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Comparative studies on the non-isothermal DSC curing kinetics of an unsaturated polyester resin using free radicals and empirical models

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Abstract

In this paper, we study the kinetics of the curing of an unsaturated polyester resin initiated with MEKP by means of DSC. DSC runs were performed at different heating rates. The experimental curves were fitted using two kinetic models: one involving the concept of free-radical polymerization, and the other an empirical model that does not take into account the different steps involved in the curing. A computer program was developed to find the parameters involved in each kinetic model. The calculation algorithm uses the Runge–Kutta numerical integration and the "downhill simplex method". The experimental data are very well fitted by using both models. The activation energy values are in concordance with the values tabulated by Odian. In the model theoretical calculation, it is useful to know the decomposition rate constant of the initiator. We determined the decomposition constant by using two different methods. Both methods give similar values of the activation energy E_d and they are in agreement with those tabulated in the literature. © 1997 Elsevier Science B.V.

Keywords: Curing kinetics; Unsaturated polyester resin; DSC; Free-radical polymerization

1. Introduction

The curing of an unsaturated polyester (UP) resin is a free-radical polymerization in which the resin is transformed from liquid state into a rigid cross-linked molecular structure. To induce the production of free radicals in the system, organic peroxides are commonly used. Free radicals can be formed by thermal decomposition of peroxide or by chemical decomposition in ambient temperature applications [1–3]. The curing of a thermoset is complex in that several steps are involved. The curing is highly exothermal and can be monitored by thermal analysis as the differential scanning calorimetry (DSC). The composition of the groups of reactant contained in the UP resin influences not only the curing rate but also the final mechanical properties of the material. Their handling and their processing require an understanding of the reaction kinetics of polymerization during cure. For instance, given the exothermicity of these materials, the control of temperature during the cure is of great importance for the quality of the product [3].

The kinetic study of an exothermic reaction like the curing of a thermosetting resin allows us to determine how much, how fast and at which temperature range the heat is released. Any study of reaction kinetics requires the following fundamental data: reaction rate and degree of conversion of reactant(s) [3–5]. The DSC technique allows us to evaluate not only the heat

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of reaction but also the reaction kinetics. In this technique it is assumed that the rate of exchanged heat is strictly proportional to the rate of the global chemical reaction(s) at any instant as follows [6,7]

$$\frac{dH}{dt} = \Delta H_R \frac{d\alpha}{dt} \tag{1}$$

where dH/dt is the heat generated by time unit or heat flow (DSC ordinate), $d\alpha/dt$ the rate of reaction and ΔH_R is the heat of reaction obtained as the area of DSC thermogram. Therefore, it is possible to evaluate the reaction rate $d\alpha/dt$ at the time t and the degree of conversion α reached at time t by means of the following expressions:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_R}\frac{dH}{dt}, \quad \alpha = \frac{\Delta H_t}{\Delta H_R} \tag{2}$$

where ΔH_t is the heat released up to time t and it can be obtained by integration of the calorimetric signal dH/dt up to time t.

There are two possibilities to model the curing behaviour of UP resin using DSC calorimetry as the experimental technique. One uses the concept of free radical polymerization. Stevenson [8] considered several special cases, each of them based on different assumptions in order to simplify the rate expressions. Then he compared theoretical predictions with experimental results obtained by DSC. Similar methods have been developed by other investigators [9–11]. These methods are of great interest to understand the curing chemistry of UP resins, but they have a great complexity with respect to the empirical kinetic methods. The other possibility is due to Kamal et al. [12] who have considered a semi-empirical approach to express the curing kinetics of UP resin. Other investigators [13,14] have found that these empirical methods were in agreement with their experimental results obtained from isothermal DSC measurements or DSC non-isothermal measurements. This procedure is more simple than the other and it is the most widely outlined and used in the literature.

The purpose of this paper is to simulate the process of curing of a UP resin initiated with MEKP by means of DSC calorimetry. Non-isothermal experiments were made at different heating rates. The experimental curves were fitted using two kinetic models: one using the concept of free-radical polymerization and the other being an empirical kinetic model. Both models give good theoretical predictions with experimental results.

2. Theoretical part

2.1. Empirical model

This procedure is the most widely used and described in the literature. In general, a kinetic model relates the rate of reaction $d\alpha/dt$ to some function of α and T. It is commonly accepted in the kinetic analysis of chemical reactions by thermal analysis that any chemical process of reaction will obey a rate law of the form [15,16]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{3}$$

where the functional dependence upon α is separated from the dependence upon T. Here, $k(T)$ is the chemical rate constant which is given by an Arrhenius type equation dependence on the temperature $k = A\exp(-E/RT)$, where A is the frequency factor and E the activation energy of the reaction. Thus, for one reaction, using a multiple linear regression, it is possible to determine the kinetic parameters from the DSC exothermal peak obtained from either isothermal or non-isothermal measurements. When the process is isothermal, the temperature is constant, but in the non-isothermal process the temperature usually increases according to a constant heating $\beta = \mathrm{d}T/\mathrm{d}t$ ($T = T_0+\beta t$). Even though the isothermal rate expression obtained in isothermal measurements is more precise, from a theoretical point of view, than non-isothermal rate expression, non-isothermal DSC measurement is, in general, less time consuming and thus more attractive than isothermal measurement.

