Mechanism and Kinetics of Epoxy−Amine Cure Studied by Differential Scanning Calorimetry

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Received August 8, 1995; Revised Manuscript Received October 11, 1995⊗

ABSTRACT: The isoconversional kinetic analysis has been applied to nonisothermal DSC data on the cure of an epoxynovolac resin. The process reveals a dependence of the activation energy (E_α) on conversion (α). The shape of the dependence has been interpreted in the terms of the reaction mechanisms. It has been found that the model $d\alpha/dt = (k_1 + \alpha^m k_2)(1 - \alpha)^n$ used for the kinetically controlled cure gives rise to the dependence of E_α on α similar to the experimentally found one. To completely describe the diffusion-controlled cure, the effect of both T and α on the change in diffusivity has been taken into account. The equation for the specific rate constant of diffusion, $k_D(T,\alpha) = D_o \exp(-E_D/RT + K\alpha)$, has been induced. Its use allows us to obtain a model dependence of E_α on α closely matching the experimental one. A technique of predicting isothermal cure from the sole dependence of E_α on α has been considered.

Introduction

Differential scanning calorimetry (DSC) which measures the heat flow from the reacting system is a very convenient tool to study the overall epoxy−amine cure.[1−16] It is especially useful when a detailed mechanism has been established by other methods such as FTIR,[2,4,10,16−21] HPLC,[4,16−18,22,23] and NMR.[5,6,16,18] In such a case, the kinetic analysis of DSC data helps to determine those steps which most profoundly contribute to the overall process. This allows for the reduction of intricate mechanisms to an effective kinetic scheme. Another practical problem which requires the knowledge of the overall kinetics is predicting the progress of cure at different temperatures. Both problems can be solved if an adequate method of kinetic analysis is used.

Obviously, DSC data do not allow the measured heat flow to be separated into contributions from single reactions. This, in no way, means that the actual complexity of curing can be ignored in kinetic calculations. A method of kinetic analysis should allow for a possible change of the rate-limiting step (and associated Arrhenius parameters) of the process. Nevertheless, the kinetics of thermal transformations are usually described[1] by eq 1 of a single-step reaction:

$$d\alpha/dt = k(T)\, f(\alpha) \qquad (1)$$

where $f(\alpha)$ is the reaction model, α is the extent of conversion, $k(T)$ is the Arrhenius rate constant, T is the temperature, and t is the time. For nonisothermal conditions, when the temperature varies with time with a constant heating rate, $\beta = dT/dt$, eq 1 is represented as follows:

$$d\alpha/dT = (A/\beta) \exp(-E/RT)\, f(\alpha) \qquad (2)$$

where A is the pre-exponential factor, E is the activation energy, and R is the gas constant. The straightforward application of eqs 1 and 2 yields a single kinetic triplet (A, E, and the reaction model) for the overall process. This type of analysis does not allow for a possible change in the rate-limiting step.

Isoconversional kinetic analysis offers a viable alternative in this situation. The basic idea of this type of analysis is that the reaction rate at a constant conversion depends only on the temperature. In other words,

$$d \ln(d\alpha/dt)_\alpha/dT^{-1} = -E_\alpha/R \qquad (3)$$

where E_α is the effective activation energy at a given conversion. For a single-step process, E_α is independent of α and may have the meaning of the intrinsic activation energy. Multistep processes reveal the dependence of E_α on α, the analysis of which helps not only to disclose the complexity of a process but also to identify its kinetic scheme.[24]

In this study the isoconversional analysis has been applied to nonisothermal DSC data on the epoxy−amine cure. An emphasis is made on the interpretation of the dependence of E_α on α in the terms of the reaction mechanisms as well as on its use to predict the cure kinetics under isothermal conditions. The experimental dependence of E_α on α has been interpreted in the frameworks of models generally accepted to describe the cure. These models have been used solely to derive corresponding model dependencies of E_α on α. The pure numerical problem of fitting these models to the experimental data of $d\alpha/dt$ has been deliberately left aside because of two reasons. Firstly, it has been solved many times.[3,7−13] Secondly, as it follows from the present results, neither explicit model nor its parameters are necessary to predict the cure progress at a given temperature. What we really need to determine is the dependence of E_α on α alone.

