

A Kinetic Study of the Effect of Three Catalytic Systems on the Curing of an Unsaturated Polyester Resin

J. M. SALLA* and X. RAMIS

Laboratori de Termodinàmica de la E.T.S.E.I., Universitat Politècnica de Catalunya,
Diagonal 647, Barcelona 08028, Spain

SYNOPSIS

We studied by differential scanning calorimetry (DSC) the influence of three tertiary amines used as promoters on the curing kinetics of unsaturated polyester resins catalyzed with an organic peroxide. The kinetic study was made by means of the analysis of isothermal experiments and we used a kinetic model that does not presuppose knowledge of the experimental rate equation $f(\alpha)$, which relates the reaction rate $d\alpha/dt$ at constant temperature with the degree of conversion α through a rate constant k according to $d\alpha/dt = kf(\alpha)$. It is thus possible to predict the time, temperature, and degree of curing without needing to know $f(\alpha)$. This model makes a linear relation between the logarithm of time needed to reach a given degree of conversion with the inverse of the curing temperature according to the expression $\ln t = A + E/RT$ for a constant α , where A is a constant, R is the universal gas constant, and E the activation energy. The proposed model has been used to calculate the activation energies for each degree of conversion according to the type and amount of promoter used. From the relation between the time and the curing temperature for a given conversion, it is possible to predict values of curing time for different temperatures. We thus simulated curing kinetics by using the proposed model and compared them with those obtained experimentally by DSC. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A typical system of initiation for the curing of polyester resins is benzoyl peroxide (BP). It is used as an initiator because it can decompose thermally, releasing free radicals that unleash the curing process. For common formulations and normal curing times, the temperature of decomposition of BP is usually high. Many applications need a curing process at ambient temperature, in which case a promoter, normally a tertiary amine, is used to induce the chemical decomposition of the peroxide at low temperature by means of a chemical reduction. It would be very interesting to know the influence of the promoters on the curing kinetics. To this end we made isothermal studies by differential scanning calorimetry (DSC) and tried to obtain kinetic parameters that show the influence of the type and amount of promoter on the curing process.

The kinetics of curing polyester resins is normally very complex because many reactive processes occur simultaneously.¹ In the initiation stage, the initiator decomposes chemically, giving out free radicals that can react with the inhibitor, which can act as a retarder of the polymerization or as an inhibitor, reacting with all the radicals that have formed until it is exhausted. In the propagation or polymerization stage the initiator radicals can react well with the styrene or with the polyester. From this moment the chains of polymer will grow and cross each other, according to three possible reactive processes: styrene-polyester copolymerization, styrene homopolymerization, and polyester homopolymerization.^{2,3} In the termination stage there are multiple reactive processes, and all the free radicals in the reaction medium can recombine, thus ending the growth of the chains. We must also consider that at the same time as these processes, if the temperature is sufficiently high in the reaction medium there may be thermal decomposition of the initiator, which can lead to another process of polymerization. In some

* To whom correspondence should be addressed.

systems it has been possible to separate the process of polymerization associated with the chemical decomposition from the initiator of the process associated with the thermal decomposition.⁴

In many cases the calorimetric curve obtained by DSC is therefore very complex, with several exothermic peaks, corresponding to different, and clearly differentiated, reactive processes. In other cases it is not possible to distinguish several processes that in fact exist.

Besides the complexity of the curing process due to the large number of reactive processes, there are other parameters that increase the complexity of the curing of unsaturated polyester resins, such as the phenomena of gelation and vitrification, the change from chemical kinetic control to control by diffusion in the advance of the curing, and the possibility of forming different chemical or morphological structures.^{2,5}

Many authors⁶⁻⁸ have studied the kinetics of curing polyester resins using isothermal and/or dynamic experiments with DSC to obtain the reaction rate curve. They then adjusted the experimental data to a model valid for solid-state reactions,⁹ normally using the kinetic equations called autocatalytic or n order equations. These models study the whole reaction of curing as a single kinetic process without bearing in mind the different reactive processes or the different stages through which the system evolves. When the profile of the rate curve is simple, this procedure normally gives a good fit of the experimental data, though it does not permit prediction of polymerization processes outside the range of experimental data.

Other authors^{1,10,11} tried to establish a mechanistic kinetic model based on the concept of free radical polymerization and on the mechanism of reactions with diffusion control, which includes the effects of the inhibitor and the limitations imposed by diffusion in the reaction rate and in the final conversion. This model has a clear advantage over the empirical kinetic models because it can predict the effect of the type or amount of initiator on the curing process, without needing to carry out experiments every time that we change the amount or type of initiator. On the other hand, it has the drawback that in order to be applied with relative simplicity it needs a large number of simplifications. Also, the method does not allow us to predict the influence of the type and amount of promoter in the curing process, nor does it consider the influence of the possible morphologies of the cured material.

This work proposes an experimental kinetic model based on isothermal DSC curing that does

not require the knowledge of the reaction rate equation $f(\alpha)$ and only presupposes that for a given degree of conversion the reactive process has the same mechanism of reaction, regardless of the curing temperature. As can be seen, this method allows us to calculate the activation energies for each degree of curing, which show the different stages through which the reactive process passes. The method also allows us to predict the curing process outside the range of experimental data, with very good results. Furthermore, this method clearly shows the changes in the curing kinetics when the type and amount of promoter are varied; it may be that the effects unleashed by an amount of a given promoter are equivalent to those caused by the use of a different amount of a different promoter.

