

Addition of a Reactive Diluent to a Catalyzed Epoxy-Anhydride System. I. Influence on the Cure Kinetics

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SYNOPSIS

The effect of a reactive diluent (RD) on the kinetics of the curing of an epoxy resin, based on diglycidyl ether of bisphenol A (DGEBA), with a carboxylic anhydride derived from methyl-tetrahydrophthalic anhydride (MTHPA) catalyzed by a tertiary amine has been studied. The reactive diluent was a low-viscosity aliphatic diglycidyl ether, and the compositions per 100 parts by weight (pbw) of DGEBA were 10, 30, and 50 pbw of RD with the stoichiometric quantity of MTHPA and 1 pbw of catalyst. The curing kinetics was monitored by differential scanning calorimetry (DSC), and the kinetic parameters were determined from the nonisothermal DSC curves by the method described by Málek. The kinetic analysis suggests that the two-parameter autocatalytic model is the more appropriate to describe the kinetics of the curing reaction of this epoxy-anhydride system. The kinetic parameters thus derived satisfactorily simulate both the nonisothermal DSC curves and the isothermal conversion-time plots. Increasing the RD content leads to a small increase in both the nonisothermal and the isothermal heats of curing and has a slight effect on the kinetic parameters E , $\ln A$, m , and n and, consequently, on the overall reactivity of the system. On the other hand, the increase of the RD content significantly affects the structure of the crosslinked epoxy. It is confirmed that the introduction of aliphatic chains in the structure of the epoxy increases the mobility of the segmental chains in the glass transition region. The consequence of this chemical modification is a decrease of the glass transition temperature, T_g . © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Reactive diluents (RDs) are used as additives in epoxy resin formulations in order to reduce the viscosity of the initial mixture and to aid the "processability" of the resin. With this additive, the properties of both the system during curing and the crosslinked epoxy can be modified.¹ The addition of an RD in an epoxy-anhydride system improves the casting and impregnation properties of the resin when it is used in electrical or electronic components. There are two main types of RD, the epoxy-based diluents and chemical compounds with a re-

active group other than an epoxide. The presence of epoxide groups allows the crosslinking reaction of the diluent at the same time that the epoxy resin is cured by the hardener. In the case of a monoepoxy diluent, the curing reaction leads to a decrease of the crosslink density of the resin, but in the case of "polyfunctionality," the behavior of the diluent is considered to be similar to that of the basic epoxy component and the crosslink density seems not to be affected.¹

The curing reaction of the catalyzed epoxy-anhydride system has been described by various authors,²⁻⁴ but there is less information when an RD is used in the formulation of the resin.^{5,6} The objective of this article was to study the effect of an RD of diepoxide type on the kinetics of the curing of di-

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glycidyl ether of bisphenol A (DGEBA) with methyl-tetrahydrophthalic anhydride (MTHPA), catalyzed by a tertiary amine. The curing reaction was monitored by differential scanning calorimetry (DSC), and the kinetic analysis of the nonisothermal curing was performed by Málek's method,⁷ which has been used to study other epoxy-anhydride systems.⁸⁻¹⁰ The kinetic parameters obtained by this method allow a satisfactory representation of the isothermal conversion curves at temperatures for which the vitrification of the system does not occur. The effect of the RD on the glass transition region of the fully cured epoxy resin has also been analyzed. In the second part of this work, the effect of the RD on the enthalpy relaxation process has been studied and compared with the same system without the RD.¹¹

EXPERIMENTAL

Materials and Cure Procedure

The system studied in this article was a commercial epoxy resin based on DGEBA, namely Araldite F (CIBA-GEIGY), with an epoxy equivalent weight of 188.3 g.eq⁻¹, cured by a carboxylic anhydride derived from MTHPA (CIBA-GEIGY HY905) with an accelerator that was a tertiary amine (CIBA-GEIGY DY061). The reactive diluent was a low-viscosity aliphatic diglycidyl ether (Araldite DY 026) with an epoxy equivalent weight of 113.8 g eq⁻¹. The epoxy resin, the hardener, and the RD were mixed at the compositions given in Table I and stirred at room temperature for 20 min. Then, the required quantity of accelerator was added, mixed vigorously for about 20 min, and degassed in a vacuum oven at room temperature for about 15 min. Samples were encapsulated in aluminum pans in order to be analyzed in the calorimeter.

The calorimeter was a Mettler Thermoanalyser TA4000 equipped with a low-temperature-range DSC 30 differential scanning calorimetry module. Nonisothermal scans were performed at different heating rates (2.5, 5, 10, and 20 K min⁻¹) from -80 to 300°C under nitrogen atmosphere in order to cure the resin and to provide the data for kinetic analysis. A second DSC scan was made to measure the glass transition temperature (T_g) of the crosslinked epoxy by use of the following procedure. After the nonisothermal scan, the sample was freely cooled to 130°C and left 5 min at this temperature; it was then cooled at 20 K min⁻¹ to a temperature T_1 well below the glass transition (e.g., 10°C in FRD10; refer to Table I for T_g values) and immediately reheated

at 10 K min⁻¹ to a temperature about 30°C above the glass transition (e.g., 130°C in FRD10).

The kinetics of the isothermal curing reactions were also studied. In these isothermal experiments, the sample was placed in the calorimeter at room temperature, and then the temperature was raised at a heating rate of about 180 K min⁻¹ to the isothermal curing temperature, which was between 70 and 140°C. The curing time was about 3-5 h, depending on the curing temperature, in order to develop all of the exothermic heat of the curing reaction. The time required for initial temperature equilibration was between 1.25 and 1.5 min.

As in the nonisothermal experiments, the sample was submitted to a second scan to measure the glass transition of the crosslinked epoxy resin by use of the following procedure. After the isothermal period, the sample was immediately cooled at 20 K min⁻¹ to a temperature T_1 well below the glass transition and immediately reheated at 10 K min⁻¹ from T_1 to 250-300°C in order to measure the T_g and the residual heat of curing (only for the partially cured samples). The T_g determined in the second DSC scan, following either the isothermal or nonisothermal experiments, can be defined in various ways: the extrapolated onset value (T_{g0}), the midpoint value in $\Delta C_p(T_g)$, and the extrapolated end value (T_{ge}).

