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Calorimetric analysis of the polymerization reaction of a phenolic resin ☆

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Abstract

The polymerization of a phenolic resole resin, used as a matrix for glass-fiber-reinforced composite materials, was studied using differential scanning calorimetry (DSC), and a kinetic model of the complex reactive process was developed. Two distinguishable reaction peaks were obtained in the dynamic DSC thermograms and were assigned to two independent cure reactions characterized by different activation energies. The kinetic analysis, performed by regression analysis on several DSC scans obtained at different heating rates, led to the determination of kinetic constants, activation energies and reaction orders for the two different kinetic equations. Both equations were integrated in a general model of the cure process through the inclusion of a weighting factor representing the fraction of heat developed in each reaction. Good agreement between experimental and modeling results was obtained.

Keywords: DSC; Kinetics; Polymerization reaction; Resin

1. Introduction

Phenolic resins are currently being re-proposed as an alternative to unsaturated polyesters in the production of glass-fiber-reinforced composite components, molded by low pressure processes such as hand or spray lay-up and resin transfer molding.

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They are mainly considered for application in the transportation industry, as a consequence of their intrinsic fire resistance. In fact, they provide low flame spread and very low smoke emissions without the addition of halogenated fire retardants or high filler loading.

As in the case of other thermosetting matrix composites, the processing of phenolic-based materials requires a careful application of processing conditions in order to control the development of the viscosity which is dependent on the temperature and on the polymer structure. In fact, the continuous changes in the resin from a low-viscosity liquid monomer at the starting point to a solid polymer at the end of the process, affect the fiber wettability, the formation and growth of bubbles and the composite consolidation. Thus, the control of the processing of these materials by scientific bases requires an accurate knowledge of the polymerization kinetics of the matrix as a function of the applied processing temperature. It has been demonstrated in recent years that optimization and control procedures, based on the modeling of the curing kinetics and of the fundamental transport phenomena associated with the specific processing technology, can be used successfully to select the appropriate temperatures and pressures to be applied during the cure of organic matrix composites [1,2]. Unfortunately, a complete chemical characterization of the thermosetting reactions to provide a mechanistic kinetic model is a formidable task, especially for materials such as phenolic resins. Therefore, empirical kinetic models have been developed and applied in recent years to describe the curing process of different thermosetting matrices like epoxy and polyester resins [1–3]. Although some information has been reported on the polymerization kinetic analysis of phenolic matrices [4,5], no comparison between experimental and modeling predictions has been presented. In this paper the results of the calorimetric characterization of a phenolic matrix are used to develop an empirical kinetic model of the complex curing reactions. The determination of the kinetic parameters will be approached by regression analysis of dynamic thermogram data.

2. Experimental

A bicomponent commercial phenol/formaldehyde system, Resorciphen® 2074-A/2026-B, developed by Indspec Chemical Co. for pultrusion processing of glass-fiber-reinforced composites was studied. Before mixing, the phenolic component 2026B was heated at 68 °C for three hours to eliminate the partial crystallization that can occur during storage. The mixture (74% of 2074A and 26% of 2026B), whose standard composition before reaction is 94% solids and 6% water, was placed in the DSC pan, weighed and analyzed, minimizing the time between preparation and characterization because the mixture has a very brief pot-life at room temperature that can be less than one hour if the temperature rises above 28 °C.

The calorimetric characterization was carried out in a DSC Polymer Lab. operating in the range of temperatures between -150 and 600 °C. The equipment works in nitrogen atmosphere and is equipped with a liquid nitrogen cooling system. DSC thermograms were recorded in isothermal and dynamic conditions at different scan rates starting at -50 °C and each experiment was repeated at least twice. Best thermograms were obtained at heating rates between 1 and 7°C min^{-1}. Experimental data were analyzed, applying statistical software (Systat) for non-linear regression analysis.

3. Results and discussion

It has already been confirmed that the polymerization of phenol/formaldehyde resins is accomplished in two steps following the scheme of reaction shown in Fig. 1 [6]: the addition of formaldehyde to phenol to form hydroxymethyl resorcinol is the first step, and the condensation of hydroxymethyl resorcinol to form methylene and methylene-ether-bridged di- or high-molecular compounds is the second step; eventually, the methylene ether bridge may lead by disproportion to methylene-bridged resorcinol and formaldehyde. Moreover, the presence of water associated with formaldehyde in the original system and in the by-products of the reaction determines the production of an endothermic evaporation peak that can overlap the reaction peaks.