THEORETICAL ANALYSIS

Without knowing the exact reaction mechanism, it is reasonable to assume that the total reaction rate $d\alpha/dt$ at a given temperature is only dependent on the degree of curing $f(\alpha)$ according to the equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where k is the reaction constant.

For the kinetic study, many authors consider that during the curing process the reaction mechanism does not change and the equation $f(\alpha)$ has the same form. They then determine the kinetic parameters by adjusting the isothermal experiments to a kinetic model, normally the autocatalytic, or n order model. Finally, using the Arrhenius equation they calculate the frequency factor and the activation energy for the whole reactive process. As we state above, the curing process in polyester resins tends to be complex, and in many cases it is not correct to consider that the reaction mechanism remains constant during the process, or that there is a single activation energy associated with it. In our study we considered that equation $f(\alpha)$ has the same form regardless of the temperature for the same degree of conversion α .

By integrating eq. (1) for a curing time of $t = 0$ where $\alpha = 0$ to a time t with a degree of curing α , we obtain:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k dt \Rightarrow C = kt \quad (2)$$

where C is a constant. Equation (2) shows us how the time is inversely proportional to the reaction

constant k for an α regardless of the $f(\alpha)$ at a given temperature.

The dependence of the reaction constant on the temperature follows the Arrhenius law:

$$k = k_0 \exp(-E/RT). \quad (3)$$

By replacing (3) in (2) and taking logarithms, we will have:

$$\ln t = E/RT + A \quad (4)$$

where A is a constant that is the sum of the logarithm of the constant C of eq. (2) and the logarithm of the frequency factor k_0 . Equation (4), which makes a linear relation between the logarithm of the time needed to reach a curing α and the inverse of temperature, will be used to study the curing kinetics of an unsaturated polyester resin. The times needed to reach different degrees of conversion will be determined from isothermal curings with DSC at different temperatures. Equation (4) will be used to determine the activation energies. By extrapolating with this equation values outside the experimental range of temperatures, we can predict the time needed to reach a given curing, and thus simulate the curing kinetics.

EXPERIMENTAL

Materials

We used an orthophthalic-type unsaturated polyester resin with styrene as a cross-linking agent, marketed by Reposa under the name Estratil A-228. The resin is composed of phthalic anhydride, maleic anhydride, and propylene glycol with a molar relation of 3 : 2 : 5 determined by nuclear magnetic resonance (NMR). The resin was supplied with a styrene content of 35% and with hydroquinone as an inhibitor, which was not eliminated.

As an initiator we used a dispersion of benzoyl peroxide with an approximate peroxide content of 50%, supplied by Akzo Chemie under the trade name of Lucidol BW-50T.

The promoters used were *N,N*-dimethyl aniline (DMA), *N,N*-diethyl aniline (DEA), and *N,N*-dimethyl-*p*-toluidine (DMPT).

Differential Scanning Calorimetry

The calorimetric measurements were made on a DSC 20 Mettler calorimeter. Isothermal curings were performed at a range of temperatures of 5–

50°C in a nitrogen atmosphere. The curing times were generally 300 min, and in all the experiments the calorimetric curve had recovered the base line at the end of the experiment, so the material could no longer cure isothermally. After all the isothermal curings a dynamic scan was made from 0 to 250°C to determine the residual heat. Dynamic curings of 0–250°C were also made at heating rates of 2.5–10 K/min to determine the total reaction heat. All the tests contained 2% initiator; the amount of promoter varied according to the experiment.

RESULTS AND DISCUSSION

As we have said, the curing of unsaturated polyester resins is complex, and includes several reactive processes. As a result of all these processes, the system releases heat. Assuming that the curing process only has a thermal effect, the reaction advance will be directly proportional to the amount of heat generated and the maximum degree of curing reached when all the bonds that may react have done so.

Taking into account these considerations, the degree of conversion α in a time t and the reaction rate $d\alpha/dt$ in the same time may be evaluated from isothermal DSC data as follows:

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{\text{iso}}} \quad \left(\frac{d\alpha}{dt} \right)_t = \frac{(dH/dt)_t}{\Delta H_{\text{iso}}} \quad (5)$$

where ΔH_t is the heat generated in a time t , which is calculated by integrating the calorimetric signal until the time t ; ΔH_{iso} is the total heat generated in an isothermal experiment, which may be evaluated by integrating the whole calorimetric signal until the process recovers the base line; and $(dH/dt)_t$ is the calorific power generated in a time t , which is the direct calorimetric signal.

This analysis will be correct providing that the material reacts completely during an isothermal curing process. In our case, in the range of working temperatures for the different systems used, the maximum isothermal curing reaches 60–80% of the values found in a dynamic curing.

