Thermal degradation kinetics of a commercial epoxy resin—Comparative analysis of parameter estimation methods

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ABSTRACT: The thermal degradation behavior of a commercial epoxy resin, EpoFix® (Struers), has been investigated by thermogravimetry (TG), differential thermal gravimetry (DTG), and differential thermal analysis (DTA) under nonisothermal conditions in an argon atmosphere. Different methods (Kissinger, Flynn–Wall–Ozawa (FWO), Friedman isoconversion methods, and nonlinear least-squares (*NLSQ*) estimation method) have been used to analyze the thermal degradation process and determine the apparent kinetic parameters. The methods produce similar results in terms of activation energy estimations. Nevertheless, the *NLSQ* method has several advantages over the other methods in terms of both characterizing the activation energy and modeling the thermal degradation—i.e., including this model in a resin degradation process simulation. However, it is interesting to combine the *NLSQ* method with other isoconversion methods: they can reflect the dependence and variability of the activation energies during pyrolysis processes, while providing a good starting point for a nonlinear procedure, especially with respect to the activation energy *E*. This work is the first step (apparent kinetic reaction) of complete simulation of experimental oven of degradation of epoxy resin coating of impregnate nuclear fuel sample. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42201.

INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers and are widely used in many fields such as surface coatings, adhesives, painting materials, potting, composites, and so on.[1–4] In this study, the commercial epoxy resin called EpoFix® is used to coat and impregnate nuclear fuel samples for microstructural examinations. After such examinations, the epoxy resin must be separated from the nuclear fuel to prevent radiolysis.[5] For this reason, a thermal treatment process has been developed. The first step of this process involves pyrolyzing the epoxy resin coating. This study investigates the thermal degradation kinetics of this epoxy resin during pyrolysis.

Thermal analysis techniques such as thermogravimetry (TG), differential thermal gravimetry (DTG), and differential thermal analysis (DTA) are widely used to measure the thermal stability and pyrolysis behavior of the epoxy resin under different conditions.[4,6–9] It is important to estimate the kinetic parameters in order to determine the reaction mechanisms and simulate the

pyrolysis process. There are numerous studies on the degradation kinetics of different materials. Among these, some investigations have also focused on the reaction mechanisms and product yields of cured and uncured epoxy resins.[10–14]

Isothermal conditions are sometimes used to model reactions over a broad temperature range. This requires conducting a series of experiments at different temperatures, whereas a single experiment under nonisothermal conditions is theoretically sufficient for kinetic model identification. Moreover, modeling on the basis of isothermal conditions neglects the time needed to achieve the reaction temperature for the sample.[15] This is why it is preferable to use a kinetic study under nonisothermal conditions rather than resorting to using isothermal conditions.[16–24]

It should be pointed out that nonisothermal experiments using high heating rates cannot produce reliable kinetic results because the heat or mass transfers can act as the limiting phenomenon. Thus, the thermal decomposition must be carried

out at low or moderate heating rates to keep the impact of heat and mass transfers to a minimum.[25] Moreover, it is known from previous experiments that kinetic analysis based on a single heating rate is very unreliable and problematic. The use of multiple heating rates is therefore preferable.[26,27]

Several methods specifically adapted to estimate the kinetic parameters from thermogravimetry data under nonisothermal conditions have been proposed in the past.[28] For instance, iso-conversion methods by Kissinger,[29] Friedman,[30] and Flynn–Wall–Ozawa[31,32] are widely used for degradation kinetic studies of epoxy resins.[18–23]

The degradation process of polymers is very complex and influenced by both the type of materials and the operating parameters. This complexity generates a broad range of variations in the kinetic parameters found in publications. For example, the activation energies of epoxy resins found in publications range between 80 and 230 kJ mol^{-1}, with a pre-exponential factor between 10^{12} and 10^{18} s^{-1} and an order of reaction between 0.4 and 1.84. This variability could be explained by different degradation mechanisms in the epoxy resins. The thermal degradation is affected by the structure of the resin, as well as the type of curing agents and other additives used. The available literature mentions several approaches which have been used to modify the epoxy backbone to enhance the thermal properties of epoxy resins.[33–38] It is also clear that the type of atmosphere plays an important role in the degradation mechanism of epoxy resins.[39–41]

In order to model the behavior of nuclear fuels embedded in epoxy resin during the resin pyrolysis process, we must first describe the elementary composition of the resin before defining the main chemical reactions and the thermal degradation kinetics. This article investigates the pyrolysis kinetics of the commercial epoxy resin, EpoFix®, under nonisothermal conditions by means of thermogravimetric measurements. Experiments were carried out using five different heating rates (1, 3, 5, 10, and 15°C min^{-1}) and argon as carrier gas. Various methods (Friedman, Flynn–Wall–Ozawa, Kissinger, and nonlinear least squares (NLSQ) method) were used to determine the apparent kinetic parameters, the activation energy, the pre-exponential factor, and the overall rate equations of the pyrolysis reaction for a specified reaction order. The results of different methods have then been compared. The NLSQ method has several advantages over the other methods in terms of both characterizing the activation energy and modeling the thermal degradation. Primarily, the NLSQ method can simultaneously estimate the various kinetic parameters without having to repeat experiments with various heating rates. The NLSQ method is also able to take into account the presence of consecutive or parallel reactions and other complex reaction mechanisms. The major disadvantage of this method, however, is the need to initially estimate the parameters. This difficulty can be overcome by a linearization procedure or the use of isoconversion methods estimated parameters as initialization points. This is why the use of isoconversion methods can be recommended. They can reflect the dependence and variability of the activation energies during reaction.

Table I. Elemental Analysis of the Epofix® Epoxy Resin

Elemental Analysis (wt %)				
C	H	O	N	Other elements
69.9 ± 0.3	8.15 ± 0.5	3.4 ± 0.2	15.9 ± 0.8	2.65 ± 18

EXPERIMENTAL

Materials

The epoxy resin studied in this article is EpoFix® which is distributed by Struers S.A.S. It was used in this study to coat and impregnate samples of nuclear fuel for microstructural examinations. This polymer is based on bisphenol A (acetone ≡ A) and epichlorohydrin; it is known as the DGEBA epoxy resin (DiGlycidyl Ether of Bisphenol A). The epoxy curing agent used was EpoFix® Hardener (triethylenetetramine TETA).

Samples of the epoxy resin were prepared by mixing 75 wt % of EpoFix® resin with 25% of the curing agent. After curing, an epoxy resin powder was obtained by grinding. An elemental chemical analysis of the sample is listed in Table I.

