

# Kinetic Analysis of Two DSC Peaks in the Curing of an Unsaturated Polyester Resin Catalyzed With Methylethylketone Peroxide and Cobalt Octoate

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The curing of an unsaturated polyester resin catalyzed with methylethylketone peroxide and cobalt octoate as promoter is studied by DSC at different heating rates. A high promoter/peroxide ratio is used. The DSC curves show two exothermic peaks. It has been assumed that they represent two independent cure reactions. A set of kinetic parameters for each DSC peak has been obtained. They describe the overall cure process using an empirical kinetic model. Nth order and autocatalytic kinetic functions have been employed. A computer program was developed to calculate the degrees of conversion associated with each peak, and to evaluate the kinetic parameters. The calculation algorithm uses the Runge–Kutta numerical integration and the ‘downhill simplex method.’ This methodology permits to find all kinetic parameters simultaneously. DSC experimental data are very well fitted. The simulated first peak occurs always before the second one, and the fraction of reaction heat associated with the first peak over the overall reaction heat decreases with heating rate. Moreover, activation energies are in good agreement with the tabulated values for typical free radical polymerization induced by thermal and redox decomposition of the peroxides. POLYM. ENG. SCI., 47:62–70, 2007. © 2006 Society of Plastics Engineers

## INTRODUCTION

The unsaturated polyester (UP) resins cured with styrene are widely used in many industrial fields by their great benefits and their relatively low cost [1]. Before making any mechanical or physical analysis on such materials, it is important to characterize the kinetics of the curing. It has been shown that differential scanning calorimetry (DSC) is a powerful and useful thermal analysis technique to determine cure kinetics of thermoset resins [2–5].

The curing of an UP resin is a free radical polymerization in which the resin is transformed from the liquid state into a rigid crosslinked molecular structure, which becomes insoluble and infusible. To initiate the reaction a source of free radicals is needed, by means of heat or a catalytic system. Organic peroxides (initiators) are commonly used as the source of free radicals. In the cold process, this reaction can be initiated by addition of metallic salts or amines (initiator + promoter system), depending on the peroxide used [6–8]. UP resins cured with promoter exhibit two exothermic DSC peaks, whereas the resins without promoter show only a single exothermic DSC peak [9, 10].

Even though there are several controversial interpretations about the origin of these exothermic peaks [10–15], the first peak can be attributed to the polymerization initiated by a redox decomposition of methylethylketone peroxide (MEKP), and the second one to the polymerization initiated by the thermal decomposition of MEKP at high temperatures.

The kinetic models used to monitor the curing process of a thermosetting material, may be phenomenological or mechanistic models. Mechanistic models take into account the different reactive groups that take part in the cure process. They give a better prediction and interpretation of the cure reactions but they are, in general, very complex, and involve difficult computations. So, in most studies of the cure processes by DSC, researchers prefer the use of phenomenological models that facilitate simple computations with kinetic parameters such as activation energy, reaction order, and pre-exponential factor. In the present work, a phenomenological model will be used to obtain the kinetic parameters of the curing.

A number of phenomenological models, that use a generalization of the ASTM Test Method E698 [16, 17], have been developed to characterize the cure process with two or more DSC exothermic peaks. In these models, some or all of the following steps are undertaken: (1) to separate the different peaks by means of a Gaussian distribution (it is an necessary step when a DSC thermo-

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gram displays one or more shoulders [18], (2) to find the Arrhenius parameters by means of the ASTM E698 method, (3) to evaluate the rest of the kinetic parameters by means of a nonlinear regression technique, and (4) to determine the relative weight of each reaction rate to the total. Grentzer et al. [19] used the ASTM E698 methodology to monitor the cure of novolac modified vinyl ester and they found an activation energy for each DSC peak. Focke and Smit [20] also used this method in the curing of a phenolic resin. In this article, an original kinetic model is proposed. The main advantage of the latest method respect to the ASTM E698 one, is that the kinetic parameters are calculated simultaneously. Gaussian distributions are not used either.

The aim of this study is: (a) to analyze the two DSC exothermic peaks in the DSC curing of an UP resin with MEKP peroxide as initiator and cobalt octoate as promoter, (b) to separate the two reactive processes, obtaining a set of kinetic parameters and also the overall heat fraction associated with the first peak, and (c) to shed some light onto the still unsolved problem of the two peaks appearing during an UP resin cure.

## EXPERIMENTAL PART

### *Materials and Calorimetric Instrumentation*

A commercial UP resin was used in this study. Reposa S.A. supplied the UP resin under the commercial name Estratil A-228. The base of polyester consists of phthalic anhydride, maleic anhydride, and propylene glycol with a mole ratio of 3:2:5 obtained by  $^1\text{H}$  NMR. The NMR peak for maleic anhydride was very small because maleate isomerizes to fumarate extensively during the synthesis of UP resins. The average weight of the UP was 1696 g/mol and the equivalent molecular weight per mole  $\text{C}=\text{C}$  was 465 g/mol. The resin contains an average of 3.64 vinylene groups per polyester molecule. It was supplied with 35 wt% of styrene as a crosslinking agent. The resin system has approximately 2:1 styrene: polyester  $\text{C}=\text{C}$  molar ratio.