This is why for the correction of the degree of conversion and the reaction rate it must be borne in mind that the material does not completely cure isothermally, and the heat ΔH_{iso} is not the total reaction heat. For the total reaction heat ΔH_{tot} , we took a value of 340 J/g calculated as the average value of the reaction heats obtained on curing the resin dynamically between 0 and 250°C at heating rates of 2.5–10 K/min. We assumed that in these

conditions the material does cure completely. It is important to take into account also that the heat obtained as a sum of the heat ΔH_{iso} and the residual heat ΔH_{res} obtained in a dynamic postcuring after each isothermal experiment in no case exceeds 300 J/g, a value rather far from the total heat obtained dynamically. This is because in isothermal tests part of the reaction heat cannot be recorded by the calorimeter. As pointed out by several authors,^{12,13} at low temperatures at the start and end of the reaction the heat cannot be detected by DSC if it falls below the sensitivity of the apparatus, and at high temperatures part of the reaction heat may be lost during the heating of the sample and the stabilization of the DSC.

For a more precise calculation of the degree of conversion and the reaction rate, it will be necessary to correct eq. (5), bearing in mind the above considerations.

The corrected degree of conversion and the corrected reaction rate are defined as:

$$\alpha_t^c = \frac{\Delta H_t^c}{\Delta H_{\text{tot}}} \quad \left(\frac{d\alpha}{dt} \right)_t^c = \frac{(dH/dt)_t^c}{\Delta H_{\text{tot}}} \quad (6)$$

where ΔH_t^c and $(dH/dt)_t^c$ would be, respectively, the corrected isothermal heat released in a time t and the corrected calorific power generated in a time t if a heat equal to $\Delta H_{\text{tot}} - \Delta H_{\text{res}}$ could be detected isothermally. As ΔH_t^c and $(dH/dt)_t^c$ cannot be determined experimentally, it is possible to calculate them if we accept the following relations as correct:

$$\frac{\Delta H_t}{\Delta H_{\text{iso}}} = \frac{\Delta H_t^c}{\Delta H_{\text{tot}} - \Delta H_{\text{res}}} \quad (7)$$

$$\frac{(dH/dt)_t}{\Delta H_{\text{iso}}} = \frac{(dH/dt)_t^c}{\Delta H_{\text{tot}} - \Delta H_{\text{res}}} \quad (8)$$

From here it is possible to find the values of ΔH_t^c and $(dH/dt)_t^c$. Replacing them in expressions (6), we obtain the corrected degree of conversion in time t and the corrected reaction rate in a time t , with the value:

$$\begin{aligned} \alpha_t^c &= \frac{\Delta H_t (\Delta H_{\text{tot}} - \Delta H_{\text{res}})}{\Delta H_{\text{iso}} \Delta H_{\text{tot}}} \\ &= \alpha_t \left(\frac{\Delta H_{\text{tot}} - \Delta H_{\text{res}}}{\Delta H_{\text{tot}}} \right) \end{aligned} \quad (9)$$

$$\begin{aligned} \left(\frac{d\alpha}{dt} \right)_t^c &= \frac{(dH/dt)_t (\Delta H_{\text{tot}} - \Delta H_{\text{res}})}{\Delta H_{\text{iso}} \Delta H_{\text{tot}}} \\ &= \left(\frac{d\alpha}{dt} \right)_t \left(\frac{\Delta H_{\text{tot}} - \Delta H_{\text{res}}}{\Delta H_{\text{tot}}} \right). \end{aligned} \quad (10)$$

Figure 1 shows the degree of conversion according to time using eqs. (5), (9), and that which would be obtained by using eq. (5) modified according to $\alpha_t' = (\Delta H_t / \Delta H_{\text{iso}}) \cdot (\Delta H_{\text{iso}} / \Delta H_{\text{tot}})$. It is considered that the most correct option corresponds to eqs. (9) and (10), which are those used in this work to evaluate the degree of conversion and the reaction rate at a time t .

For the kinetic analysis of the curing process for the three catalytic systems investigated we used eq. (4), applying to it different degrees of conversion. The curing times were obtained from the curves degree of conversion versus curing time at different temperatures. These curves were calculated from isothermal experiments in DSC using eq. (9).

Figure 2 shows the curves α versus t at different curing temperatures, and the method for obtaining the curing times for a given degree of conversion at different temperatures for a system using DEA as a promoter. For each degree of conversion it is possible to correlate the logarithm of curing time against the inverse of the temperature by using eq. (4). Figure 3 shows the curves $\ln t$ versus $1/T$ for the same system, and Table I shows the linear regressions of these curves with the value of the ordinate at the origin, the slope of the straight lines, which is directly related to the activation energy, and the regression coefficient.

This same study was made with the same proportions of resin, initiator, and promoter with the other two promoters (DMA and DMPT) in order

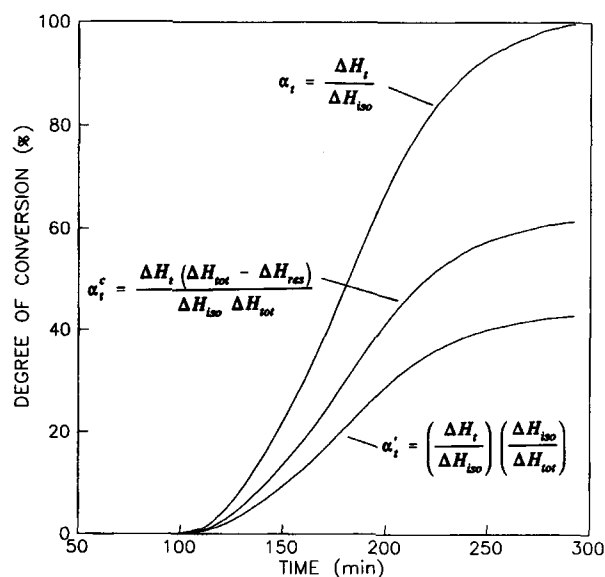


Figure 1 Degree of conversion as a function of time calculated according to different expressions. System with 0.1% DMA. $T = 15^\circ\text{C}$.