A DSC thermogram corresponding to the system studied and obtained in dynamic conditions is shown in Fig. 2. Two peaks are clearly visible and it is generally accepted that they correspond [6] to the main reactions described in Fig. 1: formaldehyde addition and formation of ether and methylene bridges, respectively. However, our objective was not to develop a fundamental understanding of the resole curing chemistry, but to derive a usable empirical model describing the curing process. Although a small water evaporation peak was observed in all the thermograms, its contribution has been neglected by interpolation of the main peaks without disturbing the general kinetic analysis. Furthermore, it must be noted that the main exothermic peaks of the thermograms are quite distinguishable, allowing their separate analysis.

In order to perform integration of the thermogram peaks, it is assumed that the partial area under the thermogram curve, computed as a function of time, is proportional to the reaction conversion. In fact, it is conventional to define the degree of cure

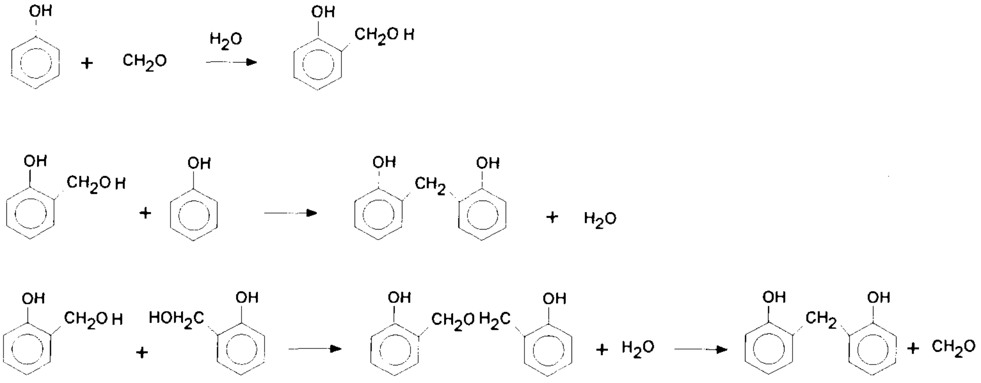

Fig. 1. Reaction scheme of a phenol/formaldehyde system [6].

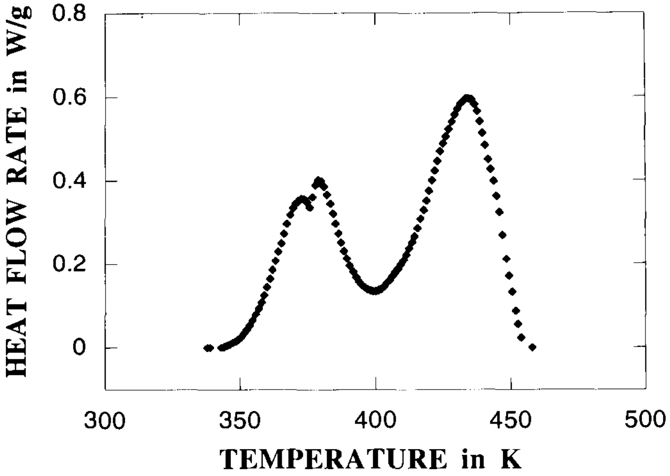

Fig. 2. Dynamic DSC thermogram of the phenolic system obtained at 7°C min^{-1}.

α as the ratio of the fraction of heat Q developed up to a given time t to the total heat evolved during the reaction Q_{tot} [7]

$$\alpha = \frac{\int_0^t \frac{dQ}{dt} dt}{Q_{\text{tot}}} \tag{1}$$

The reaction rate is then defined in the following form

$$\frac{d\alpha}{dt} = \frac{\frac{dQ}{dt}}{Q_{\text{tot}}} \tag{2}$$

Using these definitions we can easily obtain the diagram of the reaction rate as a function of the degree of conversion. A typical diagram, obtained from Fig. 2 results, is shown in Fig. 3. The possibility of separating the two reactions allows the formulation of an empirical kinetic model with the assumptions [4] that the two exothermic peaks can be assigned to two independent reactions, and that each reaction follows an nth order concentration dependence