For the curing of the resin a catalytic system was used: a 50% solution of MEKP in dibutyl phthalate (supplied by AKZO with commercial name BUTANOX M-50) with a 6% cobalt octoate ( $\text{CoO}$ ) solution in phthalate (provided also by AKZO). The resins contain between 70 and 125 ppm of hydroquinone as an inhibitor to prevent premature polymerization of resin during shipping and handling. The existence of an induction time before polymerization during a DSC run proves the presence of inhibitor. Ideal inhibitors should not affect the rate of cure after the induction time.

The calorimetric measurements were carried out in a METTLER DSC 30 calorimeter. All DSC measurements were done in hermetic aluminum pans. A standard sample was prepared by mixing 10 g of UP resin with a fixed proportion of initiator and promoter (100:1:0.1) for about 1

min. The required amount of sample (20 mg) was weighed into a previously weighed sample pan, sealed, and placed in the DSC for each measurement. The pan can fill up to 40 mg. After each run, the weight of the sample was determined again to check any weight loss because of the evaporation of the styrene monomer. No significant weight loss was observed. The dynamic scans were performed from  $-100$  to  $250^\circ\text{C}$  in a nitrogen atmosphere at different heating rates: 2, 5, 10, 15, 20, and  $25^\circ\text{C}/\text{min}$ .

From the experimental point of view, nonisothermal scans with different heating rates, can be carried out within a much wider temperature range than isothermal experiments. Then, nonisothermal scans allow discernment between the different reaction paths involved in the kinetic process because the data contain the necessary information on the time-temperature dependence of particular processes which is a prerequisite for the correct identification of the complex nature of the investigated reaction [21].

## THEORETICAL PART

### *Degree of Conversion $\alpha$ and Reaction Rate $d\alpha/dt$*

The curing of an UP resin is very complex and highly exothermal and can be monitored by thermal analysis using the DSC. The kinetic study of an exothermal 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. The quantitative DSC technique is commonly used for monitoring the process and for evaluating not only the heat of reaction, but also the reaction kinetics [22, 23]. In this technique it is common to assume that the rate of exchanged heat evolution is strictly proportional to the rate of the global chemical reaction(s) at any time as follows [24, 25]:

$$\frac{dH}{dt} = \Delta H_R \frac{d\alpha}{dt} \quad (1)$$

where  $dH/dt$  is the normalized heat generated per time unit or normalized heat flow (DSC ordinate in  $\text{mW}/\text{mg}$ ),  $d\alpha/dt$  is the reaction rate and  $\Delta H_R$  is the heat of reaction by unit of mass obtained as the area of the DSC thermogram divided by the sample mass. Therefore, it is possible to evaluate the reaction rate  $d\alpha/dt$  and the degree of conversion  $\alpha$  at time  $t$  by means of the following expressions:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_R} \frac{dH}{dt} \text{ and } \alpha = \frac{\Delta H_t}{\Delta H_R} \quad (2)$$

where  $\Delta H_t$  is the released heat per unit of mass up to the time  $t$ . It can be obtained by integration of the normalized calorimetric signal  $dH/dt$  up to time  $t$ .

The presence of more than one exothermic peak is frequently reported in the literature for epoxy curing systems [26, 27] and phenolic resins [20, 28], and it is attributed to different and independent kinetic reactions amongst their components. Two exothermic peaks appear in the DSC thermograms of the UP resin curing which will be studied next. The analysis begins with the following hypothesis:

a. The first peak, which occurs at low temperatures, is caused by Reaction 1.

b. The second peak, which occurs at high temperatures, is caused by Reaction 2.

c. The curing process involves two cure reactions with different activation energies.

The second peak should have a larger energy of activation than the first one. Assumptions (a), (b), and (c) are a test of consistence of this empirical model. Verification of this test imposes a strong restriction on the model, since Reactions 1 and 2 may or may not occur simultaneously. However, the test of consistence (assumed here) requires that Reactions 1 and 2 must be consecutive reactions: first Reaction 1, afterwards Reaction 2.

d. Each reaction obeys a rate law of the type:

$$\frac{d\alpha_i}{dt} = k_i[T]f(\alpha_i) \quad i = 1, 2. \quad (3)$$

where it has been separated the dependence upon  $\alpha$  from the dependence upon  $T$ .  $f(\alpha_i)$  is the mechanism function of Reaction  $i$ . The rate constants  $k_1(T)$  and  $k_2(T)$  differ significantly so that the position of exothermic peaks for each individual reaction is not affected by the other, and they can be clearly distinguished. The dependence upon temperature of  $k_i(T)$  follows an Arrhenius-type equation:

$$k_i(T) = A_i \exp(-E_i/RT) \quad (4)$$

where  $A_i$  is the frequency factor and  $E_i$  is the activation energy.

e. The mechanisms of Reactions 1 and 2 may not be the same. For simplicity, the same mechanism has been assumed for both reactions. Two different expressions for  $f(\alpha_i)$  have used in this study, namely the  $n$ th order  $(1 - \alpha_i)^n$ , and the autocatalytic  $\alpha_i^m(1 - \alpha_i)^n$ .