Thermogravimetric Analysis

Thermogravimetry (TG), differential thermal gravimetry (DTG), and differential thermal analysis (DTA) were carried out using a Netzsch STA 409 simultaneous TG/DTA analyzer. Samples of approximately 50 mg were tested in an alumina crucible with heating rates of 1, 3, 5, 10, and 15°C min^{-1} up to a temperature of 660°C, followed by a plateau of 2 h. These tests were performed in high-purity argon (ALPHAGAZTM2 Argon by Air Liquide) at a flow rate of 100 sccm.

The analyzer was purged before analysis (pressure lower than 0.3 mbar) and filled with high-purity argon to avoid any unwanted oxidation during heating.

TG, DTG, and DTA Analyses

Figure 1 shows the TG (weight loss) curves and DTG (weight derivative) curves as a function of temperature for different heating rates.

The initial decomposition temperature (T_i) for the different heating rates ranged between 202.3 and 293.7°C while the fractional residual mass (called char) ranged between 12.1 and 14.8% at the end of the plateau (660°C).

Figure 1 shows that an increase in the heating rate causes a slight decrease in the residual mass, i.e. 14.8% for 1°C min^{-1} and 12.1% for 15°C min^{-1}. The relative residual mass remains nearly constant for the 3, 5, and 10°C min^{-1} heating rates, i.e., between 13.6 and 13.9%. The reaction zone shifts to higher temperatures at higher heating rates. This fact may be caused by thermal resistance.

The DTG peak (minimum) becomes slightly wider and the peak height increases with the heating rate. The DTG curves show that there is only one main peak in each DTG curve. So, it is possible to consider the thermal degradation of epoxy resin under pure argon to be represented by a single apparent chemical reaction. The DTG peaks for the various heating rates tend
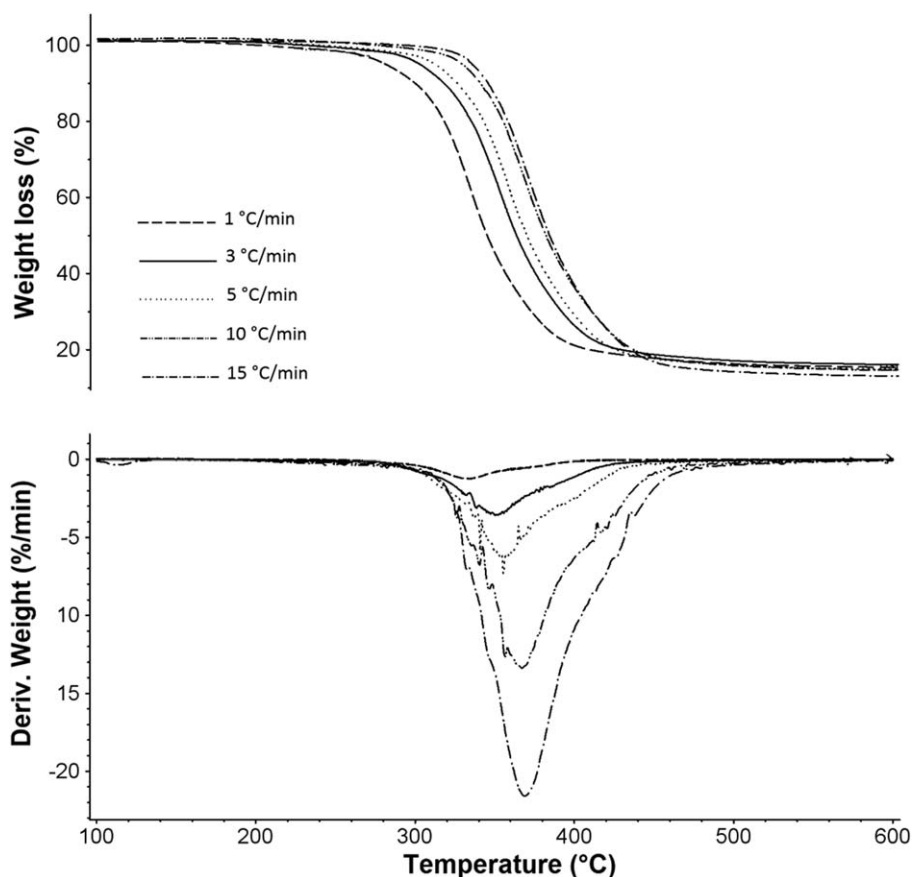
Figure 1. Weight loss (TG) and weight derivative (DTG) curves for various heating rates.

to range between 333.8 and 368.8°C. These results are consistent with those found by other authors.[18,19]

By coupling differential thermal analysis (DTA) with TG and DTG, it was possible to access the temperature difference between the sample and a reference material (empty alumina crucible). Any transformation within the resin was detectable and the related thermal effect was simultaneously measured. The DTA curves for the different heating rates are given in Figure 2. The results show the appearance of peaks (maxima) for the various heating rates for temperature ranging between 326.2 and 362.5°C. The end of the peak shifts to a higher temperature with the increase in the heating rates. Unlike Figure 1, Figure 2 also shows the existence of a second peak for each heating rate which tends to be wider than the first peak.

