Influence of Phenoxy Addition on the Curing Kinetics for Uncatalyzed and Catalyzed Cyanate Ester Resin

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ABSTRACT: The curing behavior of the dicyanate ester of bisphenol-A (DCBA) modified with poly(hydroxy ether of bisphenol-A) (phenoxy) is studied by differential scanning calorimetry in dynamic and isothermal tests at temperatures between 120 and 240°C. The addition of phenoxy to DCBA produces an increase in the reaction rate and a decrease in the temperature of maximum reaction rate for the uncatalyzed resin, and also for the system catalyzed with copper (II) acetyl acetonate/nonylphenol. The exothermic heat of curing for the mixtures is also dependent on the phenoxy content. These facts evidence a catalytic effect of phenoxy on the curing of the cyanate ester resin, even though an autocatalytic behavior is observed for all uncatalyzed DCBA/phenoxy mixtures. A simplified mechanistic kinetic model is used to calculate the kinetic parameters. For the uncatalyzed systems, a decrease in the kinetic constant for the initiation reactions, and an increase in the propagation constant are measured when the cyanate content increases. The thermal activation energy for the initiation reaction of the catalyzed systems is lower than that of the uncatalyzed ones, and it depends on the weight fraction of cyanate in the mixture. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2869–2880, 2010

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INTRODUCTION

Polycyanurates, which result from the thermal cure of dicyanate esters, are a family of thermosetting resins which posses an excellent combination of thermal, electrical, and mechanical properties, making them an ideal matrix for electronic and aerospace composite applications. The characteristic properties of polycyanurates are a high thermal stability, low outgassing, high radiation resistance, dimensional stability at solder temperatures and low moisture absorption.[1–4] In addition, they have epoxy-like processability, but their thermal stability is lower than that of other thermosetting resins such as bismaleimides, and they have some other drawbacks. For instance, like other thermosetting resins, they are too brittle to be used alone in certain structural applications.

The curing of dicyanate ester monomers occurs through thermal cyclotrimerization of cyanate ester groups to give polycyanurates. Cyanate esters can cure with or without the presence of catalyst. How-ever, uncatalyzed homopolymerization will proceed slowly at temperatures around 170–200°C, but more useful polymerization and curing rates can be achieved by the addition of specific catalysts to develop attractive curing rates. Different catalysts systems may be used for the curing to be more efficient in terms of reducing the curing temperature and attaining high conversion degrees, while minimizing weight losses by volatility. Generally, these catalyst packages comprise metallo-organic compounds such as the carboxylates and chelates of copper, zinc, manganese, cobalt, tin and nickel, in the presence of a hydrogen donor, such as an alkyl phenol, known as co-catalyst, which is used to dissolve the former. In this way, the presence of phenolic initiators and metal catalysts in the cyanate system strongly influence the kinetic evolution of the resin.

To overcome their weaknesses and to improve their performance, polycyanurates have been blended with other thermosets. Among them, epoxies[5–11] and specially, bismaleimides[12–15] have evidenced great interest. Also, for improving their low fracture toughness, cyanate esters have been frequently modified by means of the addition of certain thermoplastics and elastomers. Usually, amorphous thermoplastic polymers of high glass transition temperature, T_g, such as polysulphone[16–21] or polyetherimide[20,21] among others, are preferred as a way of

maintaining the high temperature properties of the cured cyanate ester resin. Moreover, oligomeric species, including oligosulphones, dicyanate-terminated oligomers and other thermoplastics have also been used as modifiers for the cyanate ester resins.[22–25]

When a reactive thermoplastic is used as modifier for a thermoset, more ductile and more solvent-resistant products are usually obtained than when an unreactive polymer is used.[26–28] Poly(hydroxy ether of bisphenol-A), also known as phenoxy, is an amorphous thermoplastic polymer obtained by reaction of bisphenol-A with epichlorhydrin. It has a pendant hydroxyl group in its structural repeat unit, which may act as proton donor, and which is able to react at high temperatures with other functional groups, such as esters or amides.[29–32] Moreover, it is known that the polycyclotrimerization of cyanate esters to form cyanurates is very sensitive to small amounts of impurities and catalysts. For example, it is speculated that residual phenolic OH groups, stemming from the monomer synthesis, may react with a cyanate group to form an iminocarbonate which, subsequently, may react with two more OCN groups to give a cyanurate ring, releasing the phenolic compound.[3,33] For these reasons, phenoxy has been chosen as a thermoplastic modifier for the cyanate ester resin, since it might react through the pendant hydroxyls to give materials with improved toughness compared to the unmodified ester cyanate resin.

Furthermore, it has been reported that phenoxy has also been used as modifier of the cyanate ester resins for special applications, i.e., as an insulating material to obtain a copper foil-clad adhesive sheet,[34] as insulated conductive particles,[35] or as component of an adhesive composition suitable for bonding electronic components.[36] These are well-known applications, but as far as we know, no systematic studies on the effect of phenoxy on the curing kinetics of the cyanate ester resin have been made up to date.

The conventional polymerization mechanism of cyanate esters was elucidated by Bauer et al.[6,8,37–40] and other researchers.[3,4,41–46] Nevertheless, only phenomenological kinetic models have been published. Simon and Gilham[42,47] presented a kinetic scheme for the uncatalyzed polymerization, which was based on the work originally reported by Bauer et al.[36] This kinetic scheme incorporated two terms, which represented two parallel, competing second order reactions. Usually, during the first stage of the reaction, in the kinetic-conversion regime, the uncatalyzed cyanate conversions have been fitted to a second-order autocatalytic expression which takes into account both the catalyzed and the uncatalyzed reaction.[1,2,44,48–50] But, for systems in which the temperature or the catalyst concentration is high enough

to neglect the initial phases of the reaction, a simple nth-order kinetic expression may be used to describe the experimental data.[1,2,4,50,51–53] More recently, Zhao and Hu[54] proposed a variable reaction order kinetic model to describe the kinetics of fluoromethylene cyanate ester both in the chemically controlled and in the diffusion controlled regions.

Accordingly, the aim of this article is to analyze how the addition of phenoxy modifies the curing behavior of the cyanate ester resin. To evaluate the possible influence of phenoxy on the curing kinetics of the cyanate ester resin and the probable catalytic effect of the pendant hydroxyls, the curing behavior of the uncatalyzed cyanate ester resin and that of uncatalyzed cyanate ester/phenoxy systems will be studied. Catalysts are not necessary for the curing reaction of cyanate esters. However, for real industrial applications higher curing rates are needed, thus a catalyst/co-catalyst package is frequently used. For this reason, the curing behavior of the uncatalyzed systems will be compared to that of the systems catalyzed by a catalytic solution made of copper (II) acetyl acetonate dissolved in nonylphenol. A mechanistic model will be applied to modellize the kinetic of curing.