The  $n$ th order reaction is the most simple function and, analytically, it corresponds to an autocatalytic function with  $m = 0$ . For an isothermal reaction, a  $n$ th order equation predicts the maximum of reaction rate at zero time, which is not the case for autocatalytic cure processes. However, for most of the nonisothermal cure systems, the efficiency of this model has been postulated by some workers [29–35]. This is why this model also deserves to be taken into consideration.

f. The relative contributions of these two reactions to the overall process depend on the cure time for a given

temperature range. The relationship between the total heat  $\Delta H_R$  per unit of mass and the individual heats of reaction  $\Delta H_{R,i}$  per unit of mass is:

$$\Delta H_R = \Delta H_{R_1} + \Delta H_{R_2} \quad (5)$$

where  $\Delta H_{R,1}$  and  $\Delta H_{R,2}$  are the total heat per unit of mass released during Processes 1 and 2, respectively. If we define the fraction  $y$  as the following ratio:

$$y = \frac{\Delta H_{R_1}}{\Delta H_R} = 1 - \frac{\Delta H_{R_2}}{\Delta H_R}. \quad (6)$$

The total degree of conversion ( $\alpha$ ) and the individual degree of conversion ( $\alpha_i$ ) are related by

$$\alpha = y\alpha_1 + (1 - y)\alpha_2 \quad (7)$$

$\alpha_i$  is defined as the ratio between the heat per unit of mass released up to time  $t$  ( $\Delta H_{R,i}[t]$ ), and the total heat per unit of mass released during the reaction ( $\Delta H_R$ ):

$$\alpha_i = \frac{\Delta H_{R,i}(t)}{\Delta H_R} \quad (i = 1, 2) \quad (8)$$

g. the total heat flow  $dH/dt$  per unit of mass of resin is given by

$$\frac{dH}{dt} = \Delta H_{R_1} \frac{d\alpha_1}{dt} + \Delta H_{R_2} \frac{d\alpha_2}{dt} = \Delta H_R [yk_1(T)f(\alpha_1) + (1 - y)k_2(T)f(\alpha_2)] \quad (9)$$

where 1 and 2 refer to the first and the second reaction, respectively.  $dH/dt$  is the ordinate (heat flow) of the DSC curve obtained experimentally. This expression can be transformed and written as

$$\frac{d\alpha}{dt} = y \frac{d\alpha_1}{dt} + (1 - y) \frac{d\alpha_2}{dt} = yk_1[T]f(\alpha_1) + (1 - y)k_2[T]f(\alpha_2) \quad (10)$$

which will be used when fitting the experimental data. In the Eq. 8,  $\alpha_i$ , and  $y$  are unknown. They should be obtained before fitting the experimental data ( $d\alpha/dt$ ,  $T$ ).

In the calculation procedure, the corresponding kinetic parameters are computed by applying the downhill simplex algorithm [36, 37] which generates a set of kinetic parameters and the fraction  $y$ . The Runge–Kutta numerical method [38, 39] has been used to solve the differential equations, and thus, to obtain the degree of conversion for each individual reaction ( $\alpha_i$ ). The computing algorithm gives the set of kinetic parameters that minimizes the function merit defined as

$$X^2(\vec{a}) = \sum_{i=1}^N (z_{\text{exp},i} - z_{\text{calc}}[T_i, \vec{a}])^2 \quad (11)$$

where  $N$  is the number of experimental values, and  $z$  is the reaction rate measured  $d\alpha/dt$  (exp) or calculated (calc)

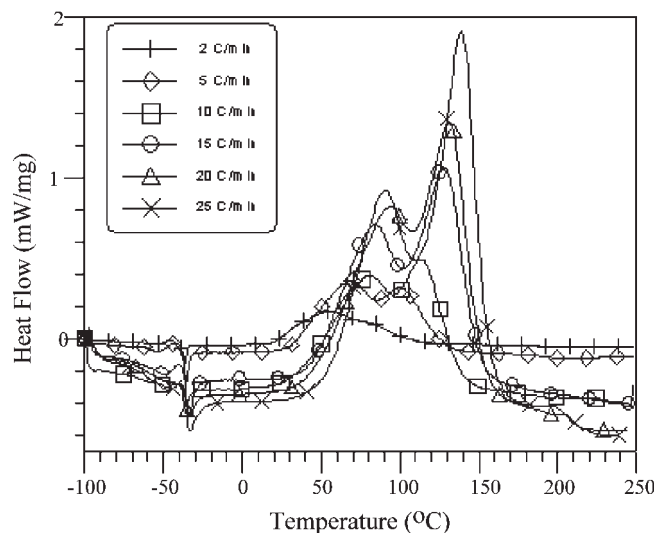


FIG. 1. DSC heat flow  $dH/dt$  versus cure temperature for nonisothermal scans at different heating rates.

from the kinetic parameters and the fraction  $y$ . Vector ( $\vec{a}$ ) contains the set of kinetic parameters and the fraction  $y$ , and  $T_i$  denotes the temperature. A smaller value for the merit function indicates better agreement between the experimental data points and the theoretical model. More information on this iterative calculation algorithm can be found elsewhere [40, 41].

## RESULTS AND DISCUSSION

### Experimental Results

The normalized heat flow curves versus temperature at different heating rates  $\beta$  are drawn in Fig. 1. In Fig. 2, the reaction rate versus the cure time at different  $\beta$  is plotted. Both figures show the existence of two exothermic peaks. The influence of the heating rate in both processes can also be observed. When the heating rate increases, the area of the first peak decreases. In Fig. 3a and 3b, the degree of conversion versus the cure temperature and the time, respectively, are drawn with  $\beta$  as parameter.