As an example and to better understand the phenomenon of epoxy resin degradation, Figure 3 simultaneously shows the T, TG, DTG, and DTA curves, giving the variation in the temperature (°C), weight loss (%), weight derivative (% min^{-1}) and
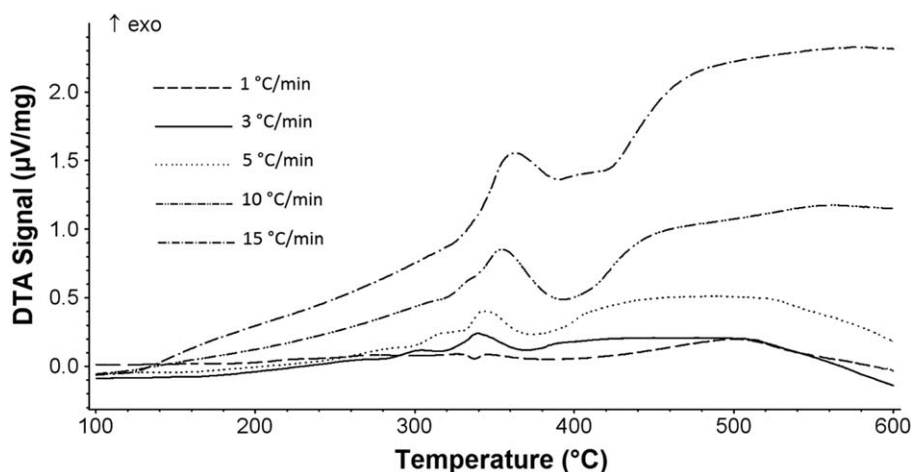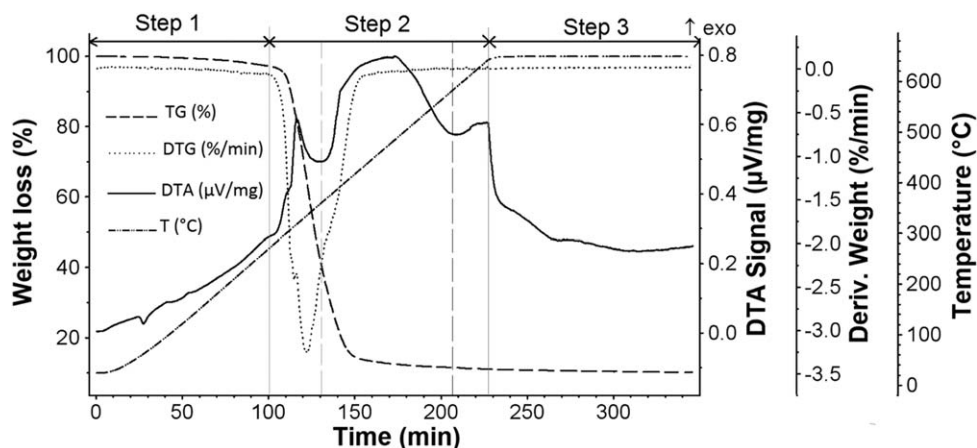

Figure 2. DTA curves for different heating rates.

Figure 3. Weight loss (TG), weight derivative (DTG), DTA signal, and temperature (T) curves of epoxy resin degradation for the 3°C min^{-1} heating rate versus time (min).

DTA signal (µV mg^{-1}) versus time (min), for a heating rate of 3°C min^{-1}.

The thermal degradation process can be divided into three steps:

Step 1—[$t < 103$ min, $T < 300°C$]: An exothermic departure from the base line was observed during the thermal phase. An endothermic peak is detected at 65°C (27.5 min), which corresponds to the vitreous transition of the epoxy resin. The TG curve shows a slight mass decrease.

Step 2—[$103 < t < 228$ min, $300 < T < 660°C$]: Some variations in the DTA signal were detected during this interval. These changes are due to the epoxy resin degradation and chemical reactions. An ideal DTA curve, corresponding to a single chemical reaction, would have only one smooth peak. In practice and in our specific case, however, it is often modified by superimposed reactions and other phenomena (transfers, etc.) and gas emissions. This interval can be broken down into three parts which show the thermal decomposition of the resin and the formation of gaseous products. The first part occurred from 300°C (103 min) to 360°C (130 min) with an exothermic peak detected at 352°C (116 min). The peak shape indicates a thermal transition at moderate speed. Most of the mass was lost during this part. The second part occurred from 360°C (130 min) to 590°C (210 min). The second peak was wider than the first and was detected with a slow thermal transition. At the end of this step, the residual weight was 15%. The last part occurred from 590°C (210 min) to the plateau (660°C, 228 min). Slight mass loss was detected within this temperature range.

Step 3—[$t > 228$ min, $T = 660°C$]: The DTA values decreased and then stabilized during this isothermal step. A slight mass loss is observed until the termination of the reaction.

The characteristics of the TG, DTG, and DTA curves for the different heating rates are shown in Table II. The kinetic parameters could be estimated on the basis of several TG measurements at different heating rates. The different steps that can be identified on the DTA curves did not correlate with a similar behavior pattern on the TG curves, even we can notice some shouldering on DTG curves. The informative content of such curves allows identifying the kinetic parameters of one single apparent reaction in spite of potential consecutive reactions. In this study, the TG curve was used to determine the reaction rate taking into account only one global chemical reaction as a function of conversion and temperature.

KINETIC MODEL

Only one apparent global chemical reaction was considered for the model of thermal degradation of the epoxy resin. It can be stated as follows:

$$A \text{ (solid)} \rightarrow B \text{ (solid)} + C \text{ (gas)}$$
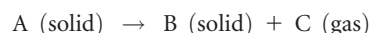
This reaction is characterized by a degree of progress α, defined as

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \tag{1}$$

where w_0, w_t, and w_f represent the initial mass of the sample, its mass at time t, and its final mass at the end of the plateau, respectively.

The rate of mass loss, $d\alpha/dt$, is supposed to be a separable function of the temperature and the degree of progress α, following

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

where k, the reaction rate constant, is assumed to be only dependent on the reaction temperature T according to the Arrhenius expression:

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where E is the activation energy (J mol^{-1}), k_0 is the preexponential factor (s^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the reaction temperature (K).

Table II. Characteristics of TG, DTG, and DTA Curves at Different Heating Rates

Heating rate (°C min^{-1})	Initial decomposition temperature T_i (°C)	Residual weight (%)	Temperature at DTG max (°C)	DTG max (% min^{-1})	Temperature at DTA max (°C)
1	202.3	14.8	333.8	1.2	326.2
3	203.9	13.6	352.0	3.8	347.8
5	239.8	13.8	355.8	7.3	344.5
10	275.5	13.9	367.1	13.4	354.7
15	293.7	12.1	368.8	21.6	362.5

For a controlled and constant heating rate $\beta = \frac{dT}{dt}$ (K s^{-1}), the overall rate equation of pyrolysis reaction becomes

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{4}$$

For $f(\alpha)$, we assumed an nth-order kinetics, $f(\alpha) = (1 - \alpha)^n$, with n representing the order of reaction.

Thereafter, eqs. (1)–(4) were used to estimate the kinetic parameters by the different methods.

ESTIMATION OF KINETIC PARAMETERS

Different isoconversion methods specifically developed to estimate the kinetic parameters from thermogravimetric data under nonisothermal conditions have been proposed based on eq. (4). The classical ones are Flynn–Wall–Ozawa (FWO), Friedman, and Kissinger methods. These methods can be classified as differential or integral.

On one hand, some authors tend to explain that polymer decompositions are probably better studied by differential methods,[28] such as Friedman's method. On the other hand, Audebert and Aubineau compared differential and integral methods investigating various polymers and came to the conclusion that integral methods were superior to differential methods in the frequent case of complex degradations.[28] All these methods are simple and easy to implement, which explain their popularity. However, Staring[42] investigated the accuracy of some model-free isoconversion methods for the estimation of activation energy and came to the conclusion that some methods based on approximations could be inaccurate. Therefore, this article compares the results obtained by the three previous methods (FWO, Friedman, and Kissinger) and a more generic one, based on least squares estimation procedure.