EXPERIMENTAL

The cyanate ester resin used in this work was 4,4′-dicyanato-2,2′-diphenylpropane, named hereafter as dicyanate ester of bisphenol-A (DCBA). It was gently supplied by Ciba under the trade name Arocy B10. It has a cyanate equivalent weight of 139 g/eq. It was used as received without further purification. Poly(hydroxyether of bisphenol-A), phenoxy, was used as thermoplastic modifier. The phenoxy employed was Paphen Phenoxy PKHH, from Phenoxy Associates. It was kindly supplied by Quimidroga (Spain). It has a number average molecular weight, $\overline{M}_n = 25,800$, and a polydispersity index, $I = 2.2$. The chemical structures of DCBA and phenoxy are given in Figure 1.

DCBA/phenoxy mixtures containing up to 20 wt % phenoxy were prepared in the following way. A weighed amount of phenoxy was dissolved in tetrahydrofurane. Then, DCBA was added to the solution and gently stirred until complete dissolution. Afterwards, the solvent was allowed to evaporate in an oven at 60°C. Finally, the mixtures were dried in a vacuum oven at 60°C until constant weight, typically for one night. The samples appeared transparent, thus indicating the total miscibility of the blends.

A catalytic solution was prepared by dissolving copper (II) acetyl acetonate in nonylphenol at 60°C, and stirring for 4 h. Catalyzed DCBA/phenoxy mixtures were prepared by adding 2 phr of this catalytic solution to the uncatalyzed mixtures, which had
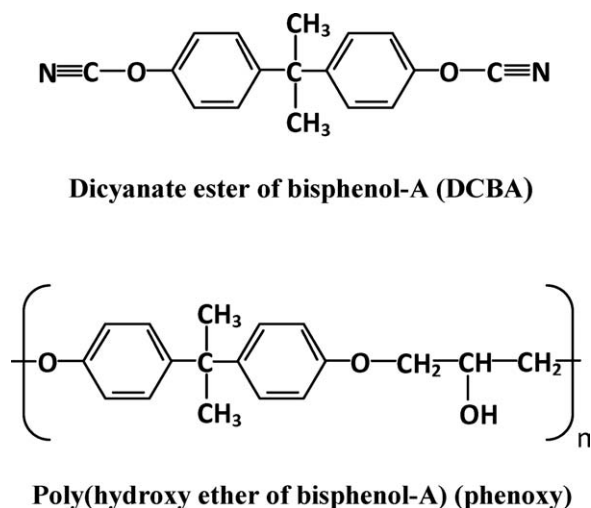
Dicyanate ester of bisphenol-A (DCBA)

Poly(hydroxy ether of bisphenol-A) (phenoxy)

Figure 1   Chemical structures of DCBA and phenoxy.

been melted at 90°C in an oil bath. The resulting catalyst concentration was 360 ppm of copper ions. Previous tests were performed with copper (II) acetyl acetonate concentrations up to 750 ppm, and nonylphenol amounts up to 4 phr to determine the optimal catalyst/co-catalyst concentration. Higher nonylphenol concentrations gave unacceptable plasticization of the samples, whereas higher copper (II) acetyl acetonate concentrations only gave a marginal decrease in the temperature of reaction.[55]

Differential scanning calorimetry (DSC) was used as a convenient tool to investigate the curing reaction under isothermal and dynamic conditions for the uncatalyzed and for the catalyzed DCBA/phenoxy blends. Calorimetric measurements were performed under nitrogen atmosphere flow on a Perkin–Elmer DSC-7 differential scanning calorimeter. The instrument was calibrated with an indium standard. Accurately weighed samples of about 6–10 mg were sealed in aluminum pans. Dynamic scans between 35 and 400°C for the uncatalyzed samples, or between 35 and 350°C for the catalyzed ones were carried out at a constant heating rate of 20°C/min. A baseline was firstly registered and it was automatically subtracted from the subsequent dynamic scan. Isothermal measurements were also performed at different temperatures between 120 and 240°C. Samples were placed in the holder at room temperature and heated to the chosen isothermal temperature at 200°C/min. No baseline subtraction was performed for the isothermal tests as the DSC trace returned to horizontal once the reaction was completed. After completion of the isothermal test, all samples were subsequently submitted to a dynamic scan to determine the residual heat of reaction. The total heat of reaction, ΔH_T, was calculated by integrating the recorded exothermic peaks for

dynamic runs, or as the sum of the isothermal heat of reaction plus the residual heat obtained in the subsequent scan. To check the reproducibility of data, at least three different tests were performed, and the measured enthalpy can be estimated to be accurate at ±5%. Conversion, α, was defined as the ratio of partial reaction heat, ΔH, to the total heat of reaction, $(\alpha = \Delta H/\Delta H_T)$ and the reaction rate was obtained as $d\alpha/dt = (dH/dt)\Delta H_T$.

RESULTS AND DISCUSSION

The polycondensation kinetics have been studied by several techniques such as DSC, Fourier transform infrared (FTIR) spectroscopy, size exclusion chromatography (SEC), Raman spectroscopy, nuclear magnetic resonance (NMR), etc. Among them, DSC has been widely used, since the polycondensation reaction is very exothermic and thus, it allows drawing the complete conversion vs. curing time curve. This is why, in Figure 2, the dynamic calorimetric curves registered during the first (continuous line) and second (dotted line) heating scans, for uncatalyzed [Fig. 2(a)] and for catalyzed [Fig. 2(b)] DCBA/phenoxy mixtures containing different amounts of phenoxy, are shown. During the first scan, both neat DCBA and DCBA/phenoxy mixtures, exhibit a sharp melting endotherm followed by an exothermic peak whose position depends on the DCBA/phenoxy ratio. Similar behavior was observed by Zhang et al.[56] for a series of cyanate resins based on phenolphthalein and its derivatives. No heat evolution is detected on the second scan, thus indicating that the reaction was completed during the first scan. In addition, a small exotherm can be detected at high temperatures, near the end of the scan, which can be attributed to degradation. Also it is noteworthy that at 60°C, temperature at which the components were blended, no reaction was detected.