$$\frac{d\alpha_i}{dt} = k_i(1-\alpha_i)^{n_i} \tag{3}$$

where α_i, ranging between 0 and 1, are the fractional conversions for each kinetic process, and the kinetic constants k_i are represented by an Arrhenius-type equation

$$k_i = k_{0i} \exp\left(-\frac{E_i}{RT}\right) \tag{4}$$

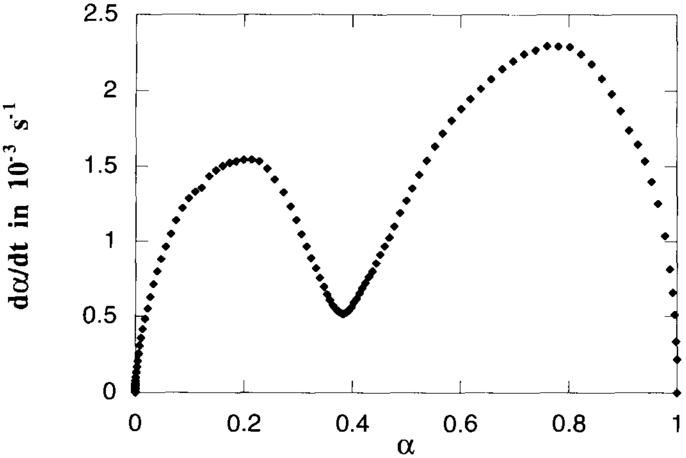

Fig. 3. Reaction rate as a function of the degree of reaction computed from the experimental data shown in Fig. 2.

Because the activation energies differ significantly, the two reactions occur in different temperature intervals in a constant heating rate experiment and the positions of the exothermic peaks of the individuals reactions are clearly distinguished.

Following these assumptions, a useful kinetic model for the whole process can be expressed through a combination of both kinetic equations

$$\frac{d\alpha}{dt}=pk_{10}\exp\left(-\frac{E_1}{RT}\right)(1-\alpha_1)^{n_1}+(1-p)k_{20}\exp\left(-\frac{E_2}{RT}\right)(1-\alpha_2)^{n_2} \tag{5}$$

where α_1 and α_2 are the degrees of reaction corresponding to each one of the processes and were computed by partial integration of the first and second peak respectively. The peaks have been integrated separately following Eq. (1) and assigning to each of them a weighting factor p which represents the fraction of the total thermogram area covered by each of them. The following expressions are defined

$$p=\frac{Q_1}{Q_{\rm tot}};\quad 1-p=\frac{Q_2}{Q_{\rm tot}};\quad Q_{\rm tot}=Q_1+Q_2;\quad \alpha=p\alpha_1+(1-p)\alpha_2 \tag{6}$$

Replacing these definitions in Eq. (5), the final expression of the model in terms of the quantities measured by calorimetry can be obtained

$$\frac{dQ}{dt}=Q_1\frac{d\alpha_1}{dt}+Q_2\frac{d\alpha_2}{dt}=Q_{\rm tot}\,[pk_1(1-\alpha_1)^{n_1}+(1-p)k_2(1-\alpha_2)^{n_2}] \tag{7}$$

One possible method [4,8,9] to compute the model parameters from dynamic calorimeteric data takes advantage of the condition that the characteristic peak in the thermogram corresponds to the point at which

$$\frac{d^2\alpha}{dt^2}=0 \tag{8}$$

which leads, after some derivations developed originally by Kissinger [8], to the condition

$$\ln\left(\frac{V}{T_p^2}\right) \approx \ln\left(\frac{Rk_0}{E}\right) - \frac{E}{RT_p} \tag{9}$$

where T_p is the peak temperature and V the heating rate. The kinetic parameters were obtained from the plot of $\ln(V/T_p^2)$ versus $1/T_p$. Then the reaction orders and the weighting factor p were obtained by a multiple regression performed on the data corresponding to the different thermograms following the method originally developed by Ozawa [9] and used by Focke and Smith [4] for a similar resin system. The values of the parameters obtained are reported in Table 1. A comparison of experimental data and model predictions is presented in Fig. 4, where although the position of the thermogram peaks is well predicted, a poor agreement was obtained in the form of the curves of heat flow measured by calorimetry and predicted by the model. Similar poor agreements were obtained for the whole range of heating rates used in the calorimetric analysis.