KINETIC ANALYSIS

The kinetic analysis starts with the basic rate equation for the degree of conversion α :

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Ae^{-x}f(\alpha) \quad (1)$$

where A is the preexponential factor, $x = E/RT$, E being the activation energy, and $f(\alpha)$ is a function of the conversion degree which can be described by some empirical kinetic models.^{12,13} The models most frequently applied to curing reactions are the *reaction order* model,

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

and the *two-parameter autocatalytic model* (*Sesták-Berggren equation*), which for a reaction with zero initial rate, is:

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (3)$$

Table I Composition of the Epoxy Systems in Parts by Weight and the Corresponding T_g

Nomenclature	DGEBA : MTHPA : RD : Accl ^a	T_g (°C)
FRD0	100 : 100 : 0 : 1	101.3
FRD10	100 : 112 : 10 : 1	96.6
FRD30	100 : 136 : 30 : 1	81.5
FRD50	100 : 160 : 50 : 1	74.2

^a Accl, accelerator agent.

According to the basic assumption that the heat flow, ϕ , generated in the curing reaction is proportional to the rate of conversion, the following equation is obtained:

$$\phi = \frac{d\alpha}{dt} \Delta H = A e^{-x} \Delta H f(\alpha) \quad (4)$$

where ΔH is the total heat of curing.

For nonisothermal DSC data, the change of the degree of conversion with temperature is

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \frac{d\alpha}{dt} = \frac{A}{\beta} e^{-x} f(\alpha) \quad (5)$$

where $\beta = dT/dt$ is the constant heating rate. Separating variables in eq. (5), integrating, and substituting eq. (4), the following integral kinetic equation is obtained:

$$\Delta H g(\alpha) f(\alpha) = \frac{E}{\beta R} \phi \left[\frac{\pi(x)}{x} \right] \quad (6)$$

where $\pi(x)$ is an approximation to the temperature integral which can be calculated by suitable expressions,^{7,14} and $g(\alpha)$ is the integral form of the kinetic model

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (7)$$

According to Málek's method,⁷ it is possible to calculate all of the kinetic parameters from a single nonisothermal DSC curve if the activation energy is previously known. The activation energy may be determined by the Kissinger method¹⁵ from the peak temperatures of nonisothermal DSC curves obtained for different heating rates. In addition, the method of Málek allows the selection of the kinetic model which best describes the DSC data by the definition of the following functions:

$$y(\alpha) = \phi e^x = \Delta H A f(\alpha) \quad (8)$$

$$z(\alpha) = \pi(x) \phi \frac{T}{\beta} = \Delta H g(\alpha) f(\alpha) \quad (9)$$

As described in Reference 7 and discussed in more detail below, the $y(\alpha)$ and $z(\alpha)$ functions permit the selection of the appropriate kinetic model and the evaluation of the kinetic parameters for the selected model.

RESULTS AND DISCUSSION

Nonisothermal DSC Curves

Figure 1 shows the DSC curves for the nonisothermal curing of the epoxy with different contents of RD at a heating rate of 10 K min⁻¹. The shapes of all of these curves are very similar, and the peak temperature is practically the same in all cases. These curves also show the glass transition of the unreacted system, the midpoint value of which decreases from -38°C in FRD0 to -57°C in FRD50, in addition to the exothermic peak between 100 and 200°C. It is observed that the heat of curing

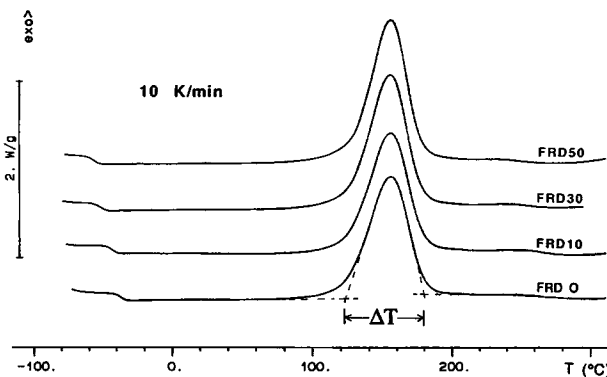


Figure 1 DSC curves for the nonisothermal curing of the epoxy-anhydride system with different contents of RD, at a heating rate of 10 K min⁻¹.

(ΔH_{NISO}) tends to increase slightly with the RD content, as shown in Figure 2(a), and that the width of the peak (ΔT) tends to decrease with increasing RD content [Fig. 2(b)].

Scans at different heating rates for the system FRD50 are shown in Figure 3 (full lines). Figure 4(a) shows the calculated values of the heat of curing (ΔH_{NISO}) which tend to increase when the heating rate decreases. A similar effect has been observed in other thermosetting systems such as polyesters¹⁶ and epoxy resins.^{17,18} At the same time, the width of the peak tends to increase with the heating rate [Fig. 4(b)].

The DSC scans at different heating rates allow us to determine the apparent activation energy of the overall process, E , by the Kissinger method, or the apparent activation energy at a constant conversion degree, E_α , by the isoconversional method,¹² which follows from the logarithmic form of eq. (4).

$$\ln \phi = \ln[\Delta H A f(\alpha)] - \frac{E_\alpha}{RT} \quad (10)$$

Figure 5(a) shows the values of E obtained by the Kissinger method as a function of the RD content; the values of E_α as a function of the degree of conversion are shown in Figure 5(b). The average values of E_α for each epoxy system are also plotted in Figure 5(a) as a function of RD content. It is observed that the activation energy E and the average of E_α do not change significantly with the RD content, in agreement with the results obtained by Patel and Patel.⁶ Additionally, Figure 5(b) shows that E_α increases gradually with the degree of conversion, as was observed in another epoxy-anhydride system.⁹

In order to perform the kinetic analysis of the nonisothermal DSC curves, following Málek's method, the DSC data were converted to $y(\alpha)$ and $z(\alpha)$ functions, following eq. (8) and eq. (9), and are thus shown in Figures 6 and 7, respectively. As described in References 7 and 8, the shape of the $y(\alpha)$ function allows the selection of the kinetic model. When the $y(\alpha)$ function decreases monotonically from a maximum at $\alpha_M = 0$ (in practice at $\alpha_M < 0.05$), the phenomenological model corresponds to the reaction order. On the other hand, when a maximum is located in the interval $0.05 < \alpha_M < \alpha_p$, α_p being the conversion degree at the peak of the DSC curve, the curing reaction may be described by the autocatalytic model. The shape of $y(\alpha)$, shown in Figure 6, together with the data of Table II, which shows the α_p values and that the maximum of the $y(\alpha)$ function lies at α_M values between 0.28 and 0.33 depending on the RD content, indicates that the two-parameter autocatalytic model is better than the reaction order model for describing the curing reaction. This result is in agreement with previous work on a catalyzed epoxy-anhydride system.⁸⁻¹⁰

Additionally, the $z(\alpha)$ function has a maximum at α_p^∞ , which is the (theoretical) value of α at the peak of a hypothetical DSC curve for which the reduced activation energy x_p tends to infinity (refer to Appendix of Ref. 7 for more details). For the two-parameter autocatalytic model, this parameter α_p^∞ allows us to determine the other kinetic parameters, namely, the preexponential factor and the exponents m and n of eq. (3), by the methods described in Reference 7. The values of α_p^∞ are found to be practically the same for all of the epoxy systems (0.59–0.60) (refer to Table II).