In isothermal DSC experiments, it is not necessary to know the equation for $f(\alpha)$, which may vary during the curing process. Applying the isoconversional adjustment [17,18], given by the expression $\ln t = A + E/RT$ ($\alpha = ct$) at a series of temperatures, it is possible to determine from the slope of this linear relation the activation energy at different degrees of conversion and, thus, to see how the reaction process evolves. Using this method, an activation energy is obtained which depends on the degree of conversion. The isoconversional adjustment has been used with success in the curing of polyester resins and epoxy resins. On the other hand, when non-isothermal experiments are performed, the function $f(\alpha)$ has to be specified.

With regard to $f(\alpha)$ [3], two functions are used to characterize the curing of a thermosetting resin: the *n*th-order reaction and the autocatalyzed mechanism of reaction. When isothermal DSC experiments show the existence of an induction time (the time needed for the reaction to start up), the autocatalyzed function for $f(\alpha)$ reproduces the curing process for UP resins better than the *n*th-order function. In this paper, the autocatalyzed function for $f(\alpha)$ is used; it is given by the following expression:

$$f(\alpha) = \alpha^m(1-\alpha)^n \quad (4)$$

where *m* and *n* are the orders of reaction. Therefore, the experimental data will be fitting according the next expression:

$$\frac{d\alpha}{dt} = Ae^{(-E/RT)}\alpha^m(1-\alpha)^n \quad (5)$$

The constants *A*, *E*, *m* and *n* of Eq. (5) are the kinetic parameters that must be determined. This expression can be written in the logarithmic form:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A - \frac{E}{R}\frac{1}{T} + m\ln\alpha + n\ln(1-\alpha) \quad (6)$$

This is the equation of a hyperplane in the hyperspace of four dimensions: $z = a + bx + cy + du$. A multilinear regression [6,19] (using the least-squares method) of the triplets $(d\alpha/dt, \alpha, T)_i$ obtained by DSC measurements allows us to determine the kinetic parameters. Sometimes, the limits of the range used in the determination of kinetic parameters for the degree of conversion do not correspond to $\alpha = 0$ and $\alpha = 1$. This is so because the beginning ($\alpha = 0$) and the end ($\alpha = 1$) of the calorimetric curve cannot be fitted with the least-squares method [20]. These problems can be avoided if the procedure of calculation explained in Appendix A is used. In this procedure, the corresponding kinetic parameters are computed by applying the downhill simplex algorithm and the Runge–Kutta numerical method to solve differential equations.

2.2. *Free-radical method*

The kinetics of the curing reaction of an UP resin initiated with an organic peroxide can be approached by a mechanism of free-radical polymerization. This consists of a sequence of steps: initiation, inhibition, propagation and termination. The reactive components in a commercial resin consist of an unsaturated polyester [E], styrene [S], an inhibitor [Z] and an initiator [I]. On the basis of some experimental evidences and theoretical interpretations, the system of equations with 16 or more parameters [8] which rigorously describe the process of polymerization with their different steps, can be simplified assuming [11,21,22]:

1. The polymerization reaction does not start until the inhibition reaction goes to completion. (The free radicals produced by thermal decomposition of peroxide are neutralized by quinone stabilizers during the induction period.)
2. Any carbon double bond in the polyester chain or styrene monomer has the same rate constant of reaction with an initiator radical [I·]. Therefore, the sum of concentration of polyester resin [E] and styrene [S] will be represented by [M].
3. The rate constant of decomposition k_d has a dependence on temperature given by an Arrhenius-type equation: $k_d = A_d\exp(-(E/RT))$.
4. The degree of conversion is defined as:

   $$\alpha = \frac{[M]_0 - [M]}{[M]_0} \quad (7)$$

   where $[M]_0$ is the initial concentration of monomer and $[M]$ the concentration at time *t* monomer.
5. The propagation step is characterized by a single average rate constant k_p. Normally, the following empirical expression is used:

   $$k_P = k_{P_0}(1-\alpha)^n \quad (8)$$

   where k_{P_0} has a dependence on temperature as the following Arrhenius relationship:

   $$k_{P_0} = A_P\exp(-E_p/RT) \quad (9)$$

6. The rate expression for propagation step can be written as [8,11]:

$$-\frac{1}{[M]_0}\frac{d[M]}{dt} \equiv \frac{d\alpha}{dt} = k_p(1-\alpha)[R\cdot] \qquad (10)$$

This expression allows us to compare the calculated reaction rate with the experimental reaction rate.

7. The termination step can be considered negligible. This is especially true when termination is hindered by gelation at the early stages of the reaction. On the other hand, Han and Lee [11] have proved that the value of k_t has little effect on the isothermal simulation of the reaction curing by free-radical polymerization, indicating that the termination plays only a small role in determining the system parameters.