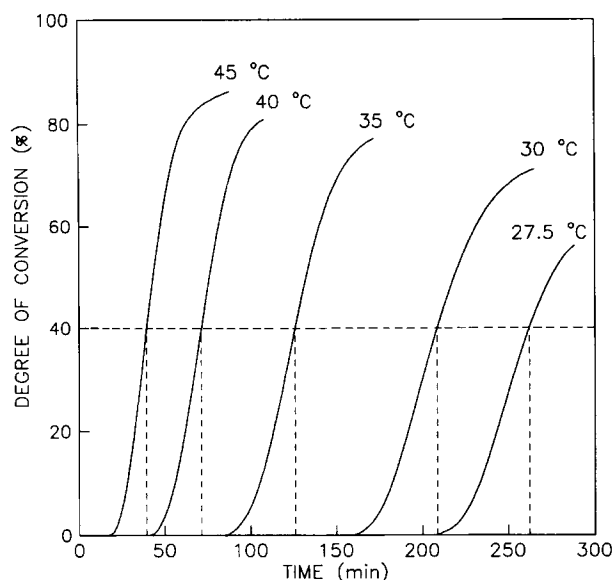


Figure 2 Experimental curves' degree of conversion versus curing time at different temperatures for a system with 0.1% DEA.

to compare the effect of the type of promoter on the curing kinetics.

Table II and Figure 4 show the comparative results of the activation energies for the three systems. We see how the activation energy does not only vary with the type of promoter but it also varies with the degree of conversion. In general, for all the promot-

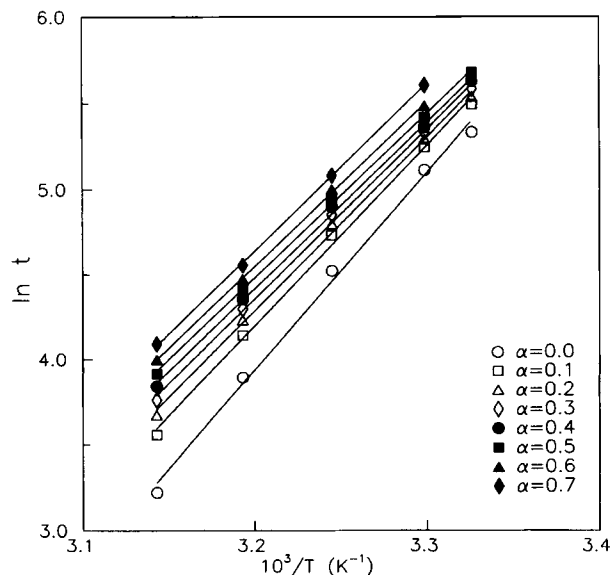


Figure 3 Correlations of the logarithm of time versus the inverse of the temperature for different degrees of conversion according to the equation $\ln t = E/RT + A$ for a system with 0.1% DEA.

Table I Linear Regressions According to $\ln t = E/RT + A$ for a System With 0.1% DEA

Conversion (%)	E/R	A	Correlation Coefficient
0	10961.3	-31.08	-0.999
10	10601.6	-29.73	-0.999
20	10196.4	-28.34	-0.999
30	9966.1	-27.54	-0.999
40	9741.5	-26.75	-0.999
50	9623.1	-26.32	-0.999
60	9618.2	-26.23	-0.999
70	9779.0	-26.66	-0.999

ers used the activation energy takes a maximum value at the start of the reaction, then decreases slightly, then remains practically constant, and finally shows a certain tendency to increase. This behavior may be due to the autocatalytic effect of the curing process when the reaction has started, and to the phenomena of gelification, vitrification, and high viscosity shown by the reaction medium when the conversion increases.

In many free radical polymerizations the autoacceleration in the polymerization rate is characteristic as the reaction advances. Normally it is to be expected that the reaction rate decreases with time, when the concentrations of reactive species and initiator decrease as the conversion increases. On the other hand, in this type of process the reaction rate increases as the reaction advances due to the effect of autoacceleration. At higher conversions, the rate may decrease again due to the effect of vitrification, which is very pronounced at low temperatures.¹⁴ This effect may overlap with the important increase in viscosity at high conversions, which also leads to the decrease in the reaction rate.¹⁵ This can be seen in Figure 5, which shows the reaction rate according to the degree of curing for the system with DMA as a promoter.

