resorcinol-added phenolic resin. The 10 wt% system has shown to be a transition between the phenol-formaldehyde and the more reactive resorcinol-formaldehyde curing reactions, displaying a merged double peak in its DSC thermograms. The addition of resorcinol has been shown to decrease the curing times of phenolic resins by up to 71% without a detrimental effect to its carbon yield. Thus, these results validate the addition of resorcinol for reducing curing times of resoles without the potential corrosion and contamination issues associated with catalysts while still maintaining the original carbon yield.

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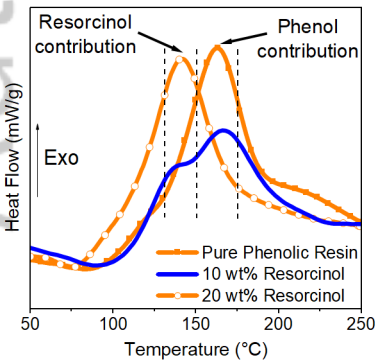
Table of Contents



Resorcinol-added phenolic resins show a complex curing reaction behavior, where resorcinol and phenol play competing roles. Differential Scanning Calorimetry is used with pure, 10, 20 and 30 wt% resorcinol added phenolic resins to fit different curing methods. Isoconversional model-free models are able to best predict isothermal curing times for these systems.