A second method was then used applying non-linear regression analysis to all the experimental data obtained in the entire set of dynamic scan thermograms. The only

Table 1. Parameters of the kinetic model computed using peak temperature data

Pre-exponential constant/s^{-1}	$k_{10} = 2.25 \times 10^{19}$	$k_{20} = 7 \times 10^6$
Activation energy/K	$E_1/R = 18180$	$E_2/R = 9170$
Reaction order	$n_1 = 3.50$	$n_2 = 1.31$
Weighting factor	$p = 0.32$	$(1-p) = 0.68$

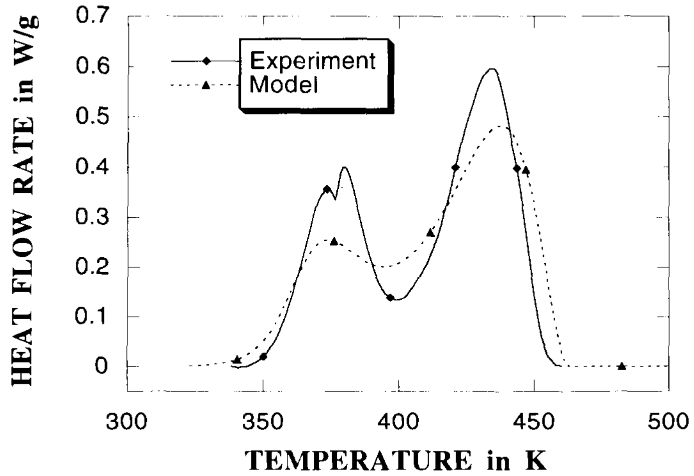

Fig. 4. Comparison between experimental DSC data obtained at 7°C min^{-1} and model predictions obtained with the kinetic parameters computed from reaction peak data.

parameter that is possible to estimate a priori is the weighting factor p considering that the peaks are clearly distinguishable. Therefore, p is given by the value of the degree of conversion at which the first reaction finishes

$$p=\frac{\int_0^{t_1}\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t}{Q_{\mathrm{tot}}}=\frac{Q_1}{Q_{\mathrm{tot}}} \tag{10}$$

The value of $p=0.36\pm0.01$ was estimated as the average of results of different thermograms. Then the values of the degree of reaction of the single reactions were obtained according to the following calculation scheme

$$\alpha_1=\frac{\int_0^{t}\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t}{Q_1}=\frac{\int_0^{t}\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t}{pQ_{\mathrm{tot}}}=\frac{\alpha}{p};\quad \alpha_2=0 \quad \text{for} \quad T\leq T_1 \tag{11}$$

$$\alpha_1=1;\quad \alpha_2=\frac{\int_{t_1}^{t}\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t}{Q_2}=\frac{\int_0^{t}\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t-\int_0^{t_1}\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t}{(1-P)Q_{\mathrm{tot}}}=\frac{(\alpha-p)}{(1-p)} \quad \text{for} \quad T\geq T_1 \tag{12}$$

The availability of α_1 and α_2 values allowed a direct application of regression analysis to Eq. (5) to estimate the Arrhenius parameters reported in Table 2. Then, the results of the model, in terms of curves of heat flow rate as a function of temperature, were compared with experimental data as reported in Figs. 5 and 6, for two different heating rates. Better results were obtained with this method than with the method adopted before, as evidenced in the comparison between Figs. 4 and 5. The same conclusion was obtained for all the heating rates tested.

In the thermograms shown in Figs. 5 and 6, the endothermic peak due to water evaporation is evident and has not been considered in the model. In fact that part of the thermogram was not included in the regression analysis. The position of this endothermic peak appears erratic and seems to depend on the heating rate and probably on the characteristics of the polymer network being formed in the process. In controlled processes at low heating rates, it always occurs at long times when the cross-linked polymer is already formed and further foam development is not allowed. Although this information provided by the calorimetric characterization is very useful for processing purposes, it was not included in the model developed to avoid further complexities.