The autoacceleration, understood as the production of free radicals by the exothermicity of the reactive process, could explain the results obtained in relation to the activation energy (Table II, Fig. 4) and to the reaction rate (Fig. 5). At the beginning, it is the amount and type of promoter that according to the temperature causes the decomposition of the peroxide and the start of curing. This would be in agreement with the values of the activation energy found for $\alpha = 0$. Later, the exothermicity of the process would lead to an additional production of free radicals that would be in accordance with the acceleration of the rate and the decrease in the acti-

Table II Activation Energy at Different Degrees of Conversion for Three Systems Using 0.1% of Different Promoters

Promoter	<i>E</i>							
	Conversion (%)							
	0	10	20	30	40	50	60	70
DMPT	65.7	61.9	62.6	63.2	64.1	64.5	66.2	67.1
DMA	67.8	66.2	64.1	62.2	60.1	59.5	58.3	64.2
DEA	91.1	88.2	84.8	82.9	81.0	80.0	80.0	81.3

vation energy that are observed, regardless of the promoter. Finally, whether due to the viscosity of the medium, to the phenomenon of the vitrification, or to the process of termination of the reaction, the curing rate decreases and the activation energy, after passing through a minimum, increases.

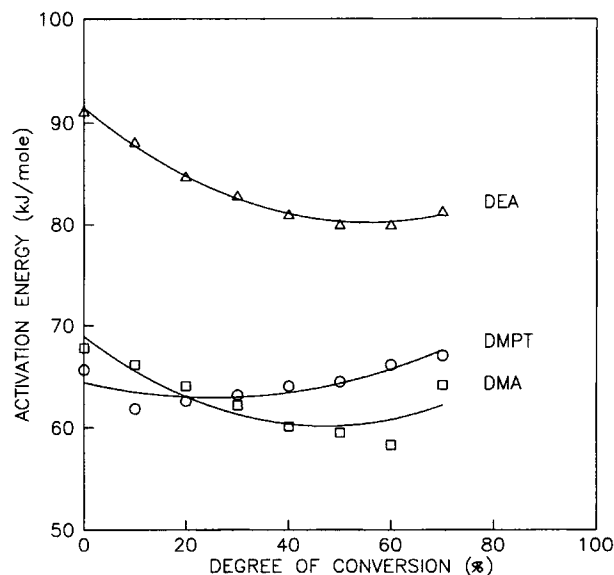
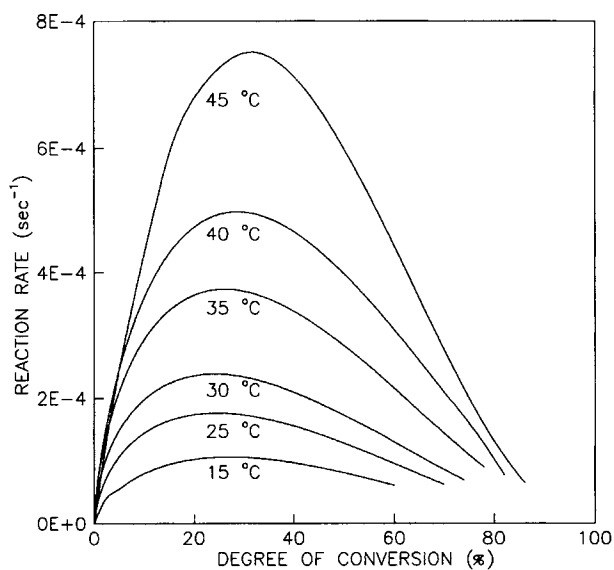
The fact that the minimum activation energy occurs at different degrees of conversion is attributed basically to the effectiveness of the promoter (Fig. 4).

In previous works, the effect of autoacceleration in unsaturated polyester resins has also been detected. It was seen that the autoacceleration was reinforced not only by the catalytic system but also by the reactive mass.¹⁶

Assuming that the lower the activation energy is the more efficient the promoter is, it is possible to compare the effectiveness of the different promoters

(see Table II). We can see how DEA is far less efficient for any degree of conversion than DMA and DMPT, which show a more similar behavior. This effect is shown in Figure 6, which compares at the temperature of 25°C the experimental curves degree of conversion versus curing time for the three promoters used. Whereas DMPT and DMA show similar curing times, those of DEA are far higher.

Figure 7 shows the experimental curves of reaction rate against degree of conversion for the same systems and at the same temperature. We can see how at the beginning of the reaction the rates are different, which must be attributed to the effect of the promoter and the phenomenon of autoacceleration. From a certain degree of conversion, the reaction rate becomes similar for the three systems and the last conversions are practically equal and

**Figure 4** Activation energy versus degree of conversion for three systems using 0.1% of different promoters.**Figure 5** Reaction rate versus degree of conversion at different curing temperatures for a system using 0.1% DMA.

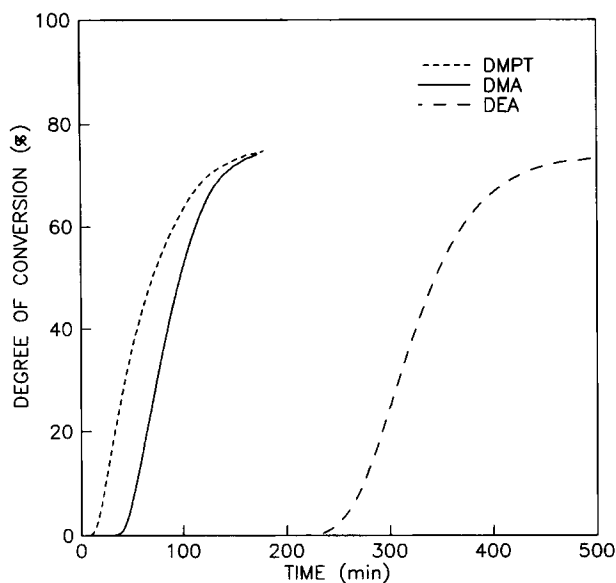


Figure 6 Experimental curves at 25°C degree of conversion versus curing time for three systems using 0.1% of different promoters.

independent of the effectiveness of the promoter used.