If the scans of the uncatalyzed and the catalyzed systems are compared, it can be seen that the first ones show a single exothermic peak. However, a shoulder can be noticed in the exothermic peak for all the catalyzed mixtures. Similar results were obtained by Gomez et al.[53] when monitoring the cyanate conversion in presence of different concentrations of the catalytic system. The shoulder at low temperature has been attributed either to the formation of intermediate imidocarbonate species, or to a possible effect of heat on the catalyst to produce the active species.[57]

In Figure 3, the peak and shoulder temperatures, T_p and T_s, obtained from the DSC traces, are reported. As can be seen, neat uncatalyzed DCBA displays a maximum reaction rate at 327°C. When phenoxy is added to DCBA, the curves shift towards lower temperatures. Consequently, T_p decreases at
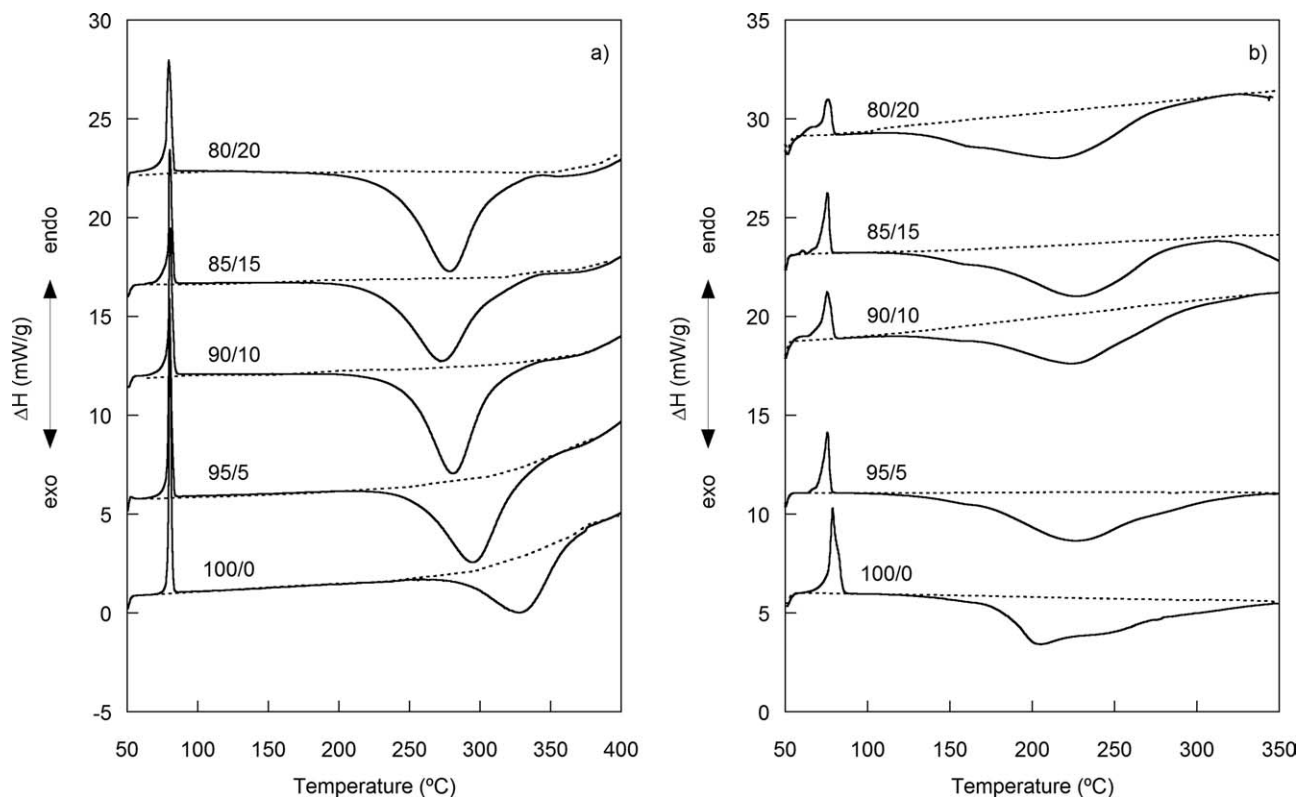
Figure 2 Dynamic thermograms for curing of (a) uncatalyzed DCBA/phenoxy mixtures, and (b) catalyzed DCBA/phenoxy mixtures of different compositions. First (——) and (⋯⋯) second heating scan. Curves have been shifted vertically for clarity.

increasing phenoxy contents and reaches a minimum at 15 wt %. Although reactions between phenoxy and DCBA may occur, these results show evidence of a catalytic effect of phenoxy on the polymerization of DCBA, which probably takes place through the hydroxyl group pendant from the main backbone chain of phenoxy. In fact, it has been stated that cyanate ester groups can react with amino, alcohol or phenol groups, and that the resultant product catalyses the cyclotrimerization reaction, increasing the overall reaction rate.[58,59] On the other side, the increase in T_p observed when the phenoxy content increases from 15 to 20 wt % could be related to the increase in the viscosity of the reacting medium which hinders the mobility of the reactant species and counteracts the catalytic effect of phenoxy.

For the catalyzed mixtures, the main effect of the presence of the catalyst is a shift of the curves towards lower temperatures. As seen in Figure 3, for these catalytic mixtures, T_p also varies with phenoxy content, but, for the high temperature shoulder this dependence is weaker. The greater scattering bars displayed by the T_p values of the uncatalyzed mixtures is attributed to a higher sensibility to the
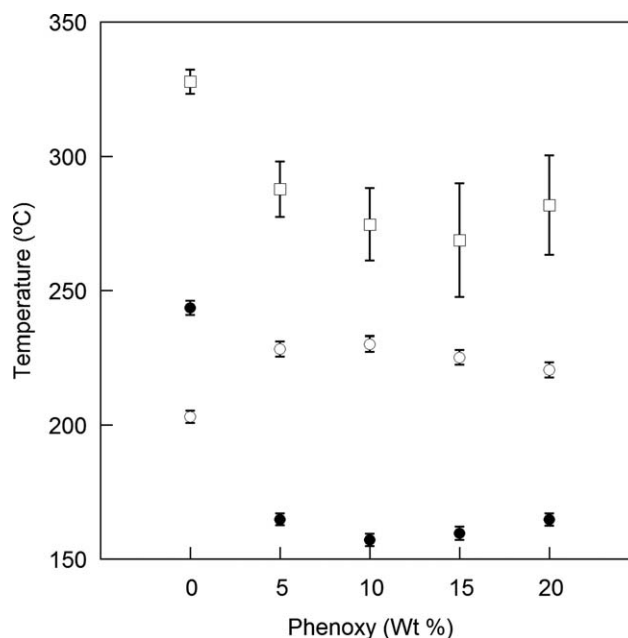

Figure 3 Characteristic temperatures obtained from the dynamic DSC traces. (□) Peak temperature for uncatalyzed DCBA/phenoxy mixtures, (○) Peak temperature for catalyzed DCBA/phenoxy mixtures, (●) Shoulder temperature for catalyzed DCBA/phenoxy mixtures.