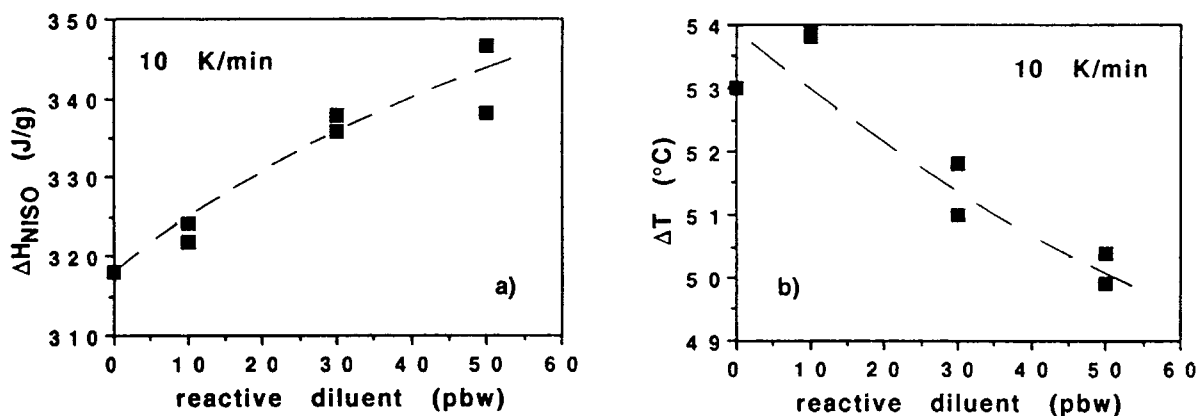


Figure 2 Nonisothermal heat of curing (ΔH_{NISO}) at 10 K min^{-1} (a) and width of the peak (ΔT) (b) for epoxy systems with different contents of RD. Lines are drawn as visual guides.

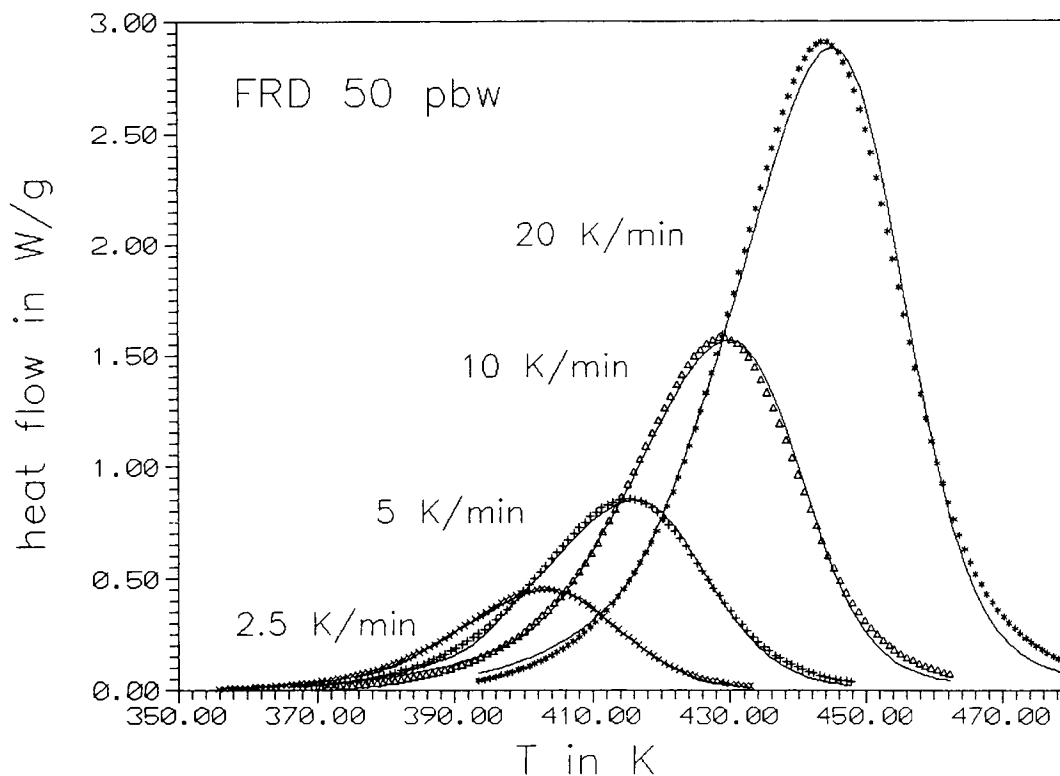


Figure 3 Experimental DSC curves (full lines) and calculated DSC curves (symbols) for the epoxy-anhydride system with 50 parts by weight (FRD50) of RD at different heating rates.

The values of m and n obtained in this way are shown as a function of RD content in Figure 8(a). Both m and n can be seen to increase slightly with the RD content [Fig. 8(a)]. The dependence of $\ln A$ on RD content [Fig. 8(b)] is similar to that observed in the apparent activation energy E . This effect is a consequence of the correlation between these two parameters, as shown in Figure 9, where the linear relationship between $\ln A$ and E

$$\ln A = aE + b \quad (10)$$

gives the values $a = 0.273 \text{ (mol k J}^{-1}\text{)}$ and $b = -3.805$ with a correlation coefficient = 0.98, where a and b are constants for this epoxy system. Such a relationship implies a so-called "compensation effect," which has been observed in other series of curing reactions, such as a catalyzed epoxy-anhydride system with different degrees of crosslinking⁹ or in the nonisothermal degradation of polymers, as reported by Budrugaec and Segal.¹⁹

The kinetic parameters thus derived satisfactorily simulate the experimental nonisothermal DSC curves, as can be seen in Figure 3 (symbols). This agreement confirms that the autocatalytic model is

appropriate to describe the kinetics of the curing reaction of this epoxy system.