Therefore, considering these simplifications and assumptions, the system of equations describing the curing process of an UP resin can be reduced and can be written as:

Initiator:

$$\frac{d[I]}{dt} \equiv -k_d[I] = -A_d\exp(-E_d/RT)[I] \qquad (11)$$

Monomer:

$$\frac{d\alpha}{dt} = A_p\exp(-E_p/RT)(1-\alpha)^{1+n}[R\cdot] \qquad (12)$$

Radical:

$$\frac{d[R\cdot]}{dt} = fA_d\exp(-E_d/RT)[I] \qquad (13)$$

where f is the efficiency of the initiator. Han and Lee [11,22] have pointed out that the value of f, in the isothermal curing, decreases with the degree of conversion as a consequence of the so-called caging effect. For simplicity, the greatest number of works mentioned in the literature using a constant value for f [23]. In this work, we have taken a constant value for f, which does not depend on the degree of conversion.

This system of equations allows us to simulate dynamic curing of a UP resin. Moreover, the initiator concentration [I], the radical concentration [R], the degree of conversion α and the rate of reaction $d\alpha/dt$ can be obtained as a function of temperature (or time). This system of equations can be solved only by means of numerical methods such as the Runge–Kutta procedure for three variables dependent (α, [I] and [R·])(see Appendix A). In solving this system, the next initial conditions, $[I]=[I]_0$, $[R]\equiv[R]_0=f[I]_0$ and $\alpha=0$ for $t=0$, must be taken into account.

The six numerical kinetic parameters (f, A_d, E_d, A_p, E_p and n) can be obtained by solving the system of equations by the Runge–Kutta method and comparing the calculated values $d\alpha/dt$ with the experimental values $d\alpha/dt$ until there is a good agreement within a prescribed tolerance. The calculation procedure uses the numerical Runge–Kutta and the "downhill simplex method" due to Nelder and Mead for finding the set of kinetic parameters that minimizes the merit function (see Appendix A).

2.3. Determination of the decomposition constant of peroxide

The number of kinetic parameters to be determined can be reduced to the following four parameters: f, A_p, E_p and n, since the kinetic parameters A_d and E_d corresponding to the initiator decomposition can be found. These parameters A_d and E_d can be determined from the half-life values reported for thermal decomposition of the peroxide and they are generally tabulated [1]. However, there is a difficulty. These parameters for decomposition constant are normally obtained in different conditions from those in which the peroxide decomposes during the curing. Therefore, these values may vary slightly according to the mode in which the initiator decomposes in the experiments realized and care must be taken in applying these data. For this reason, several authors [23,24] have proposed the following method to determine the decomposition constant of the initiator.

This method is based on the onset of polymerization in the DSC thermogram. Assuming that the polymerization does not start until the inhibitor is completely consumed during the induction period (t_{ind}), the following expression can be obtained [23–25]:

$$m[Z]_0 = d[I]_0\int_0^{t_{ind}} e^{-k_d t}dt \qquad (14)$$

where $[Z]_0$ is the initial concentration of inhibitor, m the number of molecules that react with the free radicals formed (in the case of hydroquinone $m=2$), $[I]_0$ the initial concentration of initiator, d

the number of free radicals generated by thermal decomposition of the peroxide (in this case $d = 2$) and k_d the reaction constant of decomposition. This expression can be used to determine the decomposition constant k_d of peroxide if these quantities are known: m, d, $[Z]_0$, $[I]_0$ and t_{ind}.

In an isothermal DSC run, the temperature is constant and the foregoing expression can be integrated easily. When the DSC measurements are carried out at different heating rate (non-isothermal conditions), before the integration is done, the expression must be replaced by the following equation,

$$m[\mathrm{Z}]_0 = d[\mathrm{I}]_0 \int_0^{T_0} \frac{1}{\beta} \mathrm{e}^{-k_d t} \mathrm{d}T \qquad (15)$$

The second term of the equation is called the temperature integral and can be evaluated by introducing the variable $x = E_d/RT$ and taking into account the Doyle approximation [26]. Therefore, the following is obtained:

$$\log \beta = C - \frac{0.4567 E_d}{R} \frac{1}{T_0} \qquad (16)$$

where β is the heating rate and T_0 the onset temperature of dynamic DSC peak. The constant C can be easily demonstrated, and is given by:

$$C = \log A_d - 2.315 + \log \frac{E_d}{R} + \log \left(\frac{m[\mathrm{Z}]_0}{d[\mathrm{I}]_0} \right) \qquad (17)$$

Eq. (16) shows a linear dependence of the reciprocal absolute onset temperature T_0 on the logarithm of the heating rate β. The activation energy E_d (kJ/mol) can be calculated from the slope of the straight line, either graphically or by linear regression. The factor frequency A_d (s^{-1}) can be estimated from the ordinate intersection of the straight line obtained using Eq. (17).