TABLE I
Enthalpy of Reaction for Uncatalyzed and For Catalyzed DCBA/Phenoxy Mixtures Measured From Dynamic Calorimetric Scans

Phenoxy (wt %)	ΔH_T kJ/eq. cyanate	
	Uncatalyzed	Catalyzed
0	82.4	91.3
5	94.9	95.2
10	110.1	96.7
15	116.8	103.6
20	117.5	108.6

presence of water and/or small impurities which can cause several side reactions.[48]

The enthalpy of reaction for the uncatalyzed and for the catalyzed DCBA/phenoxy mixtures measured from the dynamic DSC scans is shown in Table I. It can be seen that the heat evolved for the neat system displays similar values than those reported in bibliography. Also, the heat evolved for the modified systems depends on the phenoxy content in the mixture, both for the uncatalyzed and for the catalyzed systems. In fact, not only does phenoxy accelerate the cyclotrimerization of the cyanate ester resin, but it greatly increases the total heat of reaction, probably by a change in the reaction path. It has been demonstrated[60,61] that when an hydroxyl provider like 4-nonyl phenol is added to the cyanate ester resin, the cyclotrimerization of the ester cyanate groups is not the only reaction which takes place, since the addition of the 4-nonyl phenol to the cyanate ester occurs simultaneously. Similar simultaneous reactions might take place between the pendant hydroxyl groups of phenoxy and the ester cyanate resin. These additional reactions would be responsible for the additional heat of reaction evolved. Consistent values were obtained for dynamic runs and also for the sum of the isothermal heat of reaction and the residual heat obtained in a subsequent scan.

Isothermal DSC scans at various temperatures were also performed to obtain the kinetic data for the uncatalyzed and for the catalyzed systems. In Figure 4, the isothermal DSC traces for uncatalyzed DCBA/phenoxy mixtures at 240°C are shown. It is seen that neat DCBA reacts very slowly at 240°C, and even at times longer than 60 min the reaction is not completed, since the plot do not reach the horizontal base line yet. Moreover, some additional heat is evolved during a subsequent dynamic scan, thus confirming that the reaction was not completed on the time given for the isothermal scan. On the other side, when phenoxy is added to DCBA, the curves display an autocatalytic behavior, evidenced by the maximum reaction rate occurring at a time $t > 0$. In addition, for these phe-

noxy-containing mixtures, the time for the maximum reaction rate decreases up to a phenoxy content of 10 wt % indicating the acceleration of the reaction rate with phenoxy addition. At higher phenoxy contents, the time for the maximum reaction rate increases. This could be attributed to the increased viscosity of the reacting medium as the phenoxy content in the mixtures increases, since the high viscosity would hinder the mobility of the reacting molecules. But in spite of this, for all modified mixtures, by 30 min the reaction had already stopped.

Isothermal scans were also performed on the catalyzed samples at different temperatures (Fig. 5). Thermograms registered at 180 and 240°C are shown as examples in Figure 5(a,b), respectively. At 180°C, for neat DCBA the maximum reaction rate appears at a time $t > 0$, i.e., it displays an autocatalytic behavior. For a similar catalyzed cyanate resin (LECY), Leroy et al.[52] reported that an autocatalytic term is not negligible even if the reaction is catalyzed. For the 95/5 mixture, this autocatalytic behavior has already almost disappeared, and a new shoulder, almost imperceptible, starts appearing at times between 15 and 30 min. At increasing phenoxy contents, the shoulder appears at shorter times and becomes more evident. But, for phenoxy contents
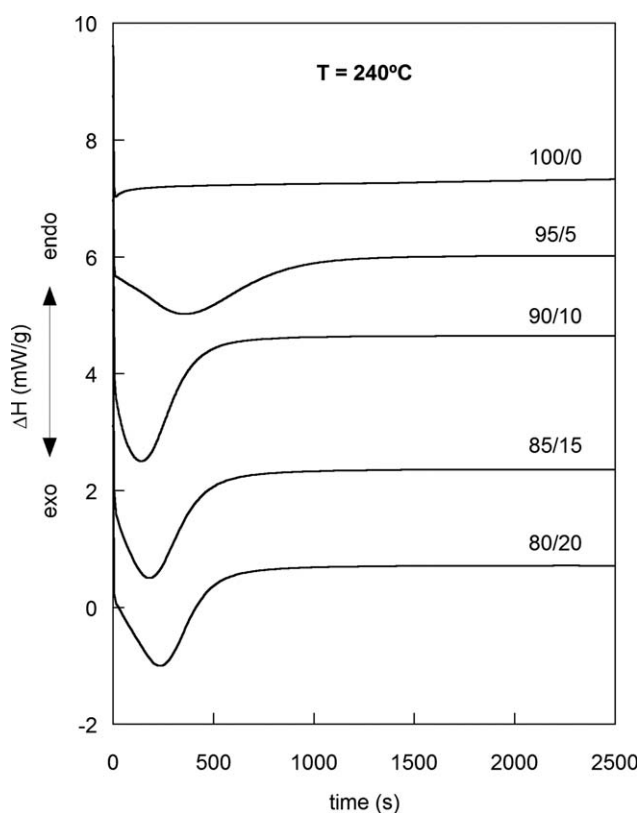

Figure 4 Isothermal thermograms for curing of uncatalyzed DCBA/phenoxy mixtures of different compositions at 240°C. Curves have been shifted vertically for clarity.
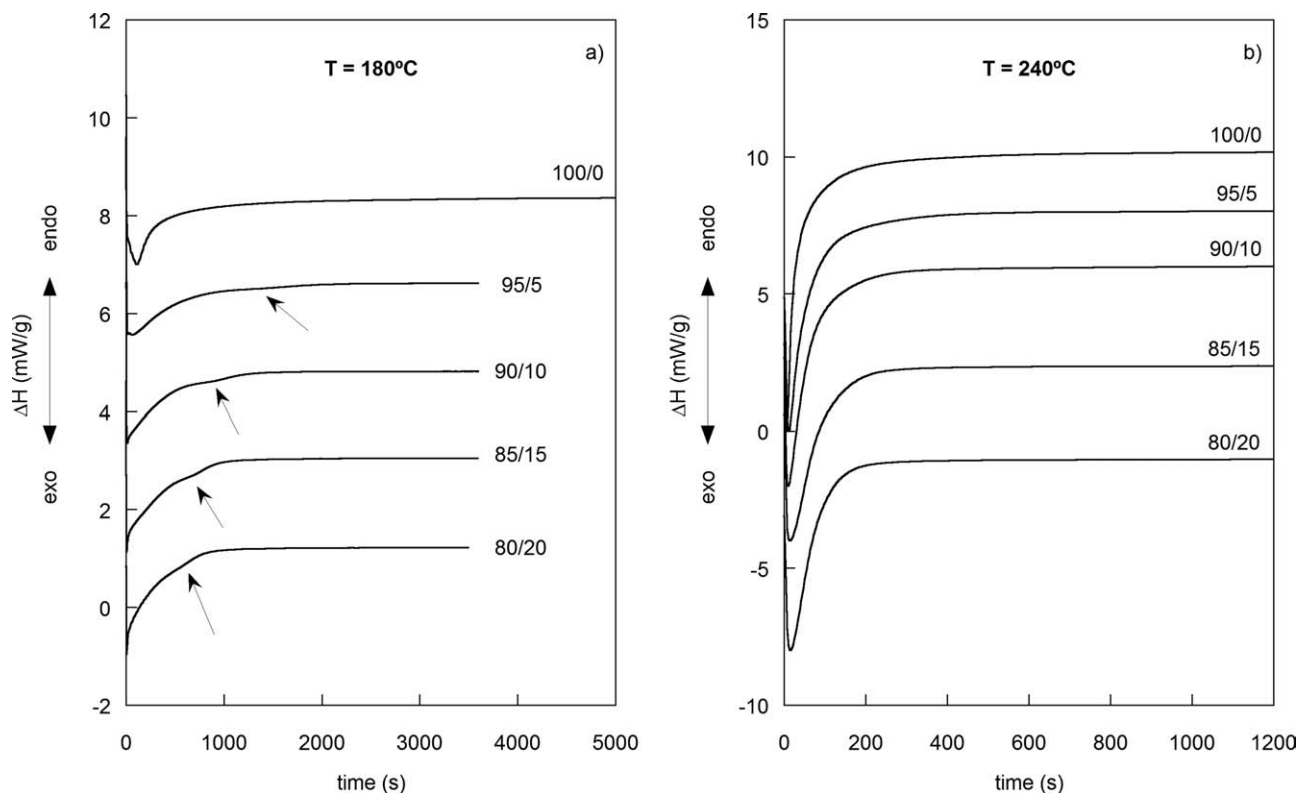
Figure 5 Isothermal thermograms for curing of catalyzed DCBA/phenoxy mixtures of different compositions (a) at 180°C, and (b) at 240°C. Curves have been shifted vertically for clarity. The arrows indicate the position of the shoulder.