The results obtained for m , n , and $\ln A$ also indicate that the introduction of aliphatic segments into the main chain of the epoxy based on DGEBA does not cause a significant change in the kinetics of the overall curing process. Only an increase of about 10% in the exothermic heat of curing is observed when the RD content increases up to 50 parts by weight.

Isothermal DSC Curves

The results of the isothermal experiments on FRD10 samples are shown in Figure 10 for four different curing temperatures, T_c . The values of the isothermal heat of curing (ΔH_{ISO}) and of the time at which the maximum occurs are shown in Figure 11. At a fixed curing temperature, it is observed that the heat of curing increases slightly with the RD content [Fig. 11(a)]. This trend is similar to that observed in nonisothermal experiments [Fig. 4(a)] and may be attributed to the presence of the aliphatic diepoxide of the RD in the curing reaction. However, there are some characteristic aspects of the isothermal

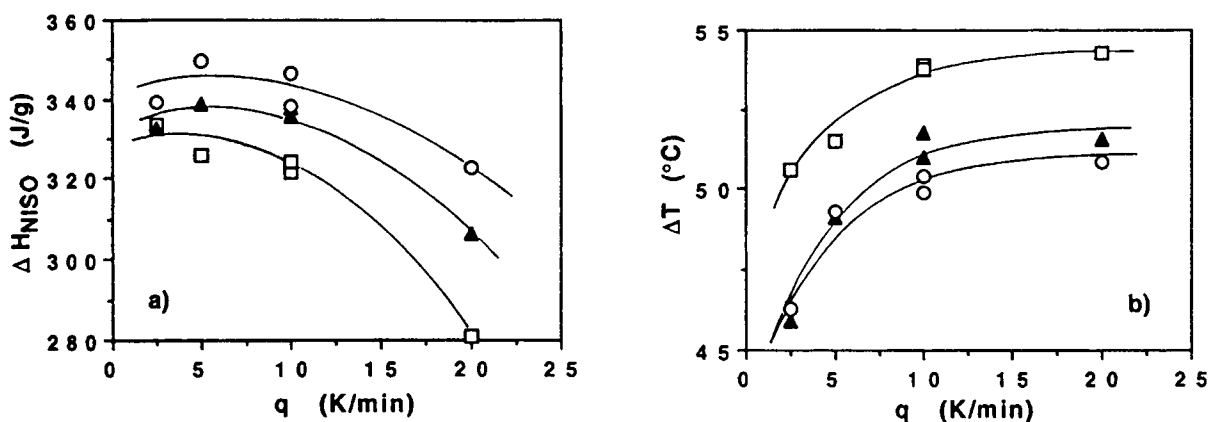


Figure 4 Dependence of the nonisothermal heat of curing (ΔH_{NISO}) (a) and width of the peak (ΔT) (b) on the heating rate for the epoxy systems: (□) FRD10, (▲) FRD30, and (○) FRD50. Lines are drawn as visual guides.

heats of curing to be highlighted. At the highest curing temperatures of 130 and 140°C, lower values of ΔH_{ISO} are observed than at 120°C. According to other authors,^{12,13,17} at these higher curing temperatures, the reaction takes place very rapidly and the heat of curing evolved during the time required for temperature equilibration is not fully recorded in the DSC curve; the result is a decrease in the value of ΔH_{ISO} . The maximum values of ΔH_{ISO} are observed in the range of 110–120°C, which is the optimal range of curing temperatures. In this range of temperatures, the values of ΔH_{ISO} are very close to those measured nonisothermally at 5 or 10 K min⁻¹ [compare the values of Figs. 11(a) and 4(a)].

Considering lower curing temperatures in the system FRD10, it is observed that the value of ΔH_{ISO} at 100°C is less than that at 110°C. This decrease could be a consequence of the vitrification of the system, which would result in a partially cured epoxy. The increase of crosslinks in the resin reduces the mobility of the reacting groups, and the curing reaction becomes controlled by diffusion.^{20–22} As a consequence of the freezing of the chemical reaction, the conversion degree tends to a practically constant limiting value, α_∞ , which is lower than unity: the system becomes partially cured after a long time of curing. On the other hand, the T_g of the system increases during the curing and becomes higher than the curing temperature. In these conditions, the system is in the glassy state, vitrifies, and is subject to the process of structural relaxation, which is easily identified in the DSC scan by a characteristic endothermic peak.^{22–25}

Bearing in mind these comments, the lower value of ΔH_{ISO} at 100°C in FRD10 cannot be clearly attributed to the vitrification process, because no re-

sidual heat of curing is observed in the second DSC scan after the isothermal curing [see Fig. 12(a)]. Additionally, the T_g of the resin cured at 100°C is practically the same as that observed in samples cured at 110 and 120°C [see Fig. 12(a)], showing that the degree of crosslinking is the same in all of these samples. Instead, it is possible that the decrease in ΔH_{ISO} on curing at 100°C may be an experimental artefact caused by a partial loss of the heat of curing due to the weak heat flow signal.

A further decrease of ΔH_{ISO} is observed in FRD10 when it is cured at 90°C. In this case, the decrease may indeed be a consequence of the vitrification of the resin during the isothermal curing. The curing temperature here is in the lower range of the glass transition region ($T_{g0} = 89.4^\circ\text{C}$) and clearly lower than the midpoint T_g (96.6°C), as shown in Figure 13. The sample is only partially cured, and a residual heat of curing is measured [see Fig. 12(a)]. In addition, an endothermic peak appears in the second DSC scan [Fig. 12(a)], indicative of a structural relaxation process during the isothermal curing. However, at this curing temperature, the sum of the isothermal and residual heats of curing, 283 and about 10 J g⁻¹ respectively, is lower than the global heat of the curing of this system (324 J g⁻¹). This difference indicates that a loss of heat of curing as a consequence of the low heat flow (about 0.04 W g⁻¹ at its maximum value) has again probably taken place.