Due to the good linearity obtained in the curves in $t - 1/T$ (see Table I and Fig. 3), for all the promoters it is possible to calculate from the curves in $t - 1/T$ the time needed to reach a given curing at a given temperature inside or outside the range of experimental measurements, and thus to simulate the curves' degree of conversion versus curing time. For a system using DMPT as a promoter, Figure 8

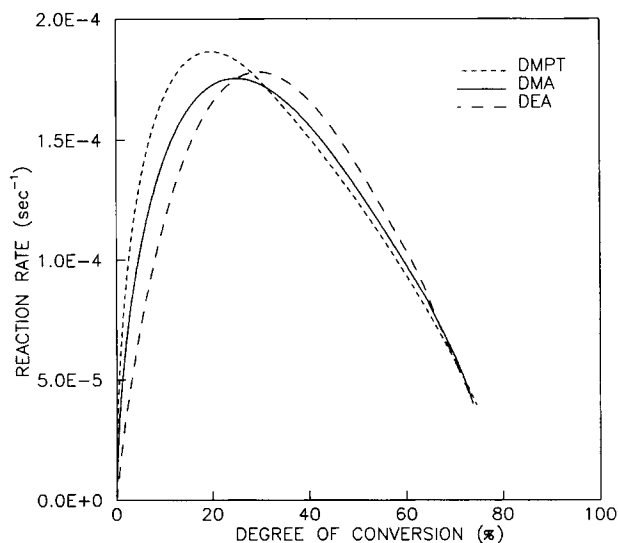


Figure 7 Reaction rate versus degree of conversion at 25°C for three systems using 0.1% of different promoters.

compares the curves simulated with the kinetic model and the results obtained experimentally with DSC. In general there is a very good fit between the calculated and experimental values. In order to establish the kinetics of the process according to eq. (4) we used a range of experimental temperatures between 35 and 15°C. As can be seen in Figure 8, in this interval of temperatures the fit between the experimental and the calculated values is very good. At the temperature of 10°C, outside the range of temperatures used to establish the kinetic equation, the fit is also quite good. However, at a temperature of 45°C the fit is not so good, probably due to the fact that at this temperature the curing process is very rapid and some of the heat is released before the calorimeter can detect it. In these cases, we think that the simulation shows more correct results than the experimental ones calculated calorimetrically. This makes us think that the isothermal method used in this work may be very useful to predict curing kinetics and curing times for rapid processes at high temperatures, where the calorimeter does not have time to detect the start of the reaction. It may also be useful for low-temperature curings where the heat at the start and end of the reactive process may be below the sensitivity of the DSC, or the times required for the curing process may be too high for experimental determination by DSC.

A complete study of the curing kinetics using this isothermal method requires the calculation of the

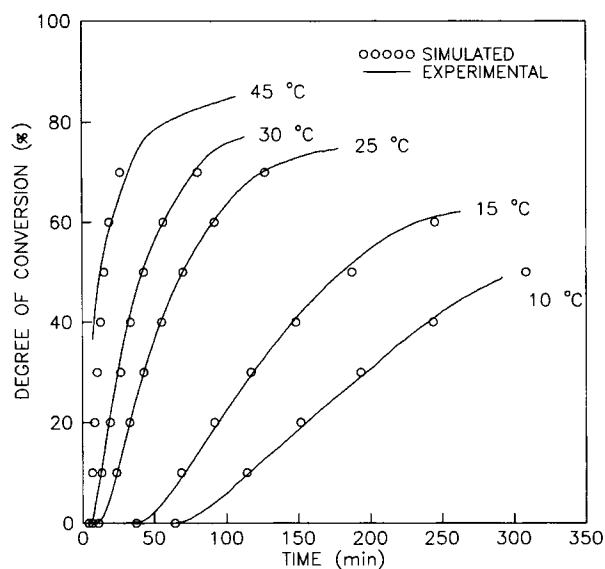


Figure 8 Comparison between the experimental curves' degree of conversion versus curing time and the curves simulated by extrapolation of the kinetic equations $\ln t = E/RT + A$ for a system using 0.1% DMPT.

activation energies and the curing times in a wide range of conversions. If we wish to compare the effect of the type and amount of promoter, it may be interesting to apply the kinetic eq. (4) only at the start of the reaction when the degree of conversion is null because it is at this instant that the effect of the promoter is most pronounced. At this conversion, the curing time may be obtained directly from the isothermal thermogram obtained by DSC, and the calculation is thus extremely simple.