higher than or equal to 10 wt %, the maximum reaction rate is at $t = 0$, thus no autocatalytic behavior is observed any longer. Similar results were obtained at lower temperatures. These results may be due to the fact that the amount of the copper (II) acetyl acetonate/nonylphenol catalyst added was not enough to fully catalyze the system which does not contain phenoxy. On the other side, when 10 wt % phenoxy or more is added, since phenoxy also has a catalytic effect, the system is fully catalyzed and then the autocatalytic behavior is not observed. Moreover, for all compositions, the samples reacting at 180°C vitrified, as could be inferred by small exotherms which were observed just after the glass transition registered in subsequent dynamic heating scans. On the other hand, at 240°C the reaction proceeds very quickly for the catalyzed samples and the shoulder on the isothermal DSC traces is not observed in any mixture.

The dynamic scans after the isothermal curing at 240°C, for the catalyzed samples, are plotted in Figure 6. The glass transition, which decreases at increasing phenoxy contents, is clearly observed at temperatures ranging from about 230 to 270°C. This single, composition dependent glass transition is indicative of the miscibility of the cured systems. At higher temperatures, the samples started to degrade.

Similar behavior during the dynamic scans was observed for samples cured at other isothermal temperatures, as well as for the uncatalyzed samples.
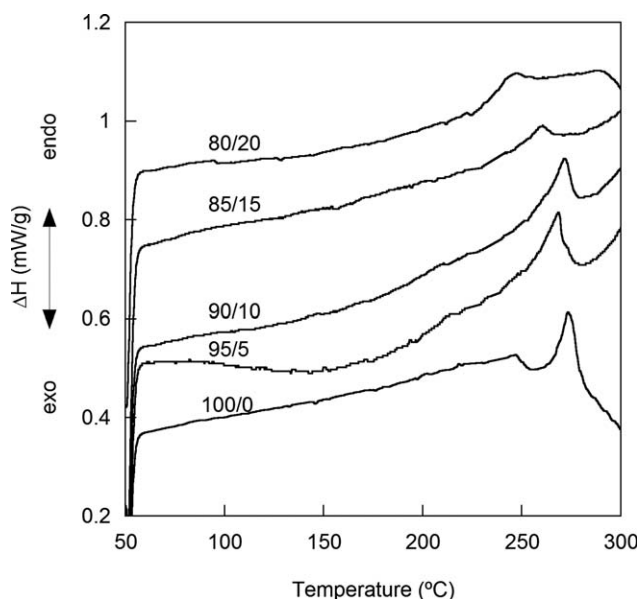

Figure 6 Dynamic thermograms, registered after the isothermal curing at 240°C, for catalyzed DCBA/phenoxy mixtures of different compositions. Curves have been shifted vertically for clarity.
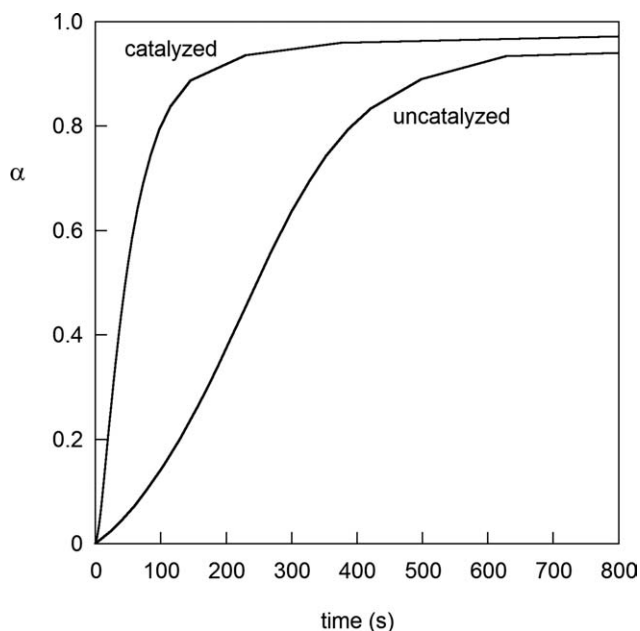
Figure 7 Isothermal extent of reaction vs. time for an uncatalyzed and for a catalyzed DCBA/phenoxy 80/20 mixture curing at 240°C.

Figure 8 Final conversion for isothermally cured catalyzed DCBA/phenoxy mixtures.

In Figure 7, the extent of reaction vs. time for an uncatalyzed and for a catalyzed DCBA/phenoxy 80/20 mixture at an isothermal temperature of 240°C is represented. For the uncatalyzed system, the slope of the α vs. t plot initially increases with time indicating an acceleration of the reaction rate with time. In this way, the autocatalytic behavior of the uncatalyzed mixtures is evidenced. On the contrary, for the catalyzed system, the slope is maximal at the beginning and then progressively decreases until the end of reaction. As expected, for the catalyzed system the reaction proceeds faster than for the uncatalyzed one. Thus, although phenoxy has some accelerating effect on the curing reaction of the cyanate ester, the reaction rate can still be increased more by the addition of another catalyst system that works cooperatively with phenoxy.