Table 1 gathers the exothermic DSC peak temperatures  $T_{p1}$  and  $T_{p2}$ , and the heat of reaction  $\Delta H_R$  per unit of mass, which was obtained as

$$\Delta H_R = \int_0^{t_c} \left( \frac{dH}{dt} \right)_T dt \quad (12)$$

where  $t_c$  is the curing time (i.e. the time to be needed for the DSC trace to return to baseline) and  $(dH/dt)_T$  is the normalized calorimetric signal (in mW/mg) during the experimental DSC run. As it can be seen in Table 1,

the amount of heat generated per unit of mass is independent of  $\beta$ . A similar result has been found in other works [42–46]. An average value of 355 J/g was assigned to the heat of polymerization of the UP resin.

The range of the heating rate used in this work, which is between 2 and 25 °C/min, has been chosen for its best performance. For values lower than 2 °C/min, some of the initial and the final reaction may be unrecorded, because of a lack of calorimeter sensitivity. Higher heating rates could be used to check whether the peaks separate more. However, for values higher than 25 °C/min, other endothermal reactions, like decomposition of the material or styrene evaporation, can occur simultaneously to curing. These processes may decrease the exothermicity of the reaction (see Refs. [41] and [46]).

Other researchers [47, 48] have reported a range of reaction heat from 292.6 to 426 J/g for UP resins. The existence of this wide range may be because of the different types of UP resins and free radical initiator systems

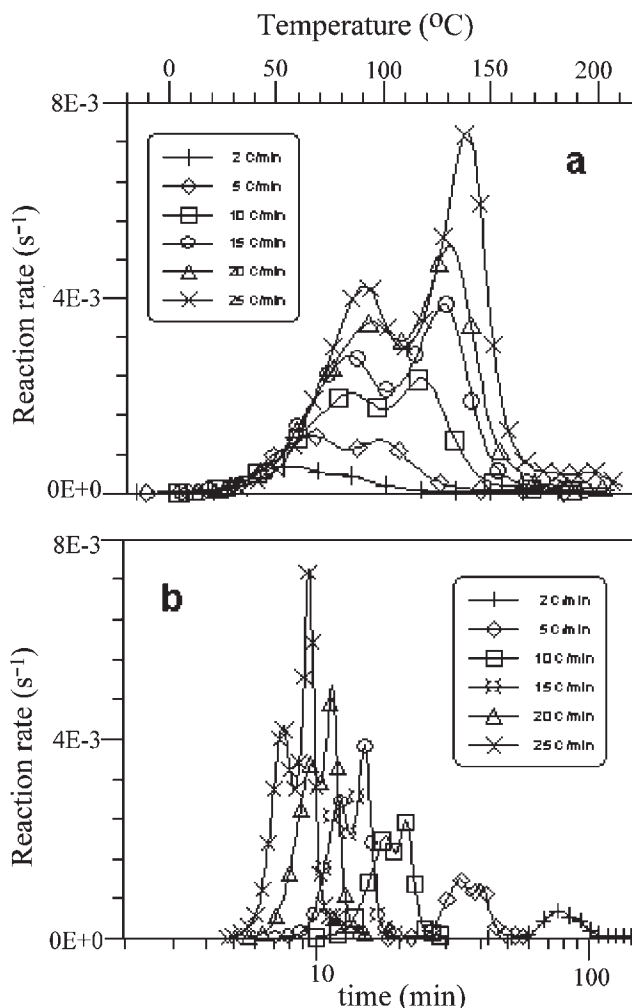


FIG. 2. Reaction rate  $dx/dt$  as a function of (a) cure temperature, and (b) cure time at different heating rates.