Another interesting result obtained in this work was the effect of the amount of promoter on the curing kinetics at the start of the reactive process ($\alpha = 0$). To this end we calculated the activation energy by means of eq. (4) for systems using DMA or DEA as a promoter. Table III shows the activation energies for the different systems used. We can clearly see for the two promoters used, how as the amount of promoter increases the activation energy decreases and the system becomes more efficient. This is shown in Figure 9, where we can see the experimental curves' degree of curing versus time at a given temperature for a system using different amounts of DEA as a promoter. Furthermore, the effectiveness of the type of promoter found are in agreement with the different nucleophilicity of the amine, and with the steric impediments, which are very important in the case of DEA, as explained in Walling and Indicator¹⁷ and Storey and Smith.¹⁸

For the same systems, Figure 10 shows the reaction rate versus curing time. Here we can clearly see how the amount of promoter has a strong influence on the reaction rate and on the curing kinetics. Table III also shows that for practically any proportion of promoter, the DEA shows far higher activation energies than the DMA and only at very high proportions does the DEA have a slightly lower activation energy than the DMA. At low amounts of the promoter DEA and DMA show very different activation energies, become more similar when the amount of promoter is increased, and finally reach

Table III Activation Energy (kJ/mol) at Start of Curing ($\alpha = 0$) for Systems Using Different Promoters and Different Amounts of Promoter

Promoter	<i>E</i>				
	Promoter (%)				
	0.05	0.1	0.5	1.0	1.5
DEA	98	91	80	62	41
DMA		67	61	53	45

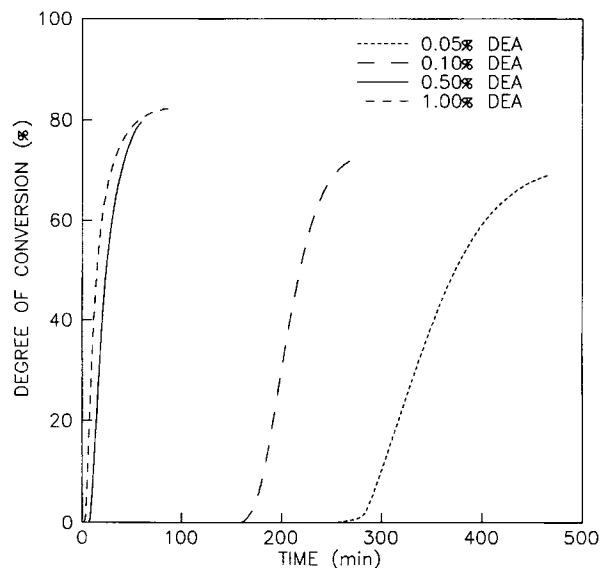


Figure 9 Experimental curves' degree of conversion versus curing time for systems cured at 30°C with different amounts of DEA.

a point where the two systems are practically equivalent. It is also important to note that for 1% DEA the system shows the same activation energy as for 0.5% DMA, which suggests that the effect of the two promoters at these amounts is equivalent. This is fully confirmed in Figs. 11 and 12, which compare at 20°C the experimental curves' degree of conversion versus time, and reaction rate against degree of conversion for the two systems. As can be seen, the two kinetic processes are practically identical.

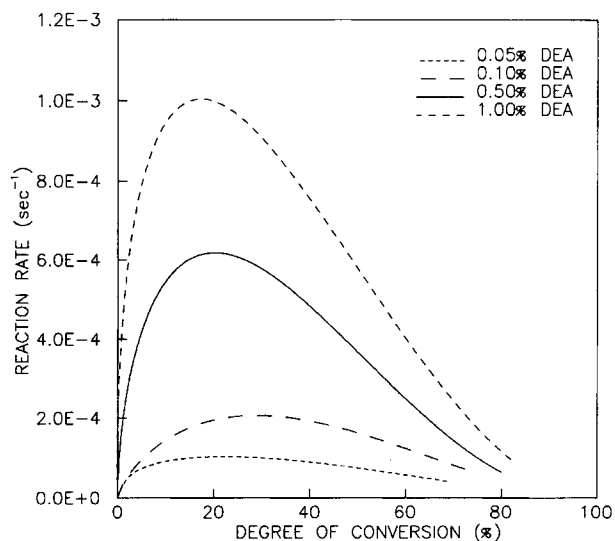


Figure 10 Reaction rate versus degree of conversion for systems cured at 30°C with different amounts of DEA.

CONCLUSIONS

1. Although it is usual to accept a single activation energy as a descriptive parameter of the kinetics of the curing process in thermostable reactions, this work shows that by usual procedures we can find activation energies that vary according to the degree of conversion.
2. The activation energies calculated may be clearly related with the effectiveness of the promoters used.
3. The variation in the activation energy during the reactive process is attributed to the effect of the promoter, to the phenomenon of autoacceleration, and to the increase in the viscosity of the medium.
4. The kinetic analysis proposed from the isothermal experimental processes allows us to characterize the curing in the different stages through which it passes. Although in this work we used a large amount of experimental information, and the obtaining of the kinetic parameters is laborious, the application of the proposed kinetic equation only at the start of the reaction is rapid and direct, and can provide useful information on the catalytic initiation system used.
5. The simulation made with the kinetic model shows an excellent agreement both inside the interval of temperatures investigated and