3. Experimental part

3.1. Materials and calorimetric instrumentation

A commercially available general purpose UP resin with commercial name Estratil A-228 was used in this study. The base of polyester consists of phthalic anhydride, malic anhydride and propylene glycol with a molar ratio of 3 : 2 : 5 obtained by ^{1}H NMR. It was supplied with 35 wt% of styrene as a cross-linking agent. In curing the resin a catalytic system was used: a 50% solution of methyl ethyl ketone peroxide (MEKP) in dimethyl phthalate, supplied by AKZO (commercial name BUTANOX M-50). The peroxide content is 33%. Elevated temperatures are required for the curing of a UP resin initiated with MEKP. For room temperature applications, it is also necessary to use MEKP together with a cobalt salt as accelerator.

The calorimetric measurements were carried out in a METTLER DSC 30 calorimeter. All DSC measurements were done in hermetic aluminium pans. A standard sample was prepared by mixing 10 g of UP resin with a fixed proportion of initiator (100 : 1) for about 1 min. The required amount of sample (20 mg) was weighed into a sample pan which is then sealed and placed in the DSC for each measurement. After each run, the weight of the sample was determined again to check any weight loss due to the evaporation of the styrene monomer. No significant weight loss was observed. The dynamic scans were performed from −100° to 250°C using a nitrogen atmosphere and different heating rates: 2, 5, 10, 15, 20, and 25°C/min.

3.2. Experimental results

Fig. 1 represents the heat generated vs. the cure temperature with the heating rate β as parameter. It can be seen from Fig. 1 that:

1. the temperature at which reaction begins increases with β;

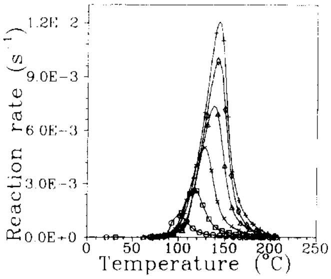

Fig. 1. Reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ vs. temperature for dynamic scans at different heating rates.

Table 1
Total heat of reaction ΔH_R, peak temperature T_p and degree of conversion of the peak α at different heating rates

β/(°C/min)	T_p/°C	ΔH_R/(J/g)	α_p
2	101.1	374.2	0.437
5	117.4	368.1	0.438
10	127.3	358.0	0.452
15	136.2	352.6	0.451
20	141.7	355.6	0.473
25	143.2	350.7	0.482

2. the exothermic peak temperature increases β;
3. the temperature at which the completion of the cure reaction occurs increases with β; and
4. the size of an exothermic peak increases with β.

Table 1 summarizes the exothermic DSC peak temperature T_p, the heat of reaction ΔH_R estimated from the area under the DSC curve and the degree of conversion $\alpha = \alpha_p$ achieved when the temperature is equal to the exothermic peak temperature. As can be seen there, the amount of heat generated by a curing reaction decreases with increasing β. Other investigators [21] have found a similar result. An average value of 359.9 J/g was assigned to the heat of polymerization of the UP resin. Other investigators [27,28] have reported a range of heat of polymerization from 292.6 J/g to 426 J/g for UP resins. This range may be due to the different types of UP resins and free radical initiator systems employed in each study [21,27].

3.3. Ozawa procedure

This method allows us to determine the activation energy E and preexponential factor A for nth-order reactions. Even for autocatalyzed reactions this method [3] gives an accurate measure of the activation energy and preexponential factor. It is based on the variation of peak exotherm temperature with heating rate. Assuming that the extent of reaction at the peak α_p is constant and independent of heating rate, Ozawa [29] derived the following expression:

$$\ln \beta = \text{const} - 1.052\frac{E}{RT} \qquad (18)$$

This expression shows a linear dependence of the reciprocal absolute peak temperature on the logarithm of the heating rate. The activation energy E (kJ/mol) is calculated from the slope of the straight line obtained (Ozawa plot), either graphically or by linear regression. A good fit was observed with a regression coefficient of $r = 0.91$. From values tabulated in Table 1, a value of $E = 72.38$ kJ/mol was obtained.

4. Results and discussion

The kinetic analysis of thermoset cures involves a search for the kinetic parameters of the process according to a mechanistic model that fits the experimental data. The required properties (degree of conversion α and reaction rate $d\alpha/dt$ as time or temperature functions) were evaluated for each non-isothermal DSC curing at different heating rate, by using Eq. (2). The dynamic heat ΔH_R was obtained as the area under the DSC thermogram and it was assumed to represent the total reaction heat of polymerization. Therefore, 100% conversion was reached in all curing reactions studied in this work.

In order to compare the results obtained and to point out differences between them, two types of adjustments were made: one using the empirical method and the other using the free-radical method. Before using free-radical method, the decomposition constant of peroxide was determined. In both cases, the kinetic parameters were computed by applying the so-called downhill simplex algorithm and the Runge–Kutta procedure (see Appendix A).