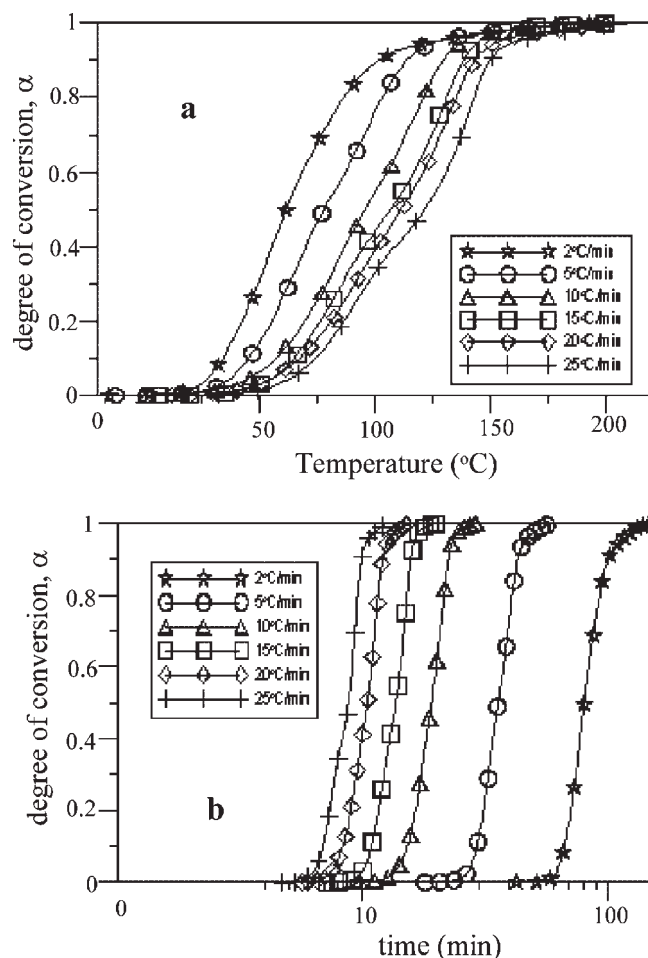


FIG. 3. Degree of conversion  $\alpha$  as a function of (a) cure temperature, and (b) cure time, at different heating rates.

employed in each study [35]. Basically, the origin of the reaction heat  $\Delta H_R$  is the crosslinking reaction between polyester double bonds and styrene double bonds. However, the organic peroxide decomposition is a highly exothermic reaction (for instance, the heat evolved in the decomposition of pure benzoyl peroxide measured by DSC is 400 J/g [7]) and different amounts of initiator can give different values for  $\Delta H_R$ . Nevertheless, the heat associated with the decomposition of initiator is comparatively negligible, given the small amount of peroxide present in the formulation. Finally, it has also been shown in the study of this UP resin with MEKP/CoO as catalytic system that the promoter has some influence on the reaction heat  $\Delta H_R$ . Nevertheless, for very large promoter/initiator ratios, the addition of more promoters produces only a slight effect on the chemical decomposition of peroxide initiator [10].

#### Ozawa and Kissinger Methods

As it is known, these methods allow the calculation of the activation energy of the reactive process by using an equation that relates  $\beta$  and temperature. In the Ozawa

calculation procedure, the following equation is derived:

$$\ln \beta = \text{constant} - 1.052 \frac{E}{RT_p} \quad (13)$$

With this expression it is assumed a linear dependence of the reciprocal absolute peak temperature ( $T_p$ ) on the logarithm of the heating rate. The activation energy  $E$  can be evaluated from the slope of the straight line obtained (Ozawa plot), either graphically or by linear regression. A good fit was observed for each peak and activation energies of 65.6 kJ/mol for the first peak and 51.5 kJ/mol for the second one were obtained. These values do not verify the consistence test, since the activation energy should be larger than that of the first peak.

Kissinger's method uses the following expression:

$$\ln \frac{\beta}{T_p^2} = \text{constant} - \frac{E}{RT_p} \quad (14)$$

According to the above equation, the activation energy can be obtained from the slope of the linear relationship between  $\ln(\beta/T_p^2)$  and  $T_p^{-1}$  (Kissinger plot). The resulting values 74.8 kJ/mol for the first peak, and 60.5 kJ/mol for the second one do not verify the consistence test neither.

#### Kinetic Parameters

The kinetic analysis of thermosetting cures involves the search for the kinetic parameters ( $A$ ,  $E$ ,  $n$ ,  $m$ ) associated with the process, according to a mechanistic model that fits the experimental data. For each nonisothermal DSC curing, the required properties (degree of conversion  $\alpha$  and reaction rate  $d\alpha/dt$  as time or temperature functions) were evaluated by using Eqs. 1 and 2. It was assumed that the dynamic heat obtained as the area of the DSC thermogram is a good approximation for the total reaction heat of polymerization. Therefore, 100% conversion was reached in all curing reactions performed at different heating rates. To compare the results obtained experimentally with the results predicted by the theoretical model, and to point out the differences between them, a series of fits were made. The corresponding kinetic parameters were computed by using the  $n$ th order reaction

TABLE 1. Total heat of reaction  $\Delta H_R$ , peak temperatures  $T_{p1}$  and  $T_{p2}$  at different heating rates  $\beta$ .

$\beta$ (°C/min)	$\Delta H_R$ (J/g)	$T_{p1}$ (°C)	$T_{p2}$ (°C)
2	354.9	54.4	78.9
5	362.7	68.0	98.7
10	356.0	74.5	112.5
15	361.8	82.2	125.2
20	352.7	90.1	127.2
25	332.4	88.2	134.7

TABLE 2. Kinetic parameters for each individual reaction, fraction  $y$ , coefficient of correlation  $r$ , and  $\chi^2(a)$  function for the different fits to experimental data.

$\beta$ ( $^{\circ}\text{C}/\text{min}$ )	$A_1$ ( $\text{s}^{-1}$ )	$E_1$ (kJ/mol)	$n_1$	$y$	$A_2$ ( $\text{s}^{-1}$ )	$E_2$ (kJ/mol)	$n_2$	$\chi^2(a)$	$R$
2	$1.152 \times 10^6$	58.0	1.865	0.654	$3.258 \times 10^{10}$	79.9	1.694	$3.667 \times 10^{-8}$	0.966
5	$4.025 \times 10^6$	57.0	0.800	0.425	$2.702 \times 10^{10}$	89.0	1.891	$2.061 \times 10^{-7}$	0.965
10	$2.906 \times 10^6$	57.1	0.875	0.423	$1.887 \times 10^{10}$	90.9	1.348	$3.157 \times 10^{-7}$	0.977
15	$2.975 \times 10^6$	56.7	0.831	0.405	$2.218 \times 10^{10}$	92.6	1.163	$1.220 \times 10^{-6}$	0.972
20	$2.121 \times 10^6$	55.6	0.855	0.383	$1.502 \times 10^{10}$	91.0	1.214	$2.634 \times 10^{-6}$	0.964
25	$1.408 \times 10^6$	54.3	0.728	0.372	$1.094 \times 10^{10}$	91.2	0.948	$1.225 \times 10^{-5}$	0.944

Experiments have been performed by considering two processes and using a  $n$ th order reaction function  $f(x)$  at different heating rates  $\beta$ .

and autocatalytic reaction for  $f(x)$ , and by applying the downhill simplex method and the Runge–Kutta procedure.