In system FRD30, a decrease of the isothermal heat of curing at $T_c < 110^\circ\text{C}$ is also observed. The lower values of ΔH_{ISO} observed at $T_c = 100$ and 90°C could be a consequence of a loss of heat during the curing of the system because there is a very low residual heat of curing, as Figure 12(b) shows. The T_g

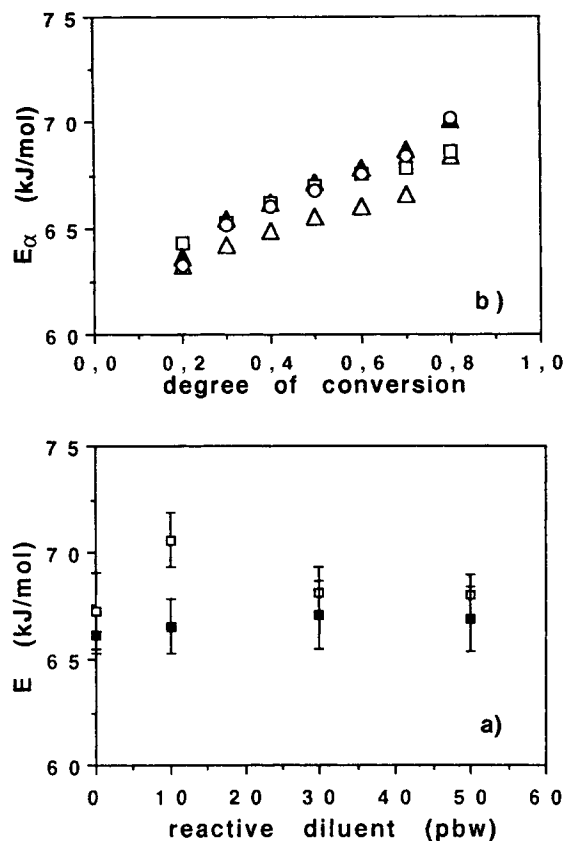


Figure 5 (a) The activation energy calculated by the Kissinger method (\square) and isoconversional average values (\blacksquare) for different contents of RD. (b) Dependence of the activation energy determined by the isoconversional method on the conversion degree for different contents of RD (Δ) FRD0, (\square) FRD10, (\blacktriangle) FRD30, and (\circ) FRD50.

values of these samples are about 79–80°C, which corresponds to the maximum T_g observed in FRD30. On the other hand, this T_g is lower than the curing temperature, which prevents the vitrification of the resin. However, at $T_c = 80^\circ\text{C}$, it is possible to observe some effects of vitrification: a) the curing temperature lies in the glass transition region, which ranges between 75.4 and 87.5°C (see Fig. 13); b) there is a residual heat of about 21 J g⁻¹; and c) a small relaxation peak is observed in the second DSC scan obtained after 8 h at 80°C, as shown in Figure 12(b). However, as for FRD10, an effect of loss of heat during the curing cannot be disregarded because the sum of the isothermal and residual heats of curing (249 and 21 J g⁻¹, respectively) is again lower than the global heat of curing (337 J g⁻¹).

The results for FRD50 show a trend similar to that for FRD30. Bearing in mind that vitrification appears when T_c is lower than the T_g , we can expect that a small effect of vitrification will occur at T_c

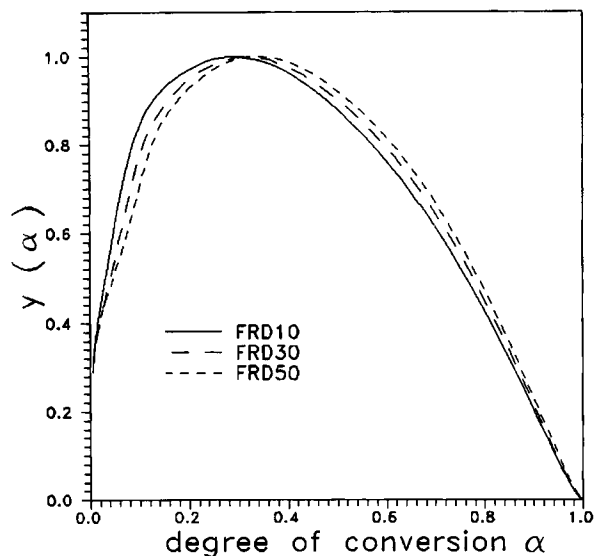


Figure 6 The $y(\alpha)$ function for different contents of RD.

= 70°C. In spite of the fact that there is a residual heat of curing, no endothermic peak is observed at the glass transition [Fig. 12(c)] and the partial cure of the resin could be a consequence of insufficient curing time. One way to investigate whether or not this is a valid interpretation of these results would be to study the curing at the same temperatures using the so-called method of residual heat of curing,^{12,22} obtaining point by point the conversion degree at different curing times; this study is currently in progress.

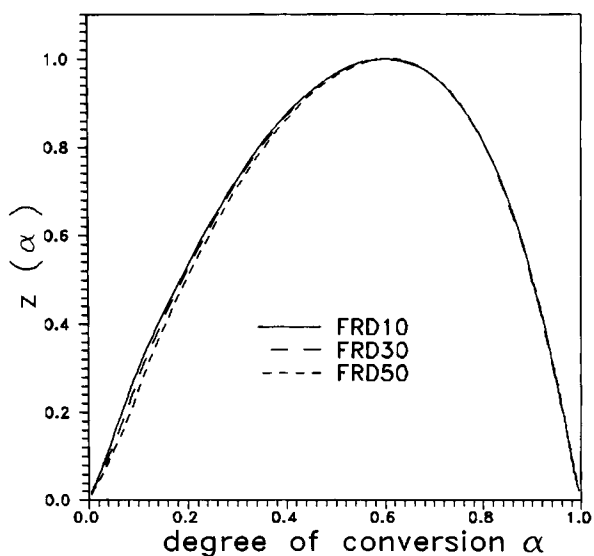


Figure 7 The $z(\alpha)$ function for different contents of RD.

Table II Average Values of α at the Maximum of the $y(\alpha)$ Function (α_M) and $z(\alpha)$ Function (α_p^z) for the Epoxies with Different RD Content

Epoxy	α_p^a	α_M	α_p^z
FRD 0	0.57	0.28	0.59
FRD 10	0.58	0.28	0.60
FRD 30	0.58	0.31	0.59
FRD 50	0.59	0.33	0.60

^a α_p is the conversion degree corresponding to the DSC peak.

The time t_p where the maximum of the isothermal DSC curves occurs is shown in Figure 11(b) as a function of the curing temperature. For any particular RD content, this time t_p decreases as the curing temperature increases, as has been observed in other epoxy resins.^{12,13,17} At a fixed T_c , the value of t_p increases slightly with the RD content.