4.1. Empirical method

Table 2 gives the kinetic parameters obtained for each heating rate considering an empirical kinetic model (Eq. (5)). The chi-square function $X^2(a)$ and the coefficient of correlation r are given too. The fitting of experimental data in the range of heating rate 5–20°C/min is better (r values closer to unity) than those obtained at other heating rates (r values smaller). In general, the kinetic parameters are not constant and show a dependence upon the heating rate. In the range of experimental heating rate, the energy of activation E seems to be constant with an average value of 90.96 kJ/mol. This value of activation energy is in concordance with the values tabulated in the literature [30] when an overall activation energy is associated with a steady-state free radical polymerization like the curing of UP resin. This overall

Table 2
Kinetic parameters, coefficient of correlation r and chi-square function for the different adjustments of experimental data using an empirical model of reaction kinetics at different heating rates

β/(°C/min)	k/(s^{-1})	E/(kJ/mol)	m	n	X	r
2	3.362×10^{10}	91.331	0.573	2.014	1.514×10^{-7}	0.953
5	2.014×10^{10}	90.603	0.542	2.089	2.487×10^{-7}	0.974
10	1.682×10^{10}	90.870	0.430	1.723	1.169×10^{-6}	0.969
15	1.109×10^{10}	90.814	0.398	1.549	2.963×10^{-6}	0.969
20	1.121×10^{10}	91.195	0.326	1.313	3.463×10^{-6}	0.971
25	1.217×10^{10}	90.933	0.302	1.343	1.747×10^{-5}	0.951

activation energy is the result of combining three separate Arrhenius-type equations for each occurring process (initiation, propagation and termination). When the reaction is initiated by thermal decomposition of the peroxide, as in our case, the overall activation energy for most free-radical polymerization is about 80–90 kJ/mol [30].

Fig. 2 gives a comparison of the calculated dα/dt vs. the cure temperature curves with experimental results at different heating rates. As can be seen, the calculated curves fit the experimental data well.

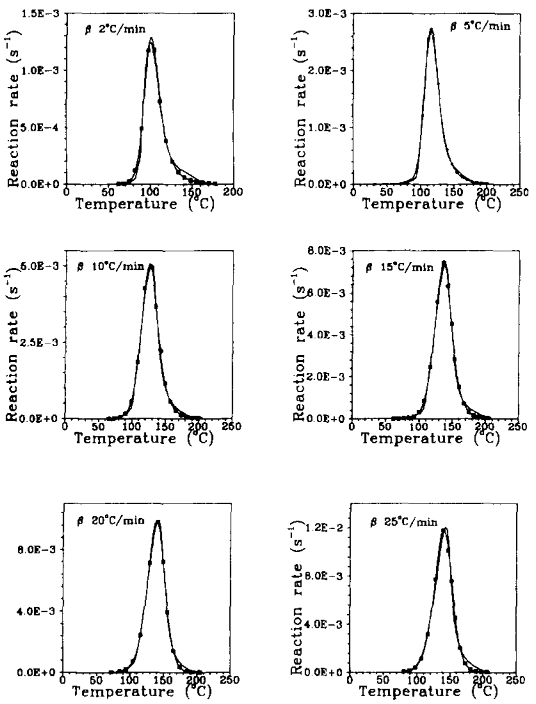

Fig. 2. Calculated dα/dt-temperature curves (- - -) using an empirical model of reaction kinetics and experimental dα/dt-temperature curves (———) at different heating rates.

4.2. Determination of the MEKP decomposition constant

Organic peroxides are widely used as initiators in free-radical polymerization since they can decompose thermally. The rate of decomposition is generally estimated from the half-life, which is the time required to reduce the active oxygen content of a peroxide solution by 50% at a given temperature. The rate of decomposition can also be estimated if the peroxide decomposition is studied by means of DSC calorimetry [31]. Another way to obtain the constant of decomposition is using the Eq. (16). In this section, we compare these methods.

Doehnert and Mageli [32] studied the kinetics of thermal decomposition of several organic peroxides used in the curing reaction of UP resins. When the decomposition is carried out in an inert solvent on attacking free radicals, the kinetics corresponds with a 1st-order reaction. Therefore, assuming a 1st-order reaction kinetics, it is possible to evaluate the activation energy from the half-life obtained at different temperatures according to the expression:

$$\ln t_{1/2} = \text{const} - \frac{E}{R}\frac{1}{T} \tag{19}$$

They found the following values: 117.95 kJ/mol and $3.93245 \times 10^{13}\ \text{s}^{-1}$ for the activation energy E and preexponential factor A of the MEKP decomposition in benzene.