The first three methods are "model-free" as regards the calculation of the activation energy.[41] They do not require any assumptions on $f(\alpha)$ and on the reaction mechanism. On the contrary, an nth-order reaction (usually a first-order reaction) is assumed for pre-exponential factor estimation.[29–32]

As already mentioned, these approximation methods are not always satisfactory and generic parameter estimation methods,[43] such as the least squares methods, can also be used. In this study, linear (LSQ) and nonlinear least squares methods (NLSQ), using Matlab® 2013.b, were also used to perform the kinetic analysis.

Flynn–Wall–Ozawa (FWO) Method

This integral method, developed by Flynn and Wall and independently by Ozawa, uses an integrated form of eq. (4) (see Appendix A). For fixed degrees of progress α, the plots of $\log(\beta) = f(1/T)$ result in straight lines with a slope proportional to the activation energy. A correction factor must be applied to the activation energy estimated to take into account some approximations (see Appendix A). Plotting the values of apparent energy activation E on the degree of progress α (Figure 4) shows that degradation mechanism can be modeled by a unique apparent chemical reaction with a constant activation energy (203 ± 12 kJ mol^{-1}) on a large range of values of α (from 0.2 to 0.9). The intercepts I_α of the straight lines are equal to $\ln(k_0 f(\alpha))$. Assuming first-order kinetics, $f(\alpha) = (1 - \alpha)$, it is then possible to determine k_0. An average pre-exponential factor ($\log(k_0) = 16.0 \pm 1.2$) has been then found for $0.2 < \alpha < 0.9$.

Friedman Method

The Friedman method is not an integral method. It is also based on the determination of the reaction rate at a given degree of progress α for various heating rates (see Appendix B). The plots of $\ln(\beta d\alpha/dT)$ versus $1/T$ at different fixed degrees of progress α show parallel lines with a slope equal to $-E/R$. Figure 4, activation energy E vs degree of progress α, shows the same behavior for Friedman method that for FWO method: constant energy activation E (227 ± 11 kJ mol^{-1}) on a large range of α values at approximately the same level. The determination of the pre-exponential factor is similar to the graphical method used in FWO method. An average pre-exponential factor ($\log(k_0) = 16.0 \pm 1.2$) has been then found, for $0.2 < \alpha < 0.9$.

Kissinger Method

Kissinger's differential method of Kissinger is based on the fact that, for a given heating rate β, the DTG curve reaches a maximum at a temperature $T_{\max}$ during the temperature rise (see Appendix C). So, $\ln(\beta/T_{\max}^2)$ is a linear function of $1/T_{\max}$, with a slope equal to $-E/R$. The activation energy estimated from the slope is equal to 226 ± 27 kJ mol^{-1}. Unlike the two previous methods, Kissinger method only provides one value of apparent activation energy, from Figure 5. The pre-exponential factor $\log(k_0)$ can then be determined from the intercept, assuming first-order kinetics. It is equal to 16.5 ± 0.1.

Least-Squares Estimation Method (LSQ and NLSQ)

The purpose of the nonlinear least-squares (NLSQ) estimation method is to obtain optimal kinetics parameters E, k_0, and n
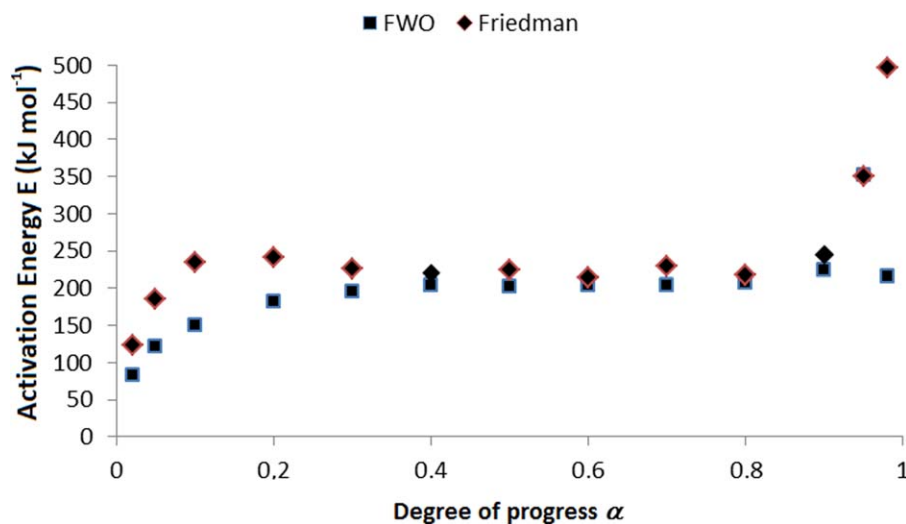
Figure 4. Apparent activation energy versus degree of progress α, for FWO and Friedman methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that minimize the sum of squares of the differences between calculated and experimental values of the degree of progress.

The first step is to choose the structure of the kinetic model. We have cosen the expression for $d\alpha/dt$ stated in the following equation:

$$\begin{cases} \dfrac{d\alpha}{dt} = k_0 \exp\left(-\dfrac{E}{RT}\right)(1-\alpha)^n \\[2ex] \text{with, for each heating rate} : \dfrac{dT}{dt} = \\[2ex] [\beta \text{ if } T \in [0, \ 660°C[0 \text{ if } T \geq 660°C \end{cases} \quad (5)$$

The three parameters E, k_0, and n were estimated simultaneously by minimizing the following criterion:

$$F = \sum_{i=1}^{nexp} \left(\alpha^i - \alpha_{exp}{}^i\right)^2 \quad (6)$$

where n_{exp} is the number of experimental data, α_i is the calculated degree of progress, and α^i_{exp} is the corresponding experimental degree of progress. The criterion F was minimized in MATLAB® 2013.b by integrating the ordinary differential equations system (5) and by using the Levenberg–Marquardt algorithm for the NLSQ problem solution.