Table 2 summarizes the set of kinetic parameters obtained for each heating rate, by considering two processes and by using an  $n$ th order function of reaction  $f(x)$  for each process. The chi-square function  $\chi^2(a)$  and the correlation coefficient  $r$  are also given. Generally speaking, the kinetic parameters depend upon the heating rate. The activation energy for each process depends on the heating rate too. Average values of 56.5 kJ/mol for the first peak and of 89.1 kJ/mol for the second one have been obtained. In this case, the test of consistence is verified. This does not always happen when the  $n$ th order model is used. For instance, in a previous work that used a  $n$ th order reaction, the beginning of the first and of the second peak were very close [41]. This would mean that the two reactive processes were simultaneous and not consecutive processes, as it had been assumed.

In Fig. 4 the computed  $dx/dt$  is plotted versus the cure temperature, together with the experimental results at different heating rates. The computed  $dx/dt$  values have been evaluated by considering two kinetic peaks and autocatalytic  $f(x_1)$  and  $f(x_2)$  functions. As it can be seen, there is a good agreement between the theoretical curves and the experimental ones. Then, it can be assessed that the autocatalytic function for  $f(x)$  reproduces the curing process for UP resins better than the  $n$ th order function. The first and the second calculated peaks are also shown in the Fig. 4 for different heating rates. It can be observed that for each heating rate, the first peak always occurs before the second peak, as required for the test of consistence. Moreover, at low heating rates, the first peak is greater than the second one. On the contrary, at high heating rates, the first peak is smaller than the second one. The beginning of the first peak takes place between 0 and 20 $^{\circ}\text{C}$ . For the second peak, the beginning takes place between 70 and 90 $^{\circ}\text{C}$ . The time of completion and the induction time (the time needed for the reaction to start up) of each peak decreases as  $\beta$  increases (see Fig. 3). In conclusion, the autocatalytic function for  $f(x)$  reproduces better the experimental results.

The kinetic parameters obtained for each heating rate by considering two independent kinetic processes of reaction and using an autocatalytic function  $f(x)$  for each

process are given in Table 3. The chi-square function  $\chi^2(a)$  and the coefficient of correlation  $r$  are also given. In general, the kinetic parameters depend upon the heating rate. The correlation coefficients for each heating rate are greater than the  $r$  values for any other fitting at the same heating rates. In these fits, the fraction  $y$  decreases as the heating rate increases. The average value of the activation energy of the second peak is 89.4 kJ/mol. For the first peak, the activation energy depends on the heating rate, with an average value of 43.1 kJ/mol. These values for the activation energies are in accordance with the values tabulated in the literature [49], which refer to a free-radical polymerization initiated by the redox decomposition of the initiator at low temperatures, and to a free-radical polymerization initiated by the thermal decomposition of the initiator at high temperatures, respectively.

It is customary practice to associate an overall activation energy to a steady-state free radical polymerization like the curing of UP resins by combining three separate Arrhenius-type equations for each occurring process (initiation [d], propagation [p] and termination [t]). In this case, the temperature dependence of the rate constant is generally given by an Arrhenius constant relationship [49]:

$$k(T) = A_0 \exp\left(-\frac{E}{RT}\right) = \frac{A_d^{1/2} A_p}{A_t^{1/2}} \exp\left(\frac{(E_d + 2E_p - E_t)/2}{RT}\right) \quad (15)$$

where  $E$  is the activation energy,  $R$  is the gas constant, and  $A_0$  is an Arrhenius constant. When the process of reaction is only initiated by the thermal decomposition of initiator, the overall activation energy for most free radical polymerizations is about 80–90 kJ/mol [49]. For instance, the values of  $E_p$ ,  $E_t$ , and  $E_d$  for free-radical polymerization of styrene with peroxybenzoate initiator are 26, 8.0, and 134 kJ/mol, respectively. Thus, the activation energy for the polymerization of styrene is  $E = E_d/2 + E_p - E_t/2 = 89$  kJ/mol. These results suggest that the second reaction considered here might be produced by a mechanism of thermal initiation. Martin et al. [40, 41] studied the curing of this resin with MEKP as initiator at different heating rates. The polymerization was only initiated by thermal decomposition of MEKP. The positions of DSC peaks coincide with the