We also studied the decomposition of peroxide directly in the DSC calorimeter using a high-pressure sealed pan to avoid the evaporation of the peroxide

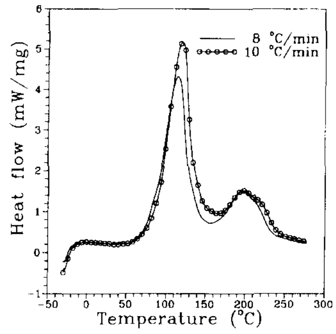

Fig. 3. MEKP decomposition scan carried out at 8 and 10°C/min, and pressure pan.

during the scanning. The evaporation phenomenon is an endothermal process and it could distort the calorimetric signal of decomposition kinetics of peroxide. In Fig. 3 we show the MEKP decompositions runs carried out at 8 and 10°C/min. These figures show two DSC peaks: the first is greater than the second, being about 80% of the total area. The first peak starts at low temperatures when free radicals are produced in the curing of UP resin to initiate the polymerization. The second occurs at high temperatures when the DSC curing of UP resin is finished (see Fig. 1). For this reason, we have used the kinetic analysis of the first peak to determine the decomposition rate of MEKP. The kinetics corresponds to a 1st-order reaction. In Table 3, we give the energies of peroxide decomposition obtained.

These values were obtained by studying the decomposition at high pressures. For the curing of a UP resin, the thermal peroxide decomposition takes place at atmospheric pressure. Therefore, the influence of the pressure on the rate constant of decomposition must be evaluated. The effect of pressure on the rate constant can be explained by means of chemical kinetics [33]:

$$\frac{\partial \ln k}{\partial P} = -\frac{\Delta V}{RT} \tag{20}$$

where k is the rate constant, ΔV the volume change in chemical species, P the pressure, R the universal gas constant and T the absolute temperature. If it is assumed that the volume change is independent of pressure, the following expression can be obtained by integration:

$$\ln k(P) = \ln k - \frac{P\Delta V}{RT} \tag{21}$$

where $k(P)$ is the rate constant at high pressure and k the rate constant at atmospheric pressure. If it is assumed that the activation energy depends only on the pressure, it can be written [34]:

$$E_d(P) = E_d + P\Delta V \tag{22}$$

The term $P\Delta V$ is generally small for liquids and solutions and it can be considered negligible. There-

Table 3
Activation energy of MEKP decomposition obtained at different heating rates.

β/(°C/min)	E_d/(kJ/mol)
5	104.3
8	118.5
10	113.9
15	115.5

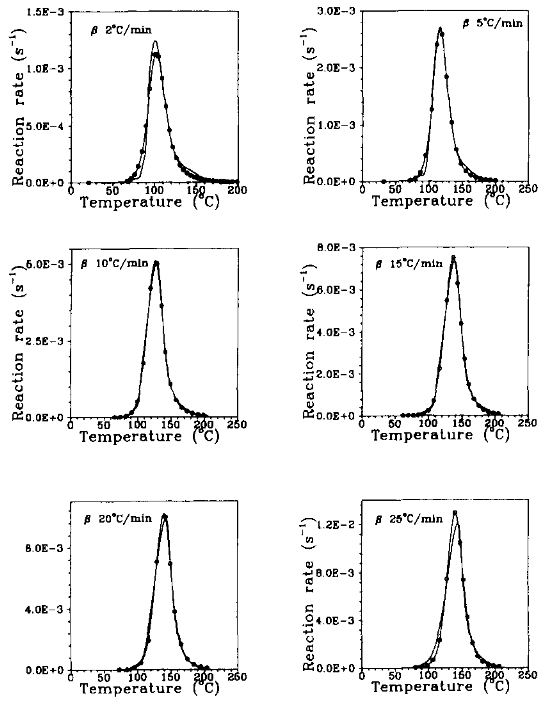

Fig. 4. Calculated dα/dt vs. temperature curves (- - -) using a free-radical model of reaction kinetics and experimental dα/dt vs. temperature curves (———) at different heating rates.

Table 4
Kinetic parameters, coefficient of correlation r and chi-square function for the different adjustments of experimental data using a free-radical model of reaction kinetics at different heating rates

β/(°C/min)	k_d/(s^{-1})	k_p/(s^{-1})	E_p/(kJ/mol)	n	f	X	r
2	2.058×10^{13}	1.385×10^{7}	56.398	0.823	0.754	2.493×10^{-7}	0.932
5	1.230×10^{13}	1.677×10^{6}	49.143	0.657	0.751	4.854×10^{-7}	0.963
10	6.652×10^{12}	3.910×10^{6}	49.385	0.874	0.746	8.058×10^{-7}	0.974
15	3.490×10^{12}	2.539×10^{6}	47.458	0.801	0.731	2.409×10^{-6}	0.972
20	3.058×10^{12}	3.779×10^{6}	47.841	0.736	0.733	6.323×10^{-6}	0.960
25	3.327×10^{12}	6.504×10^{6}	48.752	0.729	0.744	2.621×10^{-5}	0.940

fore, the values obtained at different heating rate for E_d can be used at atmospheric pressure.