Experimental Section

The epoxy resin was an epoxynovolac containing 1,4-butanediol diglycidic ether (Ciba-Geigy; araldite LY 5052) with an epoxy equivalent of 146 g/equiv and viscosity of 900−1600 mPa at 25 °C. A hardener of isophorone diamine (mixture of two stereoisomer forms of 3-(aminomethyl)-3,5,5-trimethylcyclohexylamine) with diaminodimethyldicyclohexylmethane (Ciba-Geigy; araldite HY 5052) was used to cure the resin. The

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⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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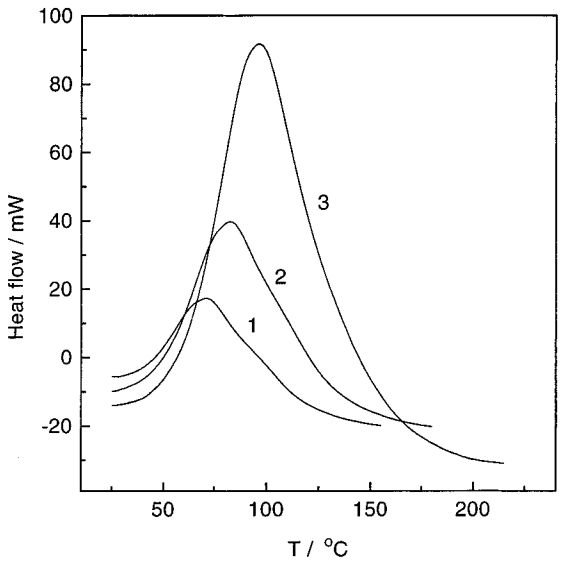


Figure 1. DSC curves for the cure at different heating rates: 1, 1.0; 2, 2.0; and 3, 5.0 °C min^{-1}.

amine equivalent of the hardener was 102 g/equiv, and viscosity was 30−70 mPa at 25 °C. Both components were commercial products and used as received. The resin and hardener were mixed at a weight ratio of 10:3.8. To slow down the reaction in the early stage of mixing, the mixture was stirred at 2 °C in an argon atmosphere and then hermetically sealed in aluminum DSC pans containing argon.

A Setaram DSC-111 instrument was used to measure the heat flow under both isothermal and nonisothermal conditions. An online PC control of DSC measurements was made possible by using an interface module and relevant software developed in our laboratory. The sampling rate was about 0.2−0.3 points/s (12−20 points/1 °C in nonisothermal mode), which is sufficient to eliminate errors in the evaluation of both enthalpy and kinetic parameters.[25] The calorimeter was previously calibrated using gallium, indium, zinc, and lead standards for temperature calibration and Joule effect for power calibration. The mass of samples was about 60 mg. Nonisothermal runs were performed at the heating rates 1, 2, and 5 °C min^{-1}. For an isothermal run, the temperature of 100 °C was taken. The glass transition temperature (T_g) of the cross-linked matrix cured for 4 h at 120 °C was measured at the heating rate of 5 °C min^{-1} and has been found to be about 126 °C. A paper[26] reports in more details on thermal properties of the system.

Results and Discussion

Kinetic Computations. In practice it is more convenient to use the integral forms of (3). The most popular integral equations independently derived by Ozawa[27] and Flynn and Wall[28] give E_α from the plot ln β_i vs $T_{\alpha,i}^{-1}$ (here i are ordinal numbers of DSC runs performed at different heating rates, β_i). Generally the E_α values found by these equations require further corrections[29] which can be avoided when using the plot[30] $\ln(\beta_i/T_{\alpha,i}^2)$ vs $T_{\alpha,i}^{-1}$. The latter has been used in the present computations of E_α at different values of α. The pre-exponential factors related to given conversions (A_α) have been evaluated through the parameters of an artificial isokinetic relationship as suggested in ref 31.

To perform isoconversional analysis, the original DSC data (Figure 1) were transformed into the form α_i vs T_i for each ith heating rate. Conversions were determined as fractional areas of a DSC peak. The resulting dependence of E_α on α for the epoxy cure is presented in Figure 2 which also shows two dependencies of a very close shape discovered[5,13] for the cure processes.