Five different optimizations were performed to estimate the kinetic parameters from the five experimental data sets associated with the five various heating rates (1, 3, 5, 10, and 15°C min^{-1}). For the purpose of comparison with FWO, Friedman, and Kissinger methods, the values of the experimental data were restricted to the 0.2–0.9 range.
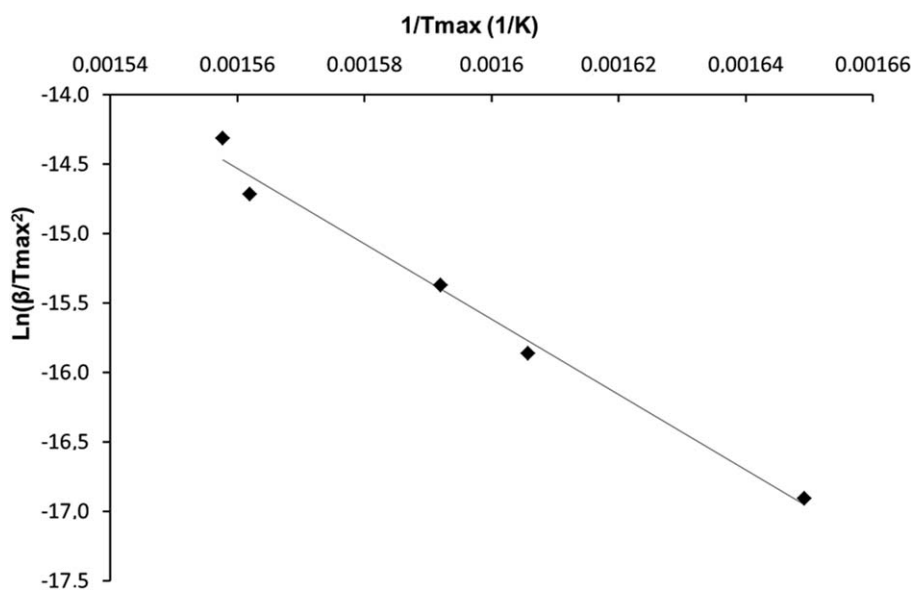

Figure 5. Plot of $\ln(\beta/T_{max}{}^2)$ versus $1/T_{max}$ (Kissinger method).

Table III. Kinetic Parameters Determined by the Nonlinear Least Squares Estimation Method ($0.2 < \alpha < 0.9$)

Heating rate β (°C min^{-1})	E (kJ mol^{-1})	log(k_0)	n
1	214 ± 4	15.5 ± 0.3	2.90 ± 0.05
3	213 ± 7	15.4 ± 0.4	2.62 ± 0.07
5	213 ± 11	15.4 ± 0.5	2.89 ± 0.13
10	212 ± 19	15.4 ± 0.7	2.86 ± 0.20
15	211 ± 24	15.4 ± 0.7	2.79 ± 0.20

Table IV. Kinetic Parameters Determined by Various Estimation Methods ($0.2 < \alpha < 0.9$)

Method	Average E ($0.2 < \alpha < 0.9$)	Average log (k_0)	n
FWO	203 ± 12	14.0 ± 0.7	1
Friedman	227 ± 11	16.0 ± 1.2	1
Kissinger	226 ± 27 (no α interval)	16.5 ± 0.1 (no α interval)	1
NLSQ	213 ± 13	15.4 ± 0.5	2.8 ± 0.1

The NLSQ estimation method requires a good set of initial parameter values to avoid poor convergence or convergence to local minima. Appropriate initial parameter values can be determined from the linearization of eq. (5a):

$$\text{Ln}\left(\frac{d\alpha}{dt}\right) = \text{Ln}(k_0) \quad -\frac{E}{RT} + \; n \; \text{Ln}(1-\alpha) \tag{7}$$

This model is linear with respect to the three following parameters: $\ln(k_0)$, $-E/R$, and order of the reaction n. They were estimated by minimizing the following criterion:

$$F = \sum_{i=1}^{nexp} (\text{Ln}(\frac{d\alpha}{dt})^i - \text{Ln}(\frac{d\alpha}{dt})^i_{\exp})^2 \tag{8}$$

The kinetic parameters for the various heating rates estimated by the LSQ method are given in Table III:

The estimated values of k_0 and E are quasi identical whatever the heating rate. The average values of E, log(k_0), and n are 213 ± 13 kJ mol^{-1}, 15.4 ± 0.5, and 2.8 ± 0.1, respectively. A fractional order of reaction greater than 2 was found for all heating rates, which often indicates a sum of consecutive or parallel reactions, or other complex reaction mechanisms.[46] This is in agreement with DTA curves. It supports the assumption that consecutive reactions may exist with different activation energies, where the reaction step with the highest activation energy becomes representative of the global reaction rate.

Figure 6 gives the variation versus time of the calculated (from Table III) and experimental degrees of progress α between 0.2 and 0.9 at various heating rates. The model shows a good agreement with the experimental degrees of progress for each heating rate.

Comparative Study and Discussion

The kinetic parameters given by the various methods are provided in Table IV.