The isothermal DSC curves allow us to determine the degree of conversion, α , as a function of the curing time according to the relationship

$$\alpha = \frac{\Delta H_t}{\Delta H_{total}} \quad (11)$$

where ΔH_t is the heat generated up to time t and ΔH_{total} is the total heat of curing, being the maximum value obtained in the nonisothermal curing: 324 (FRD10), 337 (FRD30), and 346 J g⁻¹ (FRD50). The reason for using the nonisothermal values for ΔH_{total} is that during isothermal curing at lower temperatures T_c , the occurrence of vitrification would prevent the reaction from ever proceeding to a full cure. The nonisothermal value of ΔH_{total} therefore provides a unique reference for this evaluation.²⁶ For those temperatures T_c for which a full cure is achieved isothermally, the values of ΔH_{ISO} are equal to ΔH_{total} within experimental error. The isothermal experiments are represented in the conversion-time form for FRD10 samples in Figure 14 (symbols).

The kinetic parameters obtained from the nonisothermal DSC curves allow the simulation of the isothermal experiments (full lines in Fig. 14). The results in the conversion-time plots of Figure 14 show that these kinetic parameters satisfactorily simulate the isothermal curing experiments of the FRD10 system in the range of conversion degree between 0.1 and 0.9 and in a temperature range between 100 and 120°C. A deviation can be seen at 90°C when the conversion is higher than 0.5, which may be attributed to the vitrification process. Additionally, the kinetic parameters satisfactorily also

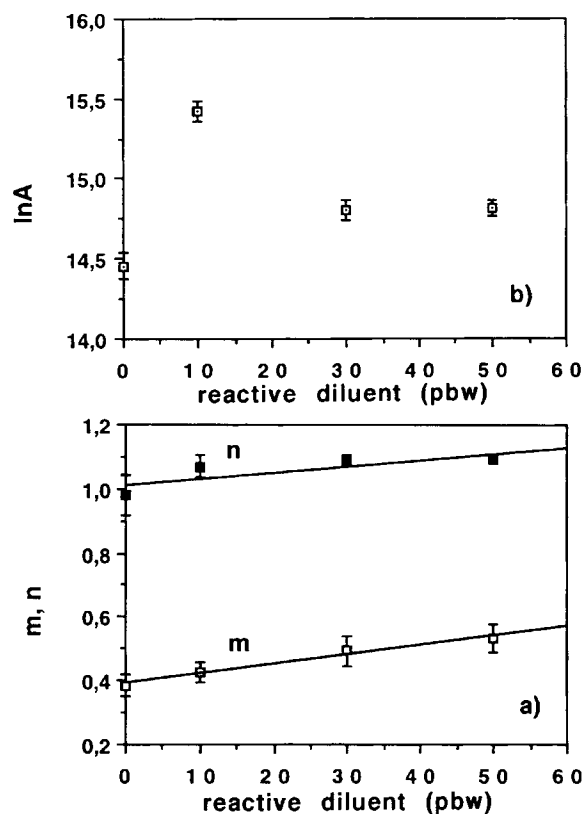


Figure 8 The variation of the kinetic parameters m and n (a) and preexponential factor (b) with the RD content.

simulate the experimental isotherms between 100 and 120°C for FRD30 and FRD50 in a range of degree of conversion between 0.1 and 0.9. A deviation has been observed in those systems where the ΔH_{ISO} is lower than the global value as the result of a loss of heat during the curing.

The isothermal conversion-time plots allow us also to calculate the apparent activation energy for

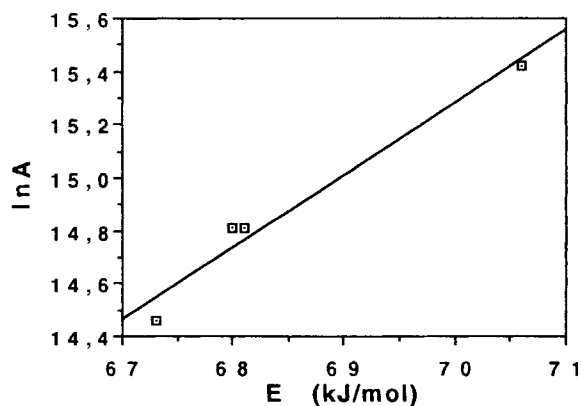


Figure 9 Correlation between the preexponential factor and the activation energy.

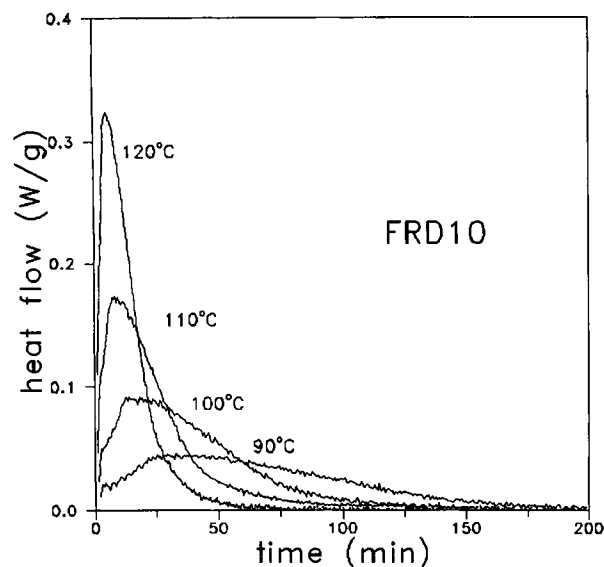


Figure 10 Isothermal DSC curves for the epoxy FRD10 at different curing temperatures.

different degrees of conversion. Rearranging and integrating eq. (1), it follows that

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T) t \quad (12)$$

and for a given curing temperature

$$F(\alpha) = \ln g(\alpha) = \ln k(T) + \ln t \quad (13)$$

where $F(\alpha)$ is a function only of the conversion degree. Assuming an Arrhenius equation for the rate constant $k(T)$, as proposed above in the Kinetic Analysis section, and rearranging, one obtains

$$\ln t = F(\alpha) - \ln A + (E/RT) \quad (14)$$

There is therefore a linear dependence of $\ln t$ on $1/T$ for a given value of $F(\alpha)$, i.e., for the same conversion degree α , and the activation energy can be found from the slope of the $\ln t$ versus $1/T$ plots. The values of the apparent activation energy, E_α , calculated from the isothermal $\alpha - t$ plots in a temperature range between 90 and 120°C, at different conversions for the systems with different RD content, are shown in Figure 15. It can be seen that these values of E_α are slightly higher than those obtained from the nonisothermal DSC scans by the isoconversional method and shown in Figure 5(b). Nevertheless, both values show a similar trend of activation energy increasing gradually with the degree of conversion.