Interpretation of E_α on α Dependence. The generally accepted scheme[32] of the amino−epoxy cure

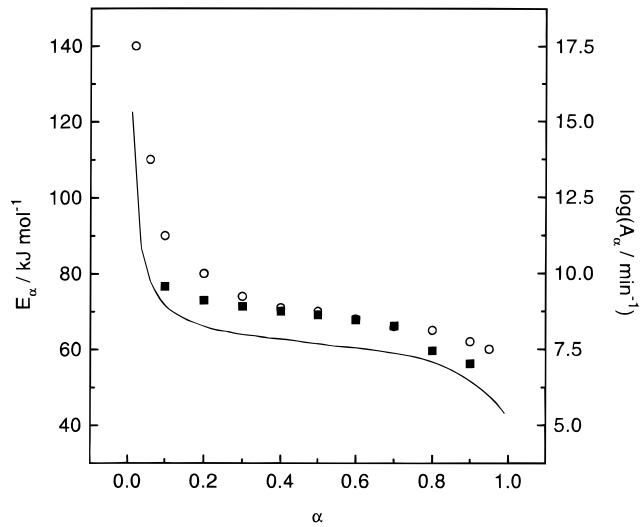
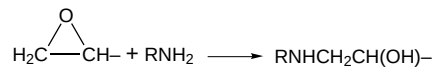
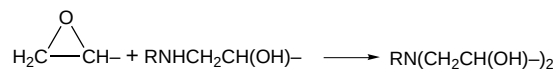


Figure 2. Dependencies of Arrhenius parameters upon conversion for the epoxy−amine cure: (−) present data, (■) ref 5, and (○) ref 13. ln A_α relates to the present data alone.

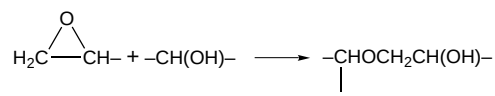
involves three main reactions of the glycidyl ether: (1) primary amine addition



(2) secondary amine addition



(3) etherification



The process of cure is autocatalytic because the hydroxylic molecules formed as a reaction product partly protonate the oxygen atom of the epoxy group, facilitating the ring-opening reactions.[32] During the cure the reaction system undergoes gelation (liquid-to-rubber) and vitrifiaction (rubber-to-glass) transitions usually described by time−temperature−transformation (TTT) diagrams.[33] Intensive cross-linking occurring in the region between the above transitions reduces molecular mobility, and the cure changes from a kinetic to a diffusion regime. The kinetics features of the cure in these regimes are discussed in the following sections.

1. Kinetically Controlled Cure. DSC analysis has shown[2] that etherification occurs at elevated temperatures once all the primary amines are exhausted. High activation energies (171.1 kJ mol^{-1} by DSC[2] and 97.3 kJ mol^{-1} by FTIR[19]) are characteristic of this process. On the whole, the overall heat release at the early stages of the cure is principally due to reactions of amino−epoxy addition.

Comparative studies[6,17,20,22,23] of the reactivity of the primary and secondary amines assign higher reactivity to the primary amines. The ratio of the rate constant of the secondary amine addition to the corresponding constant of the primary one depends on electron-donating properties[23] of an amine and may vary with the temperature.[17] Normally this ratio varies within 0.1−0.6.[6,20,22,23] According to ref 2, the secondary amine addition does not play an important role in the begin-

ning of the cure. In all likelihood the primary amine addition controls the overall heat release at lower conversions. Thus the effective value of $E_\alpha = 121$ kJ mol^{-1} at $\alpha \rightarrow 0$ (Figure 2) should be ascribed to the primary amine addition. This value is markedly higher than the activation energies reported for the primary amine additions studied by FTIR[17,19] (60.6 and 55.1 kJ mol^{-1}, respectively), HPLC[23] (58.1 kJ mol^{-1}), and DSC[2] (69.4 kJ mol^{-1}). However, in all the above cases, the reaction of the primary amine was considered as a single step so that the activation energies obtained were supposed to be constant throughout the entire interval of the amine conversion. This idea does not correspond to the autocatalytic mechanism of the process. Since the hydroxyl groups formed during the cure facilitate ring opening, it is reasonable to expect a decrease in the activation energy of the epoxy–amine cure as compared to the very beginning of the process where the nonautocatalyzed reaction occurs. The reported low values of the activation energy most likely represent some average values between the activation energies of nonautocatalyzed and autocatalyzed reactions, being closer to the latter value.

A cure model,[7]

$$d\alpha/dt = (k_1 + \alpha k_2)(1 - \alpha)(B - \alpha) \quad (4)$$

as well as its more flexible modification,[11]

$$d\alpha/dt = (k_1 + \alpha^m k_2)(1 - \alpha)^n \quad (5)$$

suggests an alternative to a single-step description of the epoxy–amine addition. Both models seem to originate from the kinetic scheme of the autocatalytic cure suggested in ref 34. Equations 4 and 5 make no distinction between the primary and secondary amine addition and are applicable when the cure is not complicated by diffusion. Diffusion imposes a restriction on the upper limit of conversions being involved in calculations by (4) and (5). Generally, this limit depends on the thermal history of cure and may be experimentally encountered as early as by $\alpha = 0.4$[7] or 0.3.[18] The latter value has been conventionally taken as the upper limit in our theoretical analysis of the kinetically controlled cure.