The final conversions, α_{max}, obtained in the isothermal runs for uncatalyzed and for catalyzed

DCBA/phenoxy mixtures at 240°C are collected in Table II. As can be seen, the final conversion reached for catalyzed and uncatalyzed system is similar both for neat DCBA and for phenoxy-containing mixtures. Moreover, α_{max} slightly increases at increasing phenoxy contents. Similar results were obtained for the catalyzed system at other isothermal temperatures, as seen in Figure 8. Moreover, the same behavior has been reported for other modified cyanate ester resins in which the modifier is able to react, or when it catalyzes the curing reaction.[61–64]

As pointed out in the Introduction section, many phenomenological kinetic models have been reported in the literature to describe the cure of cyanate esters. With this in mind, our aim is to modellize the curing kinetics of cyanante ester resins by using a mechanistic model as simple as possible. Two kinetic models, one for the uncatalyzed system and another for the catalyzed one have been chosen, which are depicted in Scheme 1. The reactive species are shown in Figure 9. As can be seen in Scheme 1, for the uncatalyzed system, two initiation reactions

TABLE II
Final Conversion for Uncatalyzed and for Catalyzed DCBA/Phenoxy Mixtures at a Curing Temperature of 240°C

Phenoxy (wt %)	α_{max}	
	Uncatalyzed	Catalyzed
0	0.93	0.93
5	0.93	0.95
10	0.95	0.96
15	0.97	0.97
20	0.98	0.99

UNCATALYZED

$$C_1 + C_2 \xrightarrow{k_{I1}} C_3 \qquad \text{I1}$$

$$C_1 + C_2 + C_4 \xrightarrow{k_{I2}} C_3 + C_4 \qquad \text{I2}$$

$$C_3 + 2C_1 \xrightarrow{k_P} C_4 + C_2 \qquad \text{P}$$

CATALYZED SYSTEM

$$C_1 + C_2 \xrightarrow{k_I} C_3' \qquad \text{I}$$

$$C_3' + 2C_1 \xrightarrow{k_P} C_4 + C_2 \qquad \text{P}$$
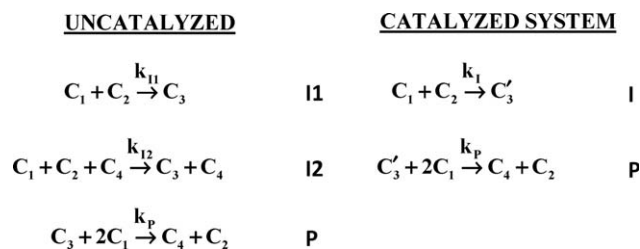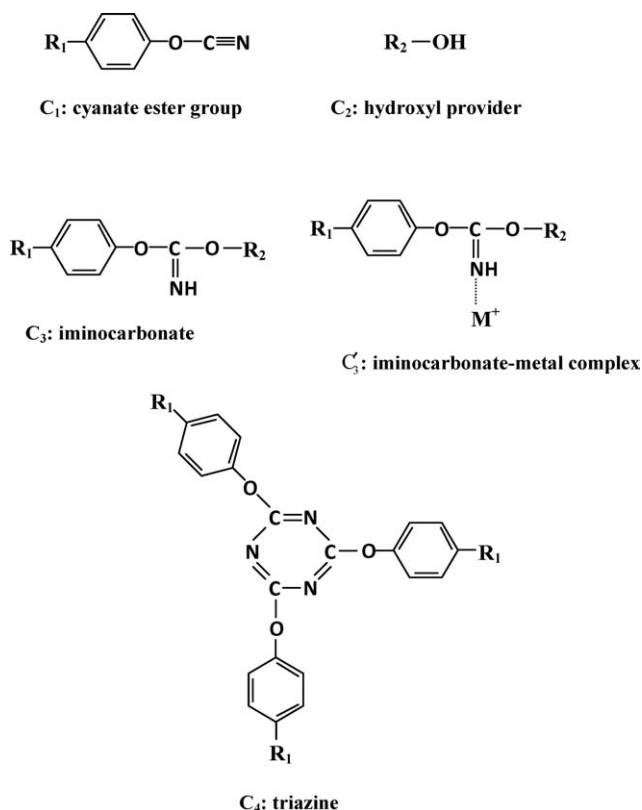
Scheme 1 Kinetic models.

Figure 9 Reactive species present during the curing of cyanate ester resin.

and one chain propagation reaction were considered.[33] The first initiation reaction, *I*1, consists on the addition of a hydroxyl group (C_2), which may be present as an impurity from the synthesis of the cyanate ester resin, to the cyanate ester group (C_1) to yield an iminocarbonate group (C_3). This reaction may be autocatalyzed by triazine groups (C_4) already formed. This is the second initiation reaction, *I*2. In the propagation reaction, *P*, the previously formed iminocarbonate reacts with two cyanate ester groups to give a triazine ring. For the catalyzed system only one initiation reaction catalyzed by a transition metal ion, *I*, giving an iminocarbonate-metal complex (C_3') and one chain propagation reaction, *P*, were taken into account.[64]

According to these simplified kinetic models, the kinetic equations for the uncatalyzed system can be written as:

$$\frac{d[C_1]}{dt} = -k_{I1}[C_1][C_2] - k_{I2}[C_1][C_2][C_4] - 2k_p[C_1]^2[C_3]$$

$$\frac{d[C_2]}{dt} = -k_{I1}[C_1][C_2] - k_{I2}[C_1][C_2][C_4] + k_p[C_1]^2[C_3]$$

$$\frac{d[C_3]}{dt} = k_{I1}[C_1][C_2] + k_{I2}[C_1][C_2][C_4] + k_p[C_1]^2[C_3]$$

$$\frac{d[C_4]}{dt} = k_p[C_1]^2[C_3]$$

while the corresponding equations for the catalyzed system are:

$$\frac{d[C_1]}{dt} = -k_{I1}[C_1][C_2] - 2k_p[C_1]^2[C_3']$$

$$\frac{d[C_2]}{dt} = -k_{I1}[C_1][C_2] + k_p[C_1]^2[C_3']$$

$$\frac{d[C_3]}{dt} = k_I[C_1][C_2] + k_p[C_1]^2[C_3']$$

$$\frac{d[C_4]}{dt} = k_p[C_1]^2[C_3']$$

These equations were made dimensionless by dividing all the concentrations by the initial concentration of the cyanate ester group, $[C_1]_0$. In this way, the dimensionless preexponential factor of the Arrhenius expression for each kinetic constant has units of time^{-1}, and is defined as:

$$A^* = A[C_1]_0^{n-1}$$

where *n* is the total reaction order of the corresponding elemental step.