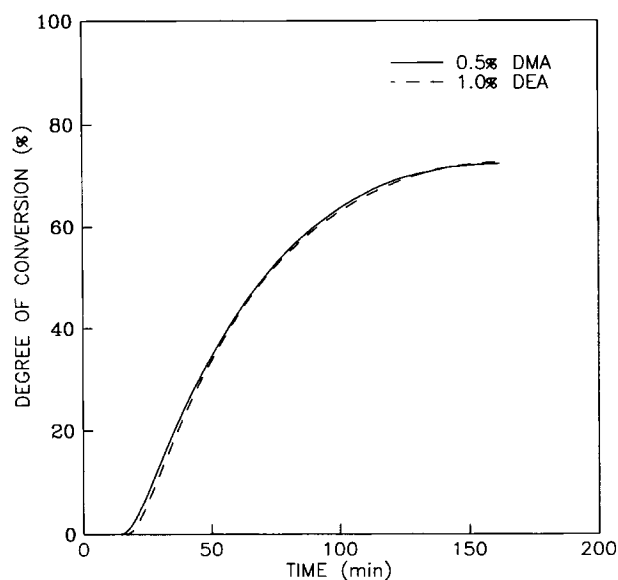


Figure 11 Comparison of the curves degree of conversion versus time for two equivalent systems using different promoters and different amounts of promoter.

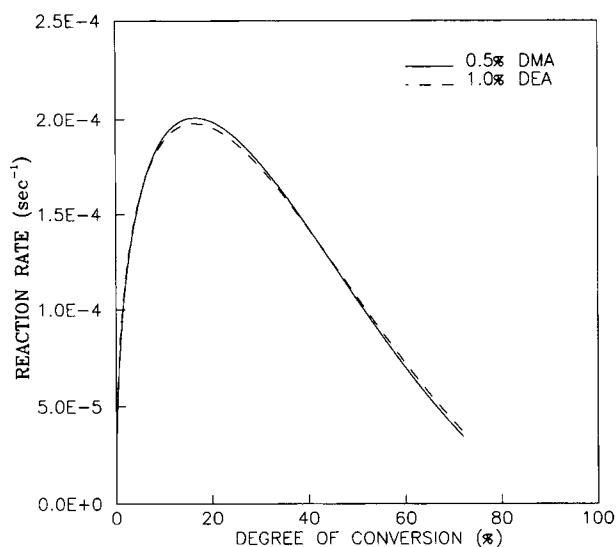


Figure 12 Comparison of the curves reaction rate versus degree of conversion for two equivalent systems using different promoters and different amounts of promoter.

outside, where a posteriori we found that the experimental results were very much in agreement. Because the isothermal experimental process is always problematic at extreme temperatures, we consider that the method used is of great interest for this type of study.

6. The results obtained show that both the type of promoter and the proportion of initiator/promoter influence the curing process, particularly at the start. However, they do not affect the last degree of conversion.
7. Though the effectiveness of the promoter depends both on the type and the proportion, an important result is that with different proportions of different promoters we can obtain a practically equivalent effect.

The research reported was supported by CICYT under Grant MAT89-377-C02-02.

REFERENCES

1. J. F. Stevenson, *Polym. Eng. Sci.*, **26**, 746 (1986).
2. Y. S. Yang and L. J. Lee, *Polymer*, **29**, 1793 (1988).
3. X. Ramis and J. M. Salla, *J. Appl. Polym. Sci.*, **45**, 227 (1992).
4. J. M. Salla, X. Ramis, J. L. Martin, and A. Cadenato, *Thermochim. Acta*, **134**, 261 (1988).
5. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci., A-1*, **8**, 2839 (1970).

6. M. R. Kamal and S. Sourour, *Polym. Eng. Sci.*, **13**, 59 (1973).
7. S. Y. Pusatcioglu, A. L. Fricke, and J. C. Hassler, *J. Appl. Polym. Sci.*, **24**, 937 (1979).
8. M. Avella, E. Martuscelli, and M. Mazzola, *J. Therm. Anal.*, **30**, 1359 (1985).
9. J. Sestak and G. Berggren, *Thermochim. Acta*, **3**, 1 (1971).
10. C. S. Chern and D. C. Sundberg, *ACS Polymer Preprints*, **25**, 296 (1985).
11. C. D. Han and D. Lee, *J. Appl. Polym. Sci.*, **33**, 2859 (1987).
12. F. Cernee, U. Osredkar, A. Moze, I. Vizivisek, and S. Lapanje, *Makromol. Chem.*, **178**, 2197 (1977).
13. R. A. Fava, *Polymer*, **9**, 137 (1968).
14. G. Odian, *Principles of Polymerization*, 3rd ed., Wiley-Interscience, 1991.
15. J. M. Barton and W. W. Wright, *Thermochim. Acta*, **85**, 411 (1985).
16. J. L. Martin, J. M. Salla, A. Cadenato, and X. Ramis, *J. Therm. Anal.*, **38**, 917 (1992).
17. C. Walling and N. Indicator, *J. Am. Chem. Soc.*, **80**, 5814 (1958).
18. R. F. Storey and D. L. Smith, *Modern Plastics*, **15**(2), 40 (1985).

Received February 23, 1993

Accepted April 5, 1993