The Kissinger method is the simplest of all methods. It provides an approximate estimate of the activation energy quickly. However, it is only based on one measurement point (at maximum rate) by experimental test at a given heating rate, namely, five experimental points. Consequently, the uncertainty of E is greater using the Kissinger method than when using the other methods. Considering a single reaction stage, this method allows to determine the overall activation energy. In the case of complex reactions where various processes are superimposed, often no straight line is obtained. Furthermore, the essential information concerning the dependence of the activation energy on the partial reaction is not provided using this method and a fixed order (here a first-order) reaction is assumed for the calculation of the pre-exponential factor.
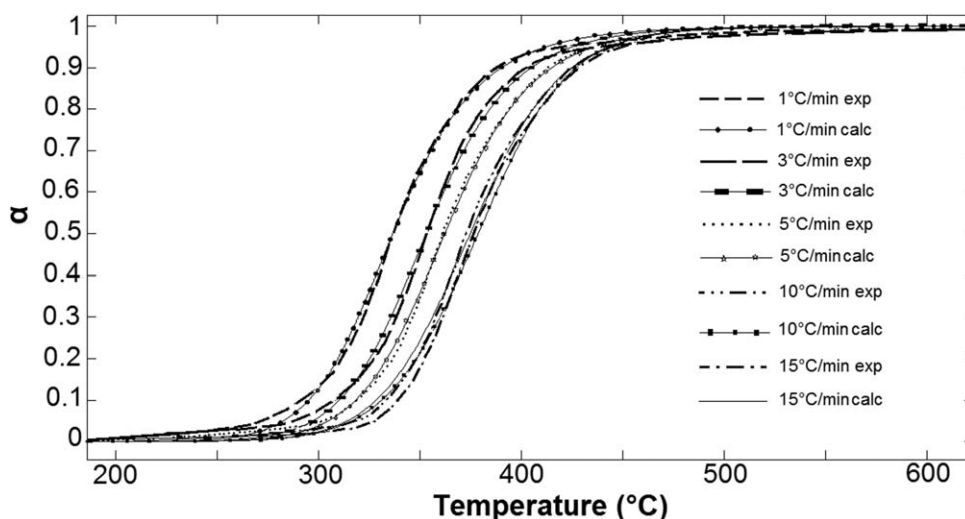
Figure 6. Comparison of calculated (NLSQ) and experimental degrees of progress α at various heating rates.
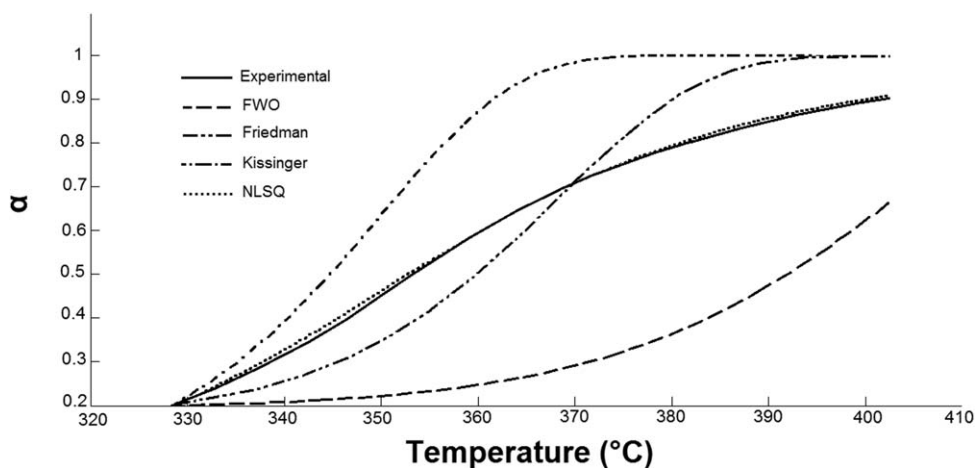
Figure 7. Comparison of experimental and calculated degrees of progress α versus temperature (°C) with different methods, for a heating rate of $3°C\ min^{-1}$.

The FWO method was used to determine the activation energy and the pre-exponential factor in our case. This method can reveal the existence of various processes in the case of complex reactions. A quasi-constant activation energy was detected for progress degree values between 0.2 and 0.9. Like the Kissinger method, a fixed order reaction (first-order in this case) must be assumed to determine the pre-exponential factor k_0.

Like the FWO method, the Friedman method does not assume a constant activation energy level. It gives a variation in the activation energy with the value of α. Similar results to those found by the FWO method were obtained. The activation energy is quasi-constant for a wide range of α, but varying energy activation levels for low and high values of α were obtained. Based on the assumption of a first-order reaction, the pre-exponential factor tends to vary with the degree of progress and a quasi-constant value for α between 0.2 and 0.9 is detected. This value is quite similar to those given by the FWO or Kissinger methods.

For the NLSQ estimation method and assuming n^{th}-order reaction kinetics (or other forms of dependence $f(\alpha)$), all three parameters (activation energy, pre-exponential factor and order of the main pseudo-reaction) can be estimated simultaneously either for all heating rates, i.e., more than 600 experimental points) for comparison with isoconversion methods, or for one heating rate only (quasi-identical values of k_0, E, and n are obtained regardless of the heating rate). The results show good agreement with experimental values and may highlight the impact of the heating rate (reaction zone shifts to higher temperatures at higher heating rates). The estimated activation energy was similar for all methods. An average value of 213 ± 13 kJ mol^{-1} (Table IV) was calculated for a wide range of reaction progress degrees ($0.2 < \alpha < 0.9$).

To compare these results, Figure 7 shows the experimental and calculated values for the degrees of progress found by FWO, Friedman, Kissinger, and NLSQ methods versus temperature (°C), for a heating rate of $3°C\ min^{-1}$ for illustrative purpose (experimental α between 0.2 and 0.9).

Unlike other methods, the NLSQ method is the only one that shows good agreement with the experimental values. Although all methods give good predictions of the activation energy, the assumption of a fixed-order reaction (first-order in our case) results in a large difference between the calculated and experimental values. This point is the main advantage of the NLSQ method. There are many other advantages of the NLSQ method. First, it can simultaneously estimate various kinetic parameters without necessary repeating experiments with various heating rates; the kinetic parameters can be estimated with a single experiment at an adequate heating rate on the whole range of α, or in a fixed range of α. Another advantage is the possibility of using the whole set of experimental thermogravimetric data (>600 in our case), whereas the FWO and Friedman methods take into account the limited number of α data (here only 8 values of α between 0.2 and 0.9), necessarily less than the experimental thermogravimetric data, and the Kissinger method takes into account the number of different heating rates (here only 5 different heating rates). Furthermore, several parameter estimations are possible (in terms of temperature or α coefficients) if multiple reactions (or other phenomena) are suspected upon analyzing the DTG curves, for example. The major disadvantage of the NLSQ method is that it is not "model-free" for the determination of the activation energy E; the structure of the model must be "a priori" provided. It also does not reflect the dependence and variability of activation energies during the pyrolysis processes, when the variation is not included in the model. Another shortcoming is the need for an initial estimation of the parameters. This point can be overcome by a linearization procedure (eq. (17)) or the use of parameters estimated by isoconversion methods as initialization points. For this reason, it is interesting to combine the NLSQ method with isoconversion methods. Isoconversion methods can provide some help to the model structure definition, by bringing out dependence or variability of the activation energies during the pyrolysis processes. They also offer a good starting point for the nonlinear procedure, especially for the energy activation E.

CONCLUSION

The degradation kinetics of the commercial epoxy resin called EpoFix® was investigated by TG, DTG, and DTA. The results show that it is possible to model thermal degradation by a single main apparent reaction. To better understand and analyze the degradation kinetics of this epoxy resin, three standard isoconversion methods were used (Kissinger, Flynn–Wall–Ozawa (FWO), and Friedman) together with an NLSQ estimation method. Activation energy values were determined by means of the Kissinger, Friedman, and FWO methods without any assumption on the function of progress $f(\alpha)$. The Kissinger, FWO, and Friedman methods also assumed a fixed-order reaction for the estimation of the pre-exponential factor k_0, which was first-order in our case. With the NLSQ method, all the three parameters (E, k_0, and n) were estimated simultaneously on the basis of an overall kinetic model.