A further analysis of both methods used in this study for the calculation of the kinetic parameters can be performed through the comparison of the application of the

Table 2. Parameters of the kinetic model obtained by non-linear regression analysis of the complete set of thermogram data

Pre-exponential constant/s^{-1}	$k_{10}=3.80\times10^{22}$	$k_{20}=6.96\times10^{10}$
Activation energy/K	$E_1/R=21030$	$E_2/R=13120$
Reaction order	$n_1=2.07$	$n_2=0.73$
Weighting factor	$p=0.36$	$(1-p)=0.64$

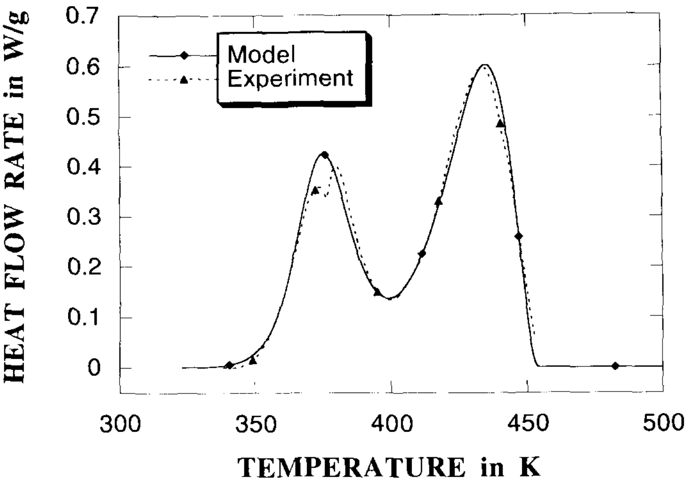

Fig. 5. Comparison between experimental DSC data obtained at 7°C min^{-1} and model predictions obtained with the kinetic parameters computed by non-linear regression analysis of the complete set of available data.

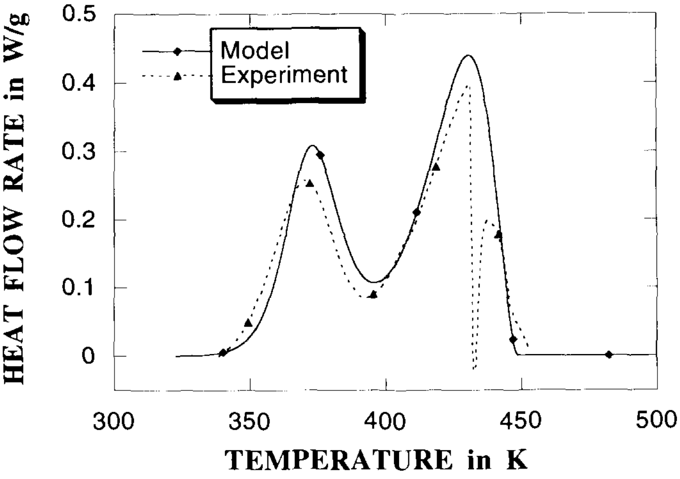

Fig. 6. Comparison between experimental DSC data obtained at 3°C min^{-1} and model predictions obtained with the kinetic parameters computed by non-linear regression analysis of the complete set of available data.

procedure indicated in Eq. (9) to model predictions and experimental data. To do this, the predicted peaks of different thermograms were reproduced by simulation of scans at different heating rates, see Fig. 7. The corresponding temperatures were used to recalculate the Arrhenius parameters as shown in Figs. 8 and 9 where the original

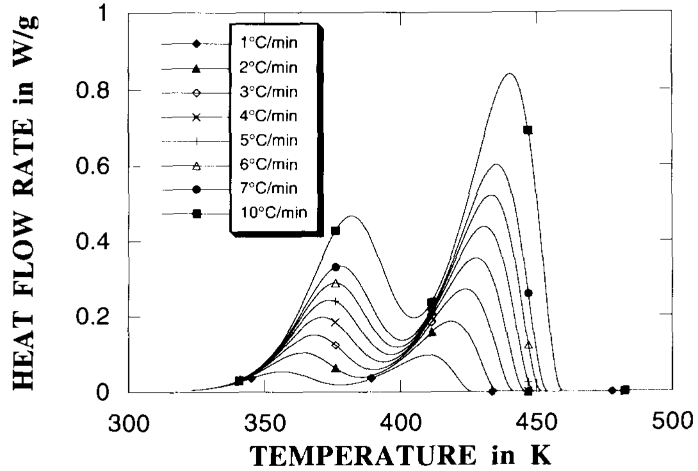

Fig. 7. Dynamic thermograms obtained by model simulation with parameters computed by non-linear regression analysis.