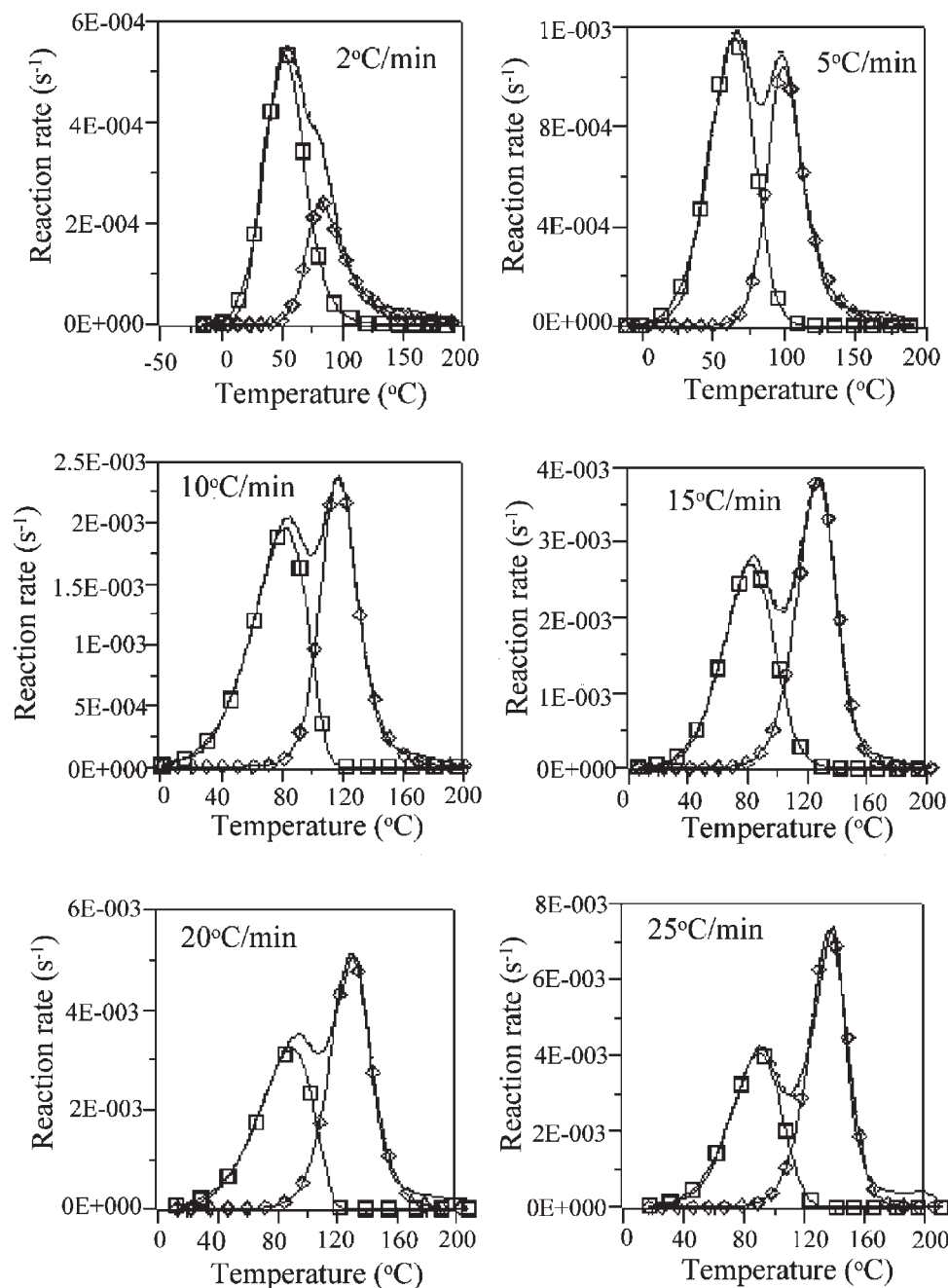


FIG. 4. The calculated  $dx/dt$  versus temperature ( $^{\circ}\text{C}$ ) curves (----) considering two processes and using an autocatalytic function  $f(x)$ , and the experimental  $dx/dt$  versus temperature ( $^{\circ}\text{C}$ ) curves ( $\square$ ) at different heating rates  $\beta$ . The first ( $\square$ ) and the second ( $\diamond$ ) simulated peaks are drawn too.

TABLE 3. Kinetic parameters for each individual reaction, fraction  $y$ , coefficient of correlation  $r$ , and  $\chi^2(a)$  function for the different fits to experimental data.

$\beta$ ( $^{\circ}\text{C}/\text{min}$ )	$A_1$ ( $\text{s}^{-1}$ )	$E_1$ (kJ/mol)	$m_1$	$n_1$	$y$	$A_2$ ( $\text{s}^{-1}$ )	$E_2$ (kJ/mol)	$m_2$	$n_2$	$\chi^2(a)$	$r$
2	$2.426 \times 10^4$	43.4	0.294	1.316	0.903	$4.887 \times 10^{10}$	89.5	0.387	2.347	$1.626 \times 10^{-8}$	0.970
5	$3.204 \times 10^4$	43.5	0.517	2.282	0.695	$4.144 \times 10^{10}$	89.3	0.352	1.638	$6.839 \times 10^{-8}$	0.980
10	$1.594 \times 10^4$	42.7	0.501	1.838	0.610	$1.913 \times 10^{10}$	89.3	0.202	1.055	$8.194 \times 10^{-8}$	0.988
15	$3.407 \times 10^4$	42.8	0.349	1.370	0.535	$1.183 \times 10^{10}$	89.4	0.380	1.424	$3.897 \times 10^{-7}$	0.984
20	$2.197 \times 10^4$	42.8	0.431	1.562	0.501	$1.514 \times 10^{10}$	89.3	0.158	0.829	$1.242 \times 10^{-6}$	0.975
25	$4.167 \times 10^4$	43.0	0.390	1.320	0.457	$1.287 \times 10^{10}$	89.9	0.360	1.123	$6.431 \times 10^{-6}$	0.959

They have been performed by considering two processes and using an autocatalytic function  $f(x)$  at different heating rates  $\beta$ .