In our case, the three isoconversion methods reveal the existence of a single key mechanism for a wide range of α with constant and similar activation energy levels, E. Nevertheless, they failed to estimate realistic values of the pre-exponential factor k_0 and the reaction order n which were used to model the thermal degradation behavior.

As for modeling the apparent kinetics of epoxy resin thermal degradation, the NLSQ estimation method provides a direct estimation of the kinetic parameters with only one heating rate experiment, without being required to repeat the experiment with various heating rates. The NLSQ method is able to take into account the existence of consecutive or parallel reactions and other complex reaction mechanisms, if it takes place into the model. The major disadvantage of this method lies in the fact that an initial estimation of the parameters is required. This point can be overcome by using a linearization procedure or isoconversion parameters as the initialization points.

Combination of NLSQ method with isoconversion methods is the good way to estimate kinetic parameters of resin pyrolysis: isoconversion methods can reflect the dependence and variability of the activation energies during the pyrolysis processes and offer a suitable starting point for the nonlinear procedure, especially activation energies, E.

NLSQ method was thus used to estimate gas evolution kinetics parameters. The apparent reaction model, detailed in this article, combined with gas evolution kinetics allows the definition of a chemical model in a CFD simulation tool. The results of this study are the first step of modeling study of the behavior of pyrolysis oven of epoxy resin coating of nuclear fuel samples, by means of coupled resin pyrolysis reactions (this work) with mass, heat, and momentum transfers in a CFD code. Thereafter, this information will be used to develop a tool for the optimal design and control of a suitable heat treatment process.

APPENDIX A: DESCRIPTION OF THE FLYNN–WALL–OZAWA (FWO) METHOD

This integral method, developed by Flynn and Wall and independently by Ozawa, uses the integrated form of eq. (4):

$$g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}=\frac{k_0}{\beta}\int_{T_0}^T \exp\left(-\frac{E}{RT}\right)dT \qquad (A1)$$

that can be roughly expressed as:[42]

$$g(\alpha)\cong \frac{k_0 E}{\beta R}\int_y^\infty \frac{\exp(-y)}{y^2}dy \qquad (A2)$$

where $y = E/RT$. The integral on the right-hand side is generally termed the temperature integral $p(y)$:

$$p(y)=\int_y^\infty \frac{\exp(-y)}{y^2}dy \qquad (A3)$$

The expression of the decimal logarithm of $g(\alpha)$ is

$$\log(g(\alpha))=\log\left(\frac{k_0 E}{R}\right)-\log(\beta)+\log p(y) \qquad (A4)$$

The *FWO* method uses in qq. (A4) the linear approximation of the logarithm of $p(y)$ suggested by Doyle:[44]

$$\log p(y)\cong -2,315-0,457y \qquad (A5)$$

This linear approximation, only valid for y in the range [20–60], leads, for a constant heating rate, to the following equation:

$$\log\left(\beta\right)\cong \log\left[\frac{k_0 E_{\text{Doyle}}}{g(\alpha)R}\right]-2,315-0,457\frac{E_{\text{Doyle}}}{RT} \qquad (A6)$$

where E_{Doyle} is the activation energy calculated by the Doyle approximation.

For fixed degrees of progress α, the plots of $\log(\beta) = f(1/T)$ result in straight lines with a slope proportional to the activation energy and equal to $-0.457\, E_{\text{Doyle}}/R$. As pointed out by Staring,[42] the Doyle approximation can be quite inaccurate depending on the value of y, leading to energy deviations higher than 10%. This is why a correction factor must be applied to the activation energy estimated on the basis of the Doyle approximation. The corrected activation energy can be calculated as:[45]

$$E=E_{\text{Doyle}}.F(y) \qquad (A7)$$

where E_{Doyle} is the activation energy calculated by the Doyle approximation and $F(y)$ is the correction factor.

The activation energy appears constant over a wide range of degree of progress α (between 0.2 and 0.9, $R^2 \geq 0.99$), with an average of 203 ± 12 kJ mol^{-1}. The quasi-identical slopes over the 0.2–0.9 range indicate that a single reaction can represent the thermal degradation on this broad range with constant activation energy. However, the slopes of the lines at $\alpha < 0.2$ and > 0.9 are clearly distinguishable from the other lines, which means that thermal decomposition is affected by other reactions or transfer mechanisms. These results are consistent with previous DTG analysis.

Using eq. (A6) and assuming first-order kinetics, $f(\alpha) = (1 - \alpha)$, the values of the pre-exponential factor k_0 can be estimated from the intercept I_α for each α value:

$$\log(k_0) = I_\alpha + \log(-Ln(1-\alpha)) - \log\left(\frac{E_{Doyle}}{R}\right) + 2.315 \quad \text{(A8)}$$

An average pre-exponential factor $(\log(k_0) = 14.0 \pm 0.8)$ can be determined for the same range of degree of progress (0.2–0.9).

APPENDIX B: DESCRIPTION OF THE FRIEDMAN METHOD

The Friedman method is not an integral method. It is based on the determination of the reaction rate at a given degree of progress α for various heating rates. By taking the logarithm of eq. (4) and after rearranging, the following equation is obtained:

$$Ln\left(\beta\frac{d\alpha}{dT}\right) = Ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + Ln(k_0) + Ln(f(\alpha)) \quad \text{(B1)}$$

The plots of $\ln(\beta d\alpha/dT)$ versus $1/T$ at different fixed degrees of progress α shows parallel lines with a slope equal to $-E/R$.

Consistent with the results found by the FWO method, the activation energy appears quasi-constant for a wide range of degrees of progress. Its average value is equal to 227 ± 11 kJ mol^{-1} for degree of progress between 0.2 and 0.9. This result (quasi constant activation energy) bears out the existence of a single apparent reaction mechanism for a wide range of degree of progress.

The intercepts I_α of the straight lines are equal to $\ln(k_0 f(\alpha))$. Assuming first-order kinetics, $f(\alpha) = (1-\alpha)$, it is then possible to determine k_0 from eq. (B1) for each α value:

$$\ln k_0 = I_\alpha - Ln(1-\alpha) \quad \text{(B2)}$$

An average pre-exponential factor $(\log(k_0) = 16.0 \pm 1.2)$ has been then found, for $0.2 < \alpha < 0.9$.