The following procedure was used to fit the proposed kinetic models to the experimental data.[65] From each experimental curve, a table containing 20–25 values of $d\alpha/dt$, α, temperature (*T*) and time (*t*), evenly distributed in the conversion range, was built up. For the isothermal runs, the recorded experimental values of temperature were selected for each point (they were almost constant). For each constant, an initial set of dimensionless preexponential factors and activation energies was selected. Predicted α and $d\alpha/dt$ values were generated by applying the Runge-Kutta method to the set of dimensionless equations and taking into account that:

$$\alpha = \frac{[C_1]_0 - [C_1]}{[C_1]_0}$$

and

$$\frac{d\alpha}{dt} = -\frac{1}{[C_1]_0}\frac{d[C_1]}{dt}$$

The following summation, including every selected experimental point of isothermal and dynamic runs, was calculated:

$$S = \frac{\sum\left[(d\alpha/dt)_{\text{exp}} - (d\alpha/dt)_{\text{model}}\right]^2}{\left[(d\alpha/dt)_{\text{max}}\right]^2}$$

where $(d\alpha/dt)_{\text{max}}$ is the maximum reaction rate for every subset of points pertaining to an isothermal or
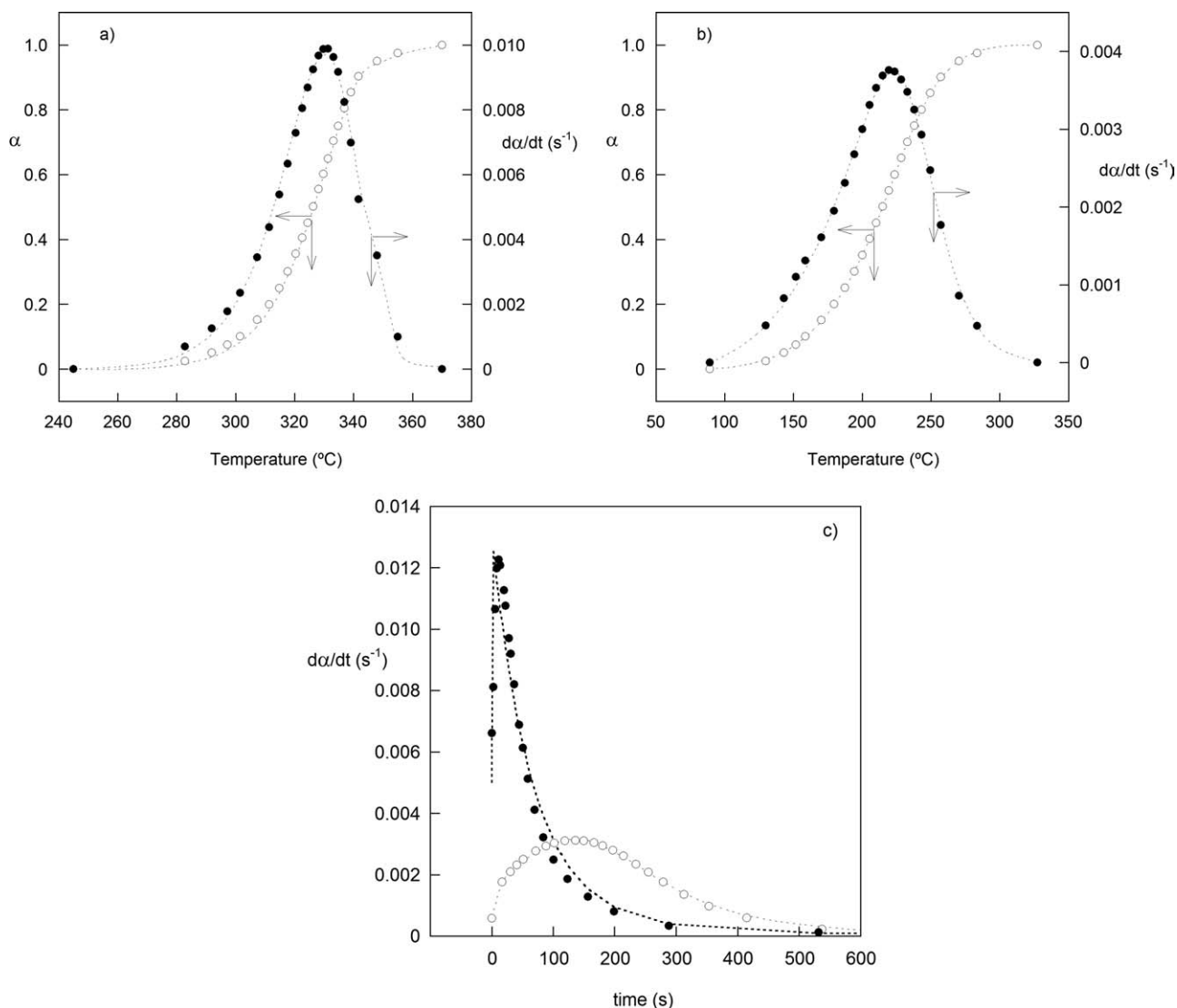
Figure 10 Fit of: (a) dynamic experimental curves for the uncatalyzed neat system, (b) dynamic experimental curves for the catalyzed system modified with 20% of phenoxy, and (c) isothermal scans at 240°C for uncatalyzed (○) and for catalyzed (●) DCBA/phenoxy 90/10 mixtures.

a dynamic run. The minimum of the S function was searched by using an optimization program that operated over the adjustable parameters. The best set obtained by using this fitting procedure let us to determine for the dimensionless constants, the corresponding pre-exponential factor, A^*, in units of s^{-1}, and the activation energy, E_a, in units of kJ mol^{-1}. As example, some of the results obtained are displayed in Figure 10. Figure 10(a,b) show the fit of dynamic experimental curves with the kinetic model for the uncatalyzed neat system and for the catalyzed system modified with 20% of phenoxy, respectively. Additionally, Figure 10(c) shows the fit of the kinetic model with experimental values for isothermal scans at 240°C for catalyzed and uncatalyzed systems modified with 10% of phenoxy. In all cases,

a good fit between the experimental data and the model is obtained.

On the other hand, the thermal activation energies for the two initiation reactions, Ea$_{I1}$ and Ea$_{I2}$, and for the propagation reaction, Ea$_P$, as well as the corresponding dimensionless pre-exponential factors, ln A^*_{I1}, ln A^*_{I2} and ln A^*_P, for the uncatalyzed systems, evaluated from dynamic calorimetric scans are shown in Table III. Also in Table III, the thermal activation energy for the initiation reaction, Ea$_I$, and for the propagation reaction Ea$_P$, tsogether with the pre-exponential factors, ln A^*_I and ln A^*_P, for the catalyzed systems, are collected. As expected, lower Ea and ln A^* values were obtained for the catalyzed systems as compared to the uncatalyzed ones for the initiation and propagation reactions. The main effect

Pre-exponential Factor and Activation Energy of Initiation and Propagation Reactions for Uncatalyzed and Catalyzed DCBA/Phenoxy Mixtures

Phenoxy (wt %)	Uncatalyzed						Catalyzed			
	$\ln A_{I1}^*$ (s^{-1})	Ea_{I1} (kJ mol^{-1})	$\ln A_{I2}^*$ (s^{-1})	Ea_{I2} (kJ mol^{-1})	$\ln A_P^*$ (s^{-1})	Ea_P (kJ mol^{-1})	$\ln A_I^*$ (s^{-1})	Ea_I (kJ mol^{-1})	$\ln A_P^*$ (s^{-1})	Ea_P (kJ mol^{-1})
0	25.2	140.2	25.6	132.1	24.7	109.9	15.3	59.9	11.7	39.2
5	27.3	143.2	25.3	127.0	23.3	107.3	13.4	60.1	12.3	45.5
10	27.9	145.2	24.1	121.8	22.7	104.3	13.2	63.6	12.7	42.9
15	28.4	145.4	23.4	116.1	22.1	104.2	13.5	63.8	12.6	42.0
20	28.6	146.5	23.3	116.0	22.3	106.0	13.2	66.3	12.0	44.8

of the phenoxy addition to the uncatalyzed system seems to be that it promotes the initiation reaction, autocatalyzed by triazine groups already formed. On the contrary, the addition of phenoxy to the catalyzed system seems to disfavor the initiation reaction. However, it must be borne in mind that conclusions obtained by only taking into account E_a, as it is frequently done in the bibliography, could be misleading because both Ea and ln A^* vary with the phenoxy content, and they can be within the limits of the kinetic compensation.