Now, we can use the Eq. (17) to determine the MEKP decomposition constant. The onset temperature T_0 was evaluated from the experimental thermograms at different heating rates. Using Eq. (16), a linear dependence of the reciprocal absolute temperature T_0 on the logarithm of the heating rate can be obtained. From the slope, the activation energy E_d can be obtained. The value of 112.35 kJ/mol has been found for E_d. The preexponential factor can be determined from Eq. (17). This expression requires a knowledge of the values of initial concentrations of initiator $[I]_0$ and inhibitor $[Z]_0$. For the initiator, the following value for $[I]_0$ was calculated: $[I]_0 = 0.01905$ mol/l. The inhibitor amount of the commercial resin A-228 is 70 ppm. With these values, a preexponetial factor of 6.55×10^{13} s^{-1} was obtained.

The three methods give different values for E_d which differ at a maximum percentage of 6%. We assumed an average value for E_d of 113.71 kJ/mol. However, the values for the preexponential factor differ much among themselves. We have considered the preexponential factor as a parameter which must be determined by means of the fit of experimental data.

4.3. Free-radical method

First the experimental data were fitted using the calculation algorithm explained in Appendix A, with five parameters to be determined: k_d, f, k_p, E_p and n. In Table 4, we give the values obtained for these parameters and the merit function and correlation coefficient for each heating rate β. As can be seen, the parameters depend on the heating rate β. If we assume that the kinetic model of free radicals is correct, these parameters should be independent of the heating rate. If we admit different values for these parameters, we can obtain contradictory results. For instance, if we consider different values of k_d, the thermal decomposition of the peroxide can take places earlier at a lower heating rate than for a different value. For this reason, we assumed one single value for k_d. This value was the average of the values tabulated in Table 4. A value of 8.2341×10^{12} s^{-1} was obtained. Then, we fitted the experimental data to determine the following parameters: f, k_p, E_p and n. The parameters obtained are tabulated in Table 5 for each heating rate. The

Table 5
Kinetic parameters, coefficient of correlation r and chi-square function for the different adjustments of experimental data using a free-radical model of reaction kinetics at different heating rates. The factor frequency of the MEKP decomposition rate is assumed constant

β/(°C/min)	k_p/(s^{-1})	E_p/(kJ/mol)	n	f	X	r
2	1.374×10^{5}	39.694	0.762	0.735	4.715×10^{-7}	0.912
5	1.254×10^{5}	39.731	0.694	0.736	6.705×10^{-7}	0.956
10	1.576×10^{5}	39.679	0.619	0.735	7.003×10^{-7}	0.976
15	1.075×10^{5}	39.676	0.295	0.735	2.350×10^{-6}	0.972
20	1.245×10^{5}	39.582	0.205	0.736	4.618×10^{-6}	0.967
25	1.857×10^{5}	39.685	0.384	0.735	1.887×10^{-5}	0.950

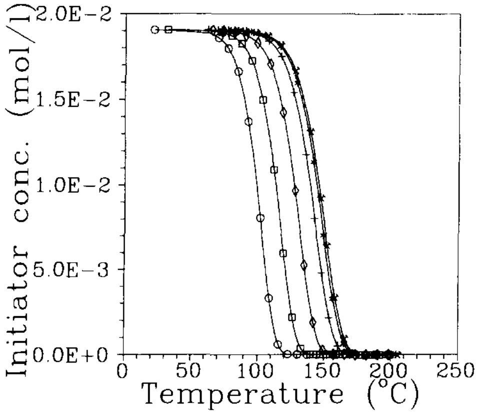

Fig. 5. Initiator concentration vs. curing temperature curves at different heating rates.

fitting of experimental data in the range of heating rate 5–20°C/min is better (r values closer to unity) than those obtained at other heating rates (r values smaller). In general, the kinetic parameters are not constant and show a dependence upon the heating rate. The activation energy for propagation E_p seems to be constant with an average value of 39.675 kJ/mol. This result is in concordance with the values given by Odian [30] for E_p (ca. 20–40 kJ/mol) in the polymerization for free radicals. The value for the efficiency of the MEKP initiator is constant too ($f = 0.735$).

In Fig. 4, we compare the experimental results with the theoretical results. As can be seen, there is a good fit. Fig. 5 gives the initiator concentration [I] as a function of curing temperature at different heating rate and Fig. 6 shows the radical concentration [R·] during the non-isothermal DSC cure at different heating rates. As can be noted, [I] decreases with cure temperature, since the rate of decomposition of initiator increases with temperature.

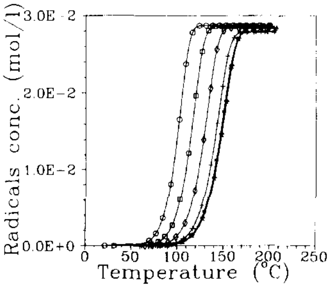

Fig. 6. Radical concentration vs. curing temperature curves at different heating rate.