Class Transition Temperature

An increase of the RD content results in a decrease of the temperature interval of the glass transition. The T_g , measured as the midpoint of ΔC_p in the second DSC scan after the nonisothermal curing, shows a linear dependence on RD content (Fig. 13). The decrease of T_g with the RD content may be attributed to the increase of the mobility of the chain segments introduced by the aliphatic epoxy chains. As will be shown in another article,¹¹ an epoxy-anhydride system such as the system FRD50 shows a higher relaxation rate than the system without RD.

Similar values of midpoint T_g were obtained in samples cured isothermally, as shown in Figure 16. In the systems with RD, the glass transition measured in samples cured isothermally is practically the same as that for those cured nonisothermally; it is only the system without RD which shows higher values of T_g for epoxies cured isothermally. This difference is a consequence of the effect of the thermal history on the network properties^{27,28} and agrees with other results ob-

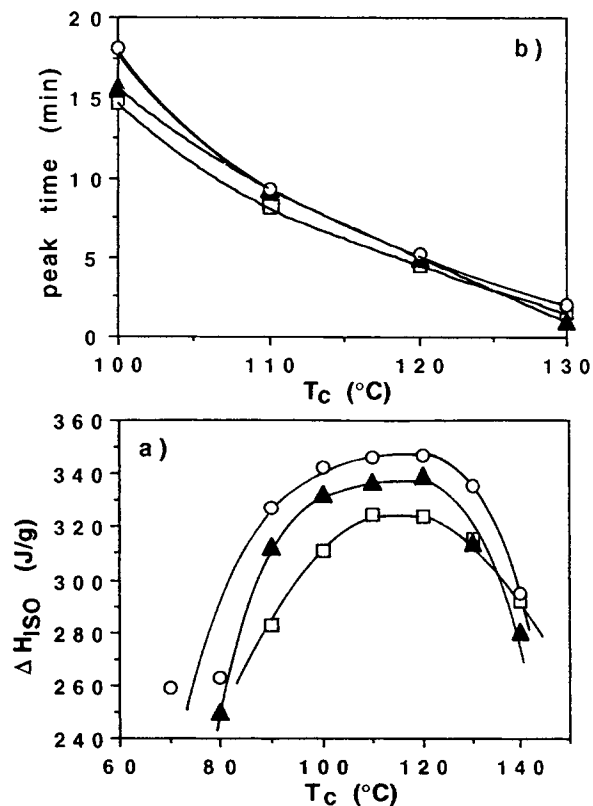


Figure 11 (a) Isothermal heat of curing and (b) time of the maximum of the peak at different curing temperatures for the epoxies (□) FRD10, (▲) FRD30, and (○) FRD50. Lines are drawn as visual guides.

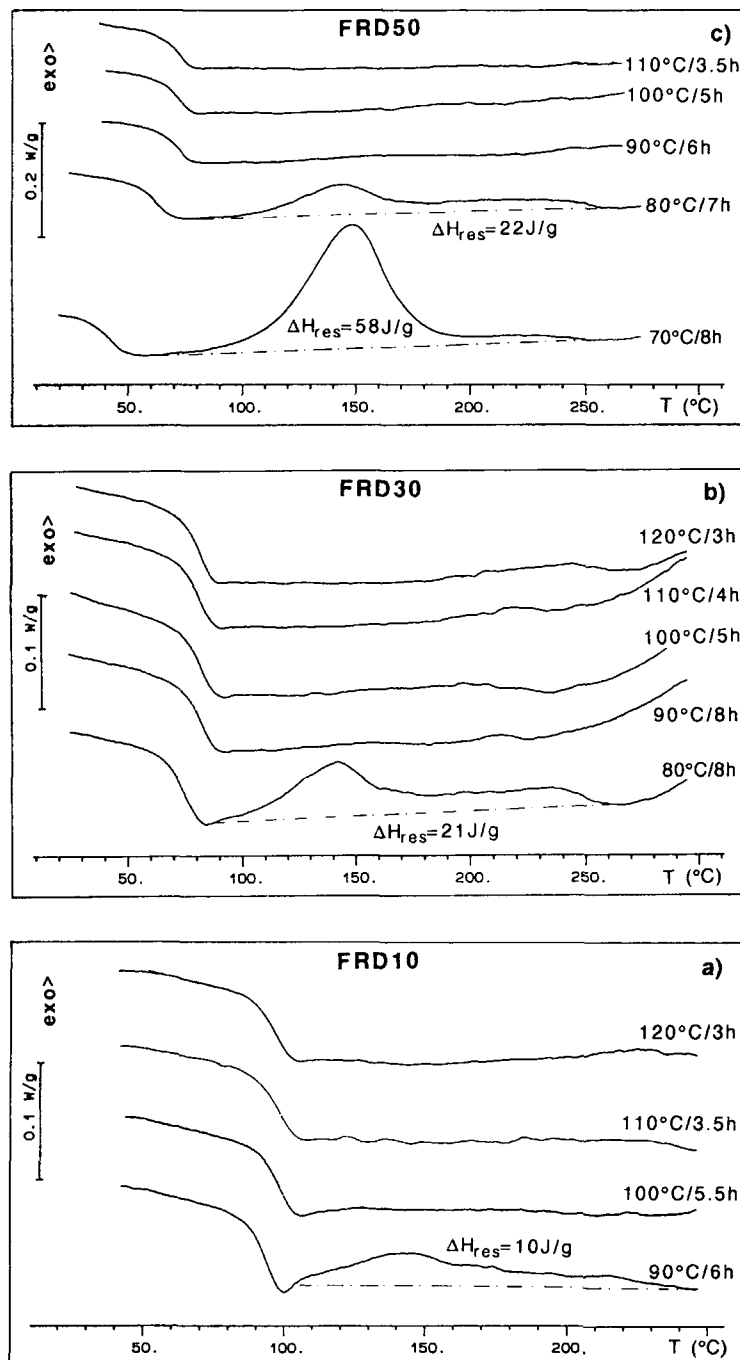


Figure 12 Second DSC scan obtained after the isothermal curing of the epoxy, cooling to 10°C at 20 K min⁻¹, and immediately reheating at 10 K min⁻¹, for different epoxy systems: FRD10 (a); FRD30 (b); and FRD50 (c). The temperature and time of the isothermal curing are shown against each curve. Residual heat of curing (ΔH_{res}) is also indicated. Refer to Figure 16 for the values of midpoint T_g .

tained on a similar epoxy resin cured with MTHPA with accelerator.²⁵

It is also found that the T_g values of these epoxies depend on the curing temperature: a slight reduction

in T_g is observed for the highest T_c in most systems (e.g., 140°C in FRD0 and FRD10 or 120°C in FRD50), in addition to that for lower values of T_c . A similar effect was reported by Meyer et al.²⁸ As