For this reason, also the kinetic constants were calculated as a tool for evaluating the reactivity of the mixtures. The kinetic constants at 240°C for uncatalyzed and for catalyzed DCBA/phenoxy mixtures with various phenoxy contents, evaluated from isothermal and dynamic calorimetric scans, are plotted in Figure 11. The initial cyanate ester concentration was taken into account. Figure 11(a) displays the variation of the kinetic constants for the first initia-

tion reaction, k_{I1}, for the second initiation reaction, k_{I2}, and for the propagation reaction, k_P, with the percentage weight content of phenoxy in the mixture for uncatalyzed DCBA/phenoxy mixtures. A slight increase of k_{I1} and k_{I2} with the phenoxy content in the mixture is seen, which would indicate the catalytic effect of phenoxy. In addition, for same phenoxy content, k_{I2} is higher than k_{I1}. This is expected behavior since the $I2$ reaction is catalyzed by the triazine rings already formed. On the contrary, the kinetic constant for the propagation reaction k_P shows a tendency to decrease with the phenoxy content. This might be the result of the increase in the viscosity of the mixtures as the phenoxy content increases, thus hindering the propagation reaction.

For the catalyzed mixtures, shown in Figure 11(b), an inverse dependence between the kinetic constant for the initiation reaction, k_I, and the phenoxy content was found. This was probably due to the fact that the modifier interferes with the formation of the
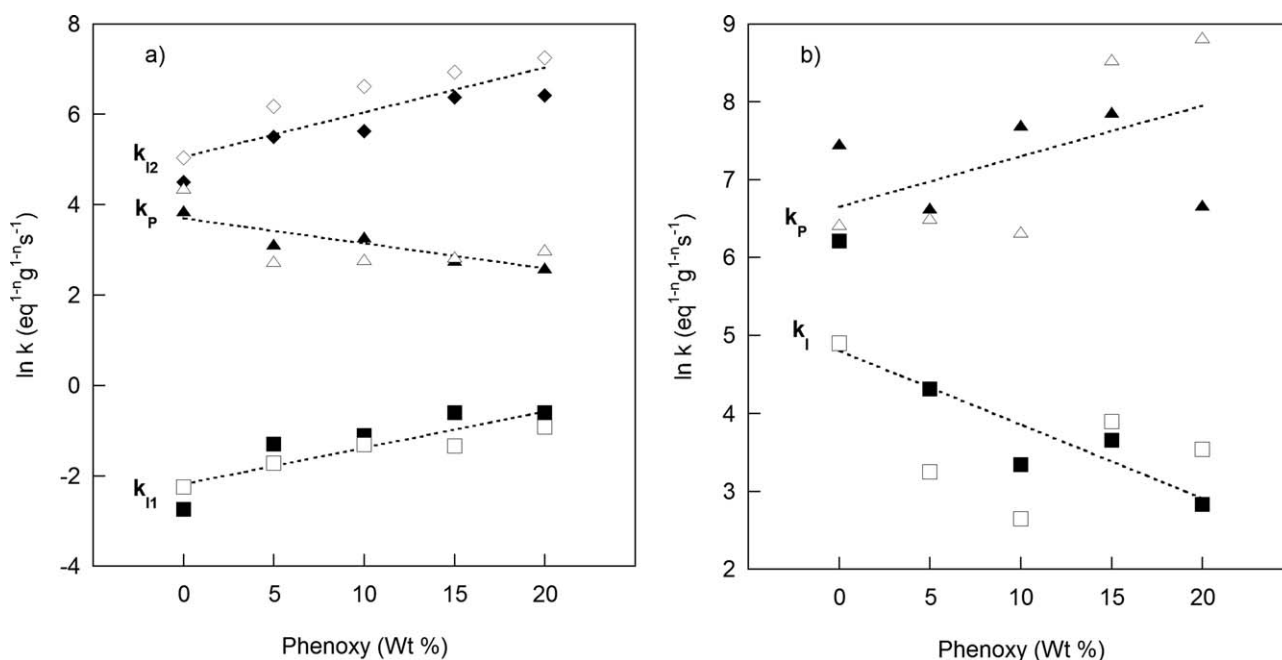

Figure 11 Kinetic constants at 240°C for (a) uncatalyzed and (b) for catalyzed DCBA/phenoxy mixtures from dynamic (filled symbols) and isothermal (open symbols) calorimetric scans.

iminocarbonate-metal complex. For the propagation reaction, the values of k_P seem to increase slightly with phenoxy contents.

CONCLUSIONS

The influence of phenoxy on the curing reactions of DCBA has been analyzed by DSC. A catalytic effect of phenoxy on the curing of the cyanate ester resin has been demonstrated, which is manifested by an increase in the reaction rate and a reduction in the temperature of maximal reaction rate for both the uncatalyzed and for the DCBA/phenoxy mixtures catalyzed with copper(II) acetyl acetonate/nonylphenol. The heat of reaction was dependent on the phenoxy content in the mixtures. The addition of phenoxy gave rise to a more exothermic reaction path.

Differences between the uncatalyzed and the catalyzed systems on the curing mechanism have also been observed. In fact, isothermal DSC tests revealed a single exothermic event for the uncatalyzed system, while two different exothermic events, occurring at different times, could be seen for the catalyzed system. In addition, the uncatalyzed systems exhibited an autocatalytic behavior, which was only seen at low phenoxy contents for the catalyzed systems. Also, the catalyzed systems reached final conversions higher than the uncatalyzed ones.

A simplified kinetic model was used to describe the reaction mechanism for the curing of cyanate ester resins in presence of phenoxy. For the uncatalyzed system, the kinetic constants for the initiation reactions increased at increasing phenoxy contents due to the catalytic effect of phenoxy, but the kinetic constant for the propagation reaction decreased because of the increase in viscosity at increasing phenoxy contents. For the catalyzed system, a reduction in the thermal activation energy was observed as compared to the uncatalyzed systems, but the catalytic effect of phenoxy was less important, probably because of interferences of phenoxy in the formation of the iminocarbonate-metal complex.

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