5. Conclusions

The curing process of a UP resin initiated with MEKP was studied by DSC at different heating rates. The kinetic analysis was performed by means of an empirical model and theoretical model that uses the concept of free-radical polymerization. We compared the fits of experimental data by using both kinetic models. The results show a good agreement between the theoretical predictions and the experimental data. The following conclusions can be drawn:

1. In the empirical model of reaction kinetics, we have proposed a calculation algorithm based on the downhill simplex method and the Runge–Kutta procedure. This calculation algorithm does not have the problems encountered in the calculation procedure based on the multilinear regression [20]. The activation energy found is in agreement with the values given by Odian [30] for an overall process of reaction.
2. Based upon the peak temperature dependence on temperature, it is possible to find the energy of activation (Ozawa method). The value obtained is smaller than the value found with the empirical model.
3. In the free-radical model of reaction kinetics, the number of unknown parameters can be reduced, assuming the decomposition rate of peroxide is known. The rate of peroxide decomposition was determined directly by means of DSC and by a method which uses the onset temperature of DSC peak corresponding to the curing of UP resin at different heating rates. Both methods give similar values for the activation energy E_d. The efficiency of the initiator value f was found to br constant with the heating rate ($f = 0.735$).
4. The kinetic parameters obtained by fitting experimental data with the free-radical model do not show a dependence on the heating rate. The activation energy E_p corresponding to the propagation step of free-radical model is in concordance with the values tabulated by Odian [30] for a free-radical polymerization.

5. Even though the experimental data are fitted very well by using both kinetic models, the free-radical method is of great interest to understand the curing chemistry of UP resins. Moreover, it allows us to obtain the initiator concentration and the radical concentration as a function of cure temperature at different heating rates. As Han and Lee [11] pointed out, one of the advantages of this kind of mechanistic model over an empirical model lies in the fact that it is not necessary to conduct new experiments to determine the parameters involved while investigating the effect of variables (initiator and monomer concentrations) on the curing of UP resin. On the contrary, the empirical model gives kinetic parameters which describe the curing without any physico-chemical significance, since the model has no exact knowledge of the individual steps of the reaction involved in the curing.

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Appendix A

Runge–Kutta procedure

The Runge–Kutta procedure [35,36] is one of the available procedures to solve a system of differential equations by numerical integration. In the empirical model, the system of equations is, in fact, a dependent-variable problem. The Runge–Kutta procedure requires starting at $\alpha_0 = 10^{-8}$ (for larger values of α_0, the solution depends on the value of α_0) and $t = 0$ and to calculate the necessary conversion α at successive increments of time Δt. The accuracy of the solution obtained by this procedure depends on the value Δt. The solution will be made more accurate by covering the integration interval in two steps instead of one by using $\Delta t = \Delta t/2$. This procedure is continuously repeated until a good degree of accuracy is obtained. It has been verified that an increment of $\Delta t = 5 \times 10^{-3}$ min provides a sufficiently accurate solution.

In the free radical model the system of equations which must be solved is a three dependent-variable problem. An increment of $\Delta T = 5 \times 10^{-3}$ min was also used to obtain an accurate solution.

A.1 Calculation algorithm

The calculation algorithm has the following steps:

1. It starts with a set of $M + 1$ directions v_i. Each vector has M-dimensions. M is the number of kinetic parameters to determine (For the empirical model, the number of kinetic parameters is four, $m = 4$). (In free-radical model, the parameters to determine are $m = 6$)
2. For each vector v_i, it evaluates $\mathrm{d}\alpha/\mathrm{d}t$ by a Runge–Kutta procedure as described.
3. It computes the X^2-merit function for each direction. The merit function (sometimes called chi-square) is defined as [37]

$$X^2(a) = \sum_{i=1}^{N} (y_{\mathrm{exp},i} - y_{\mathrm{calc}}(T_i; \mathbf{a}))^2 \qquad (\mathrm{A1})$$

where N is the number of experimental values, y represents the reaction rate measured $\mathrm{d}\alpha/\mathrm{d}t(\exp)$ or calculated (calc) from the kinetic parameters and T_i denotes the temperature. The merit function simply measures the agreement between the experimental data points and the theoretical model. A smaller value for the merit function denotes better agreement.

4. It obtains the maximum and the minimum value of $X^2(a)$.
5. If |Max-Min| < Tolerance, it ends and prints the v_i direction for the minimum value.
6. If |Max-Min| > Tolerance, it sets a new set of directions by simplex method [35] and goes back to Step 1.

Another measure of the goodness of a fit is the correlation coefficient [38] defined as

$$r^2 = \frac{S_t - S_r}{S_t} \qquad (\mathrm{A2})$$

Here S_r is the standard error of the estimate and S_t is the standard deviation, both given, respectively, by the following expressions:

$$S_r = \sqrt[2]{\frac{\sum_{i=1}^{N}(y_{\text{calc}} - y_{\text{exp}})^2}{N-M}},$$

$$S_t = \sqrt[2]{\frac{\sum_{i=1}^{N}(y_{\text{calc}} - \bar{y})^2}{N-1}} \qquad \text{(A3)}$$

where y is the average value of the experimental data. For a perfect fit, the standard error of the estimate would approach $S_r = 0$ and the correlation coefficient would approach $r = 1$. The better the theoretical model fits the experimental data; the closer the correlation coefficient approaches to unity.

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