TABLE 4. New computation of kinetic parameters for each individual reaction, fraction  $y$ , coefficient of correlation  $r$ , and  $\chi^2(a)$  function for the different fits to experimental data.

$\beta$ ( $^{\circ}\text{C}/\text{min}$ )	$A_1$ ( $\text{s}^{-1}$ )	$E_1$ (kJ/mol)	$m_1$	$n_1$	$y$	$A_2$ ( $\text{s}^{-1}$ )	$E_2$ (kJ/mol)	$m_2$	$n_2$	$\chi^2(a)$	$r$
2	$2.683 \times 10^4$	42.8	0.403	1.629	0.788	$2.487 \times 10^{10}$	88.5	0.301	1.447	$4.126 \times 10^{-8}$	0.965
5	$2.725 \times 10^4$	43.3	0.416	1.605	0.691	$2.400 \times 10^{10}$	89.8	0.312	1.404	$9.939 \times 10^{-8}$	0.970
10	$2.866 \times 10^4$	43.6	0.414	1.615	0.631	$2.353 \times 10^{10}$	89.1	0.300	1.400	$1.749 \times 10^{-7}$	0.976
15	$2.987 \times 10^4$	43.0	0.420	1.610	0.565	$2.448 \times 10^{10}$	89.3	0.310	1.414	$5.167 \times 10^{-7}$	0.971
20	$2.877 \times 10^4$	43.5	0.416	1.602	0.558	$2.572 \times 10^{10}$	89.8	0.321	1.403	$2.985 \times 10^{-6}$	0.966
25	$3.017 \times 10^4$	43.9	0.421	1.616	0.507	$3.287 \times 10^{10}$	89.5	0.350	1.423	$1.514 \times 10^{-5}$	0.950

Experiments have been performed by considering two processes and using an autocatalytic function  $f(x)$  at different heating rates  $\beta$ .

position of second peak studied here, and the values of activation energies are in concordance with the values for the second peak found here. All these results indicate that the second reaction might be produced by a mechanism of thermal initiation. When there is only a redox initiation, the value of the overall activation energy is about one half the value for nonredox initiations. That is about 40–60 kJ/mol [49].

It is reasonable to assume that two initiation mechanisms do exist in the nonisothermal curing experiments. At low heating rates, the sample temperature increases slowly and a large period of time is needed to reach high temperatures, which induce the thermal decomposition of the peroxide initiator. Therefore, the redox decomposition of peroxide initiator is the prevailing phenomenon for low heating rates. On the contrary, the temperature of the sample increases strongly when high heating rates are used. In a short period of time the temperature reaches a high value and the thermal decomposition of peroxide initiator begins rapidly. Thus, at high heating rates, the thermal decomposition competes with and prevails over the redox decomposition of peroxide initiator.

It is interesting to note that to obtain the kinetic parameters of the empirical model proposed here, it is sufficient to use the experimental data obtained with a single heating rate. Therefore, this model is very attractive because of the amount of information contained in a single temperature programmed experiment. However, although a single heating rate is sufficient to obtain the kinetic parameters, to validate the results of this empirical model, it must fit the experimental data obtained by using other heating rates, which means that the kinetic parameters should be practically independent on the heating rate. As it is observed in Table 3, the first condition is satisfied, but the second one is not. For this reason, the kinetic parameters have been calculated again so that the second condition be also satisfied. The results are listed in Table 4. Although the errors are greater than the ones shown in Table 3, the fits are reasonably good.

## CONCLUSIONS

The appearance of two peaks during an UP cure is an interesting and still non solved problem. This work has

shown that the models based on a generalization of the ASTM E698 do not satisfy the test of consistence because they give an activation energy for the first peak greater than the one of the second. A new model has been proposed, which assumes the existence of two competitive reactions. Depending on the heating rate, one of them becomes the prevailing phenomenon. It has also been obtained that the fraction of the reaction heat associated with the first peak over the overall reaction heat decreases as the heating rate increases. Nth order and autocatalytic functions have been considered as kinetic functions. The simulated peaks obtained with both functions verify the consistence test but the autocatalytic one fits better the experimental results. The activation energies obtained with this model are in agreement with the values tabulated for free radical polymerizations initiated by redox or by thermal peroxide decomposition, for the first and the second peaks, respectively.

As DSC does not give direct information on the changes of chemical structure during cure, the nature of these two exothermic peaks is unclear. Further investigation of these two reactions would be very interesting to better understand the cure mechanisms involving free radicals. Studies that use spectroscopic and structural analysis techniques, for instance, can shed some more light onto the origin of these DSC peaks.

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