APPENDIX C: DESCRIPTION OF THE KISSINGER METHOD

Kissinger's differential method of Kissinger is based on the fact that, for a given heating rate β, the DTG curve reaches a maximum at a temperature T_{max} during the temperature rise. This is based on the assumption that this maximum rate of degradation approximately occurs at a fixed degree of progress α_{max} (here 0.42 ± 0.02). At the maxima of the DTG curves, $d^2\alpha/dt^2 = 0$. The resulting expression is then rewritten to give

$$\ln\frac{\beta}{T_{max}^2} = -\frac{E}{RT_{max}} + ln[-\frac{k_0 R}{E}\frac{df}{d\alpha}(\alpha_{max})] \quad \text{(C1)}$$

According to qq. (C1), $\ln(\beta/T_{max}^2)$ is a linear function of $1/T_{max}$, with a slope equal to $-E/R$. The activation energy estimated from the slope is equal to 226 ± 27 kJ mol^{-1}.

Using eq. (C1), the logarithm of the pre-exponential factor $\log(k_0)$ can then be determined from the intercept, assuming first-order kinetics. It is equal to 16.5 ± 0.1.

REFERENCES

1. Lee, H.; Neville, K. Epoxy Resins: Their Applications and Technology. McGraw-Hill: New York, **1957**; Vol. *54*, pp 4.

2. Zhang, W.; Li, X.; Yang, R. *Polym. Degrad. Stab.* **2011**, *96*, 1821.

3. Ho, T.; Leu, T.; Sun, Y.; Shieh, J. *Polym. Degrad. Stab.* **2006**, *91*, 2347.

4. Saad, G. R.; Abd Elhamid, E.; Elmenyawy, S. A. *Thermochim. Acta* **2011**, *524*, 186.

5. Installation Pégase – INB 22, Evaluation complémentaire de la sûreté au regard de l'accident survenu à la centrale de Fukushima Daiichi, CEA/DEN/CAD/DIR/CSN DO590, 2012.

6. Kinjo, N.; Ogata, M.; Nishi, K.; Kaneda, A.; Dušek, K. *Adv. Polym. Sci.* **1989**, *88*, 1.

7. Messersmith, P. B.; Giannelis, E. P. *Chem. Mater.* **1994**, *6*, 1719.

8. Arora, S.; Lal, S.; Kumar, S.; Kumar, M.; Kumar, M. *Arch. Appl. Sci. Res.* **2011**, *3*, 188.

9. Chiang, C. L.; Chang, R. C.; Chiu, Y. *Ch. Thermochim. Acta* **2007**, *453*, 97.

10. Reich, L. *J. Polym. Sci. Part B: Polym. Lett.* **1964**, *2*, 621.

11. Montserrat, S.; Málek, J.; Colomer, P. *Thermochim. Acta* **1998**, *313*, 83.

12. Montserrat, S.; Málek, J.; Colomer, P. *Thermochim. Acta* **1999**, *36*, 65.

13. Park, J. J. *Trans. Electr. Electron. Mater.* **2012**, *13*, 204.

14. Gu, A.; Liang, G. *J. Appl. Polym. Sci.* **2003**, *89*, 3594.

15. Carrasco, F. *Thermochim. Acta* **1993**, *213*, 115.

16. Patel, J. P.; Parsania, P. H. *J. Mater. Sci.* **2013**, *2013*, ID 892371.

17. Dixit, V.; Nagpal, A. K.; Singhal, R. *Malays. Polym. J.* **2010**, *5*, 69.

18. Wang, J.; Zhan, Y.; Fang, J.; Gao, H. *J. Appl. Polym. Sci.* **2012**, *123*, 1024.

19. Chen, K. S.; Yeh, R. Z. *J. Hazard. Mater.* **1996**, *49*, 105.

20. Shan, S. Y.; Jia, Q. M.; Jiang, L. H.; Wang, Y. W. *Adv. Mater. Res.* **2011**, *213*, 502.

21. Pistor, V.; Soares, B. G.; Mauler, R. S. *Polym. Comp.* **2012**, *33*, 1438.

22. Macan, J.; Brnardić, I.; Orlić, S.; Ivanković, H.; Ivanković, M. *Polym. Degrad. Stab.* **2006**, *91*, 122.

23. Lee, J. Y.; Shim, M. J.; Kim, S. W. *J. Appl. Polym. Sci.* **2001**, *81*, 479.

24. Jimenez, M.; Duquesne, S.; Bourbigot, S. *Polym. Degrad. Stab.* **2009**, *94*, 404.

25. Gronli, M. G.; Varhegyi, G.; Blasi, C. D. *Ind. Eng. Chem. Res.* **2002**, *41*, 4201.

26. Burnham, A. K. *Thermochim. Acta* **2000**, *355*, 165.

27. Vyazovkin, S. *Thermochim. Acta* **2000**, *355*, 155.

28. Cardwell, R. D.; Luner, P. *Sci. Technol.* **1976**, *10*, 183.

29. Kissinger, H. E. *J. Anal. Chem.* **1957**, *29*, 1702.

30. Friedman, H. L. *J. Polym. Sci.* **1964**, *6*, 183.

31. Flynn, J. H.; Wall, L. A. *Polym. Lett.* **1966**, *4*, 323.

32. Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1881.

33. Wang, X.; Hu, Y.; Song, L.; Xing, W.; Lu, H. *J. Polym. Sci. Part B: Polym. Phys.* **2010**, *48*, 693.

34. Ni, Y.; Zheng, S. *Macromol. Chem. Phys.* **2005**, *206*, 2075.

35. Chin, W. K.; Shau, M. D.; Tsai, W. C. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 373.

36. Wang, C. S.; Shieh, J. Y. *J. Appl. Polym. Sci.* **1999**, *73*, 353.

37. Prime, R. B. Thermal Characterization of Polymeric Materials. Edith Turi: San Diego, **1997**; Vol. *2*, Chapter 5, pp 435.

38. Shieh, J. Y.; Wang, C. S. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 369.

39. Buch, X.; Shanahan, M. E. R. *J. Appl. Polym. Sci.* **2000**, *76*, 987.

40. Bardonnet, P. Résines époxydes (EP) - Composants: propriétés. Techniques de l'ingénieur : France, 1992, A 3465.

41. Lin, S. T.; Huang, S. K. *Polym. J.* **1997**, *33*, 365.

42. Starink, M. J. *Thermochim. Acta.* **2003**, *404*, 163.

43. Sbirrazzuoli, N.; Vincent, L.; Mija, A.; Guigo, N. *Chemom. Intell. Lab. Syst.* **2009**, *96*, 219.

44. Doyle, C. D. *Nature.* **1965**, *207*, 290.

45. Flynn, J. H. *J. Therm. Anal.* **1983**, *27*, 95.

46. Atkins, P. ; De Paula, J. Physical Chemistry. W.H. Freeman and Company: New York, **2006**, pp 797.