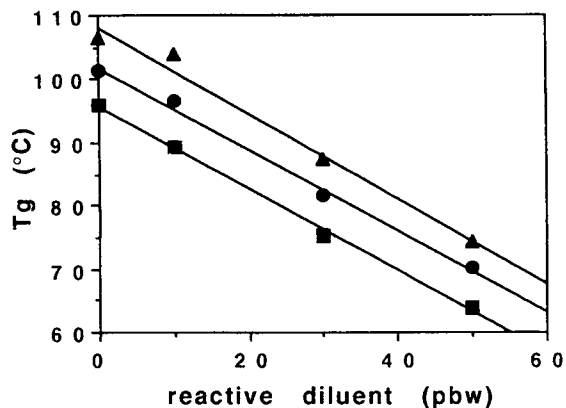


Figure 13 T_g measured in the second DSC scan after the nonisothermal curing for different RD contents: extrapolated onset (\blacksquare) $T_g(T_{g0})$, (\bullet) midpoint T_g , and (\blacktriangle) extrapolated end $T_g(T_{ge})$.

pointed out above, when the T_c is lower than the T_g of the system vitrification occurs, and hence, the system remains partially cured and the T_g is lower. This effect can be observed in FRD10 at 90°C, in FRD30 at 80°C, and in FRD50 at 70°C. Additionally, a decrease of T_g may also occur when the system remains partially cured as the result of the low curing temperature, as in FRD50 at 80°C. In these cases, the T_g of the system depends on the conversion degree of the resin.^{22,25,29}

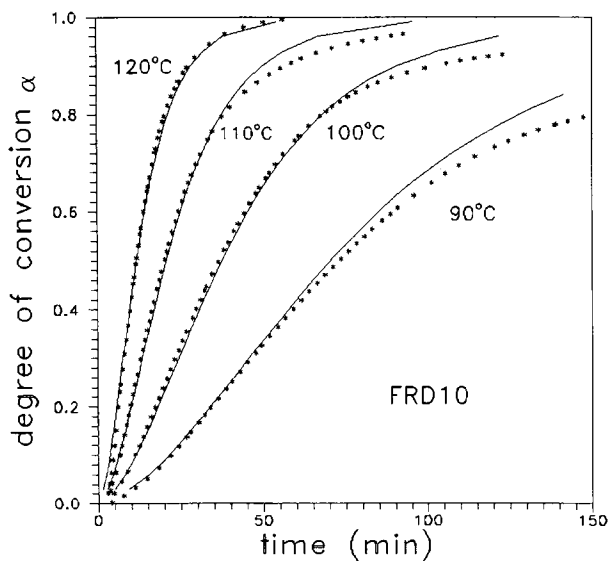


Figure 14 Experimental (symbols) and calculated (full lines) conversion-time curves for the epoxy FRD10 at different curing temperatures.

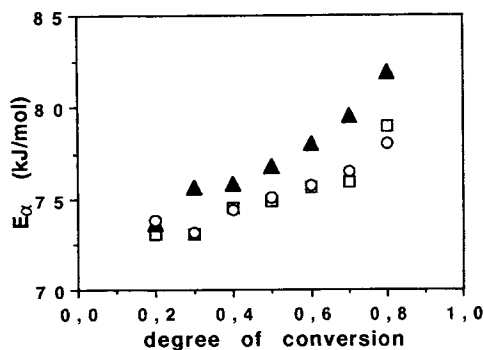


Figure 15 Dependence of the apparent activation energy on the conversion degree calculated by the isoconversional method applied to the isothermal conversion-time data, for different contents of RD: (\square) FRD10, (\blacktriangle) FRD30, and (\circ) FRD50.

CONCLUSIONS

The effect of RD on the cure kinetics of an epoxy resin cured by a carboxylic anhydride with catalyst has been studied. Kinetic analysis of the nonisothermal DSC scans performed by Málek's method suggests that the autocatalytic model is the more appropriate to describe the kinetics of the curing reaction of this epoxy-anhydride system. The kinetic

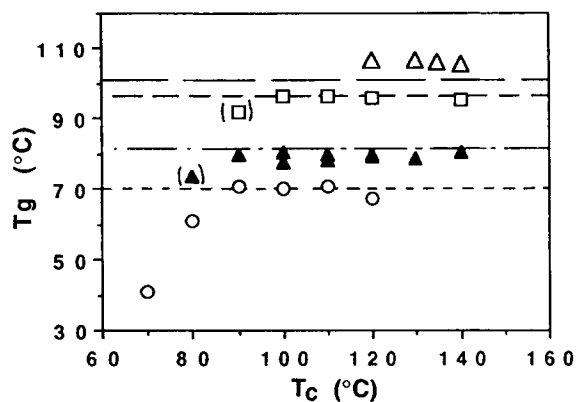


Figure 16 Midpoint T_g for different epoxy resins previously isothermally cured at the indicated temperatures: (Δ) FRD10, (\blacktriangle) FRD30, and (\circ) FRD50. The dashed lines indicate the T_g values obtained in the second DSC scan after the nonisothermal curing: (— — —) 101.3°C for FRD0, (— — — —) 96.6°C for FRD10, (— · — · —) 81.5°C for FRD30, and (— — —) 70.2°C for FRD50. The symbols in brackets correspond to the value of the midpoint T_g when there is an endothermic peak due to the structural relaxation of the system. All of the DSC curves were scanned at 10 K min^{-1} .

parameters thus derived satisfactorily simulate both the nonisothermal DSC curves and the isothermal conversion-time plots.

Increasing the RD content leads to an increase in both the nonisothermal and the isothermal heats of curing and has only a small effect on the kinetic parameters E , $\ln A$, m , and n and consequently on the overall reactivity of the system. The isothermal experiments show an effect of vitrification when the curing temperature is lower than the maximum T_g of the resin, giving a lower isothermal heat of curing, ΔH_{ISO} . Nevertheless, a decrease in ΔH_{ISO} has also been observed in systems cured at temperatures higher than the T_g ; a possible explanation for this could lie in the low heat flow signal of the DSC scan.

On the other hand, an increase of the RD content significantly affects the final structure of the epoxy. It is confirmed that the introduction of aliphatic chains in the structure of the epoxy affects the mobility of the segmental chains in the glass transition region. The consequence of this chemical modification is a decrease of the T_g .

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