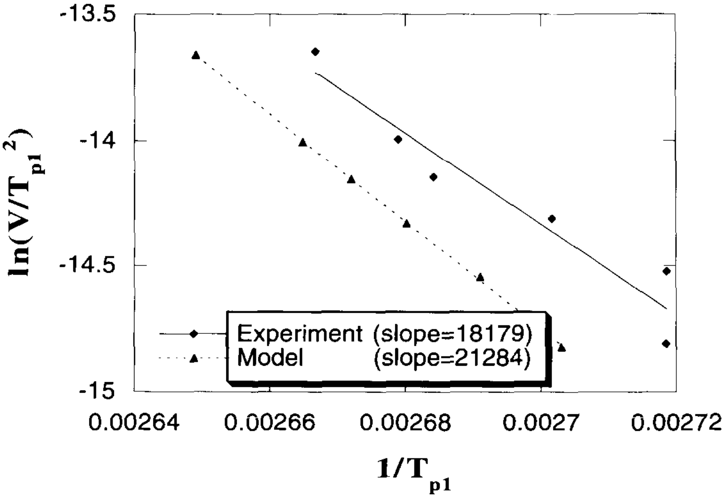

Fig. 8. Calculation of Arrhenius parameters from experimental and model data corresponding to the temperature of the first reaction peak.

calculation of the kinetic parameters, following the first method, is also shown. It is possible to observe that there is an excellent agreement between the experimental data and the predicted curves, the activation energies determined from the data peaks being very near to the estimated ones. Moreover, the experimental points are located in the same region of the estimated data, leading to a value of the activation energy estimated by the first method used, strongly affected by their dispersion. This means that the

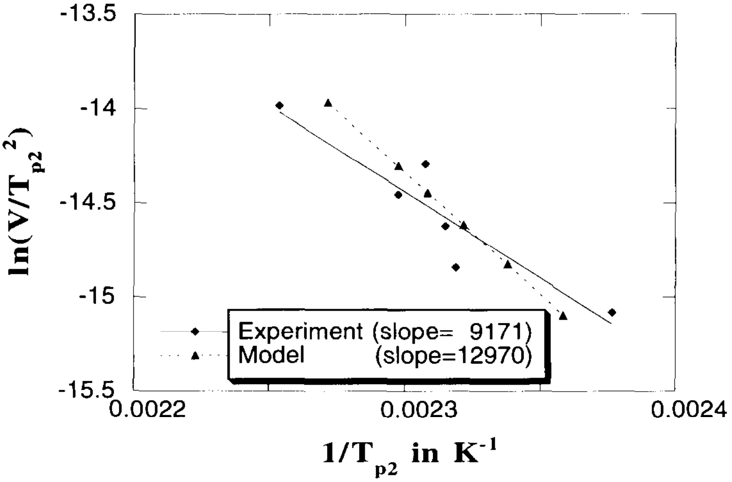

Fig. 9. Calculation of Arrhenius parameters from experimental and model data corresponding to the temperature of the second reaction peak.

procedure suggested by Kissinger [8] and Ozawa [9] and followed by Focke and Smith [4] for a similar phenolic system is precise a posteriori but can lead to highly imprecise values if used to estimate kinetic parameters a priori as a consequence of the sensitivity of the method to small errors in the determination of the peak temperature.

4. Conclusions

The kinetics of the polymerization reaction of a phenolic resin was studied by thermal analysis (DSC), monitoring the changes in enthalpy at different scan rates. A characteristic double peak appeared in each experiment and was well represented by a kinetic model with two consecutive *n*th order reactions. A critical comparison of two different kinetic methods was perfomed. Calculation of the kinetic parameters based on the position of the reaction peaks produced poor results. Only when all the information available from experimental data was used to compute the model parameters by non-linear regression analysis was good agreement between model and experiments obtained. The results of this research can be used to determine the best processing conditions for phenolic materials.

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