Model 4 assumes that the reaction is initiated by any hydrogen-bond donor molecules (HX) present as moisture or impurities.[7] In eq 4, k_1 is the rate constant of the amine addition initiated by HX molecules, k_2 is the rate constant of the amine addition internally catalyzed by the hydroxyl groups, and B is the initial ratio of diamine equivalents to epoxide equivalents. The values of E_1 and E_2 (in kJ mol^{-1}) found by eq 4 are, respectively, 79.4 and 46.0,[7] 87.8 and 46.0, 80.7 and 77.8,[8] 71.2 and 49.3,[9] and 63.2 and 48.8.[10] When model 5 has been used, the following values of E_1 and E_2 (in kJ mol^{-1}) are, respectively, reported as 64.4 and 45.6,[11] and 91.1 and 66.4, and 133.0 and 49.7.[12] A model of competitive reactions has also been applied to the cure, and values of $E_1 = 103$ kJ mol^{-1} and $E_2 = 77$ kJ mol^{-1} have been respectively found[14] for the nonautocatalyzed and autocatalyzed epoxy–amine addition. At the same time the single activation energy for the whole cure of the novolac resins takes some average values[15,16] (70.2 and 80.0 kJ mol^{-1}, respectively) between the above E_1 and E_2.

A comparison of E_1 and E_2 values with the activation energies obtained by single-step models supports our speculation that the latter values are conversion-averaged. On the contrary, E_α at $\alpha \rightarrow 0$ appears to match E_1 evaluated by eqs 4 and 5. Therefore, summing up the above results, we may accept $E_\alpha = 121$ kJ mol^{-1} as an estimate of the activation energy of the primary amine addition initiated by HX impurities.

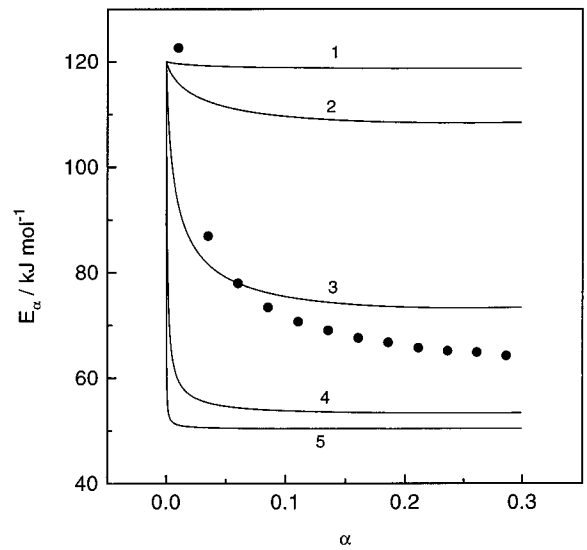


Figure 3. Dependencies of the activation energy upon conversion computed by eq 6 for different A_1 (1, 10^{18}; 2, 10^{17}; 3, 10^{16}; 4, 10^{15}; and 5, 10^{14} min^{-1}) as compared to the actual value (●).

Models 4 and 5 can be employed to further interpret the dependence of E_α on α. Let us find out the dependencies of E_α on α inherent to these models. With respect to (3), E_α can be found from (4) as

$$E_\alpha = -R\, d\ln[(k_1 + \alpha k_2)(1 - \alpha)(B - \alpha)]_\alpha/dT^{-1} = (k_1E_1 + \alpha k_2E_2)/(k_1 + \alpha k_2) \quad (6)$$

and from (5) as

$$E_\alpha = -R\, d\ln[(k_1 + \alpha^m k_2)(1 - \alpha)^n]_\alpha/dT^{-1} = (k_1E_1 + \alpha^m k_2E_2)/(k_1 + \alpha^m k_2) \quad (7)$$

The dependencies of E_α on α have been found by substituting experimental values of T and α obtained at the heating rate 1 °C min^{-1} into (6) and (7). The values of E_1 and E_2 were respectively taken as 120 and 50 kJ mol^{-1} to approximately approach the actual dependence of E_α on α (Figure 2). The value of A_2 was assigned to be 10^6 min^{-1}, and A_1 was varied to elucidate the effect of the ratio k_1/k_2 on the dependence of E_α on α. In particular, for the dependencies presented in Figure 3, k_1/k_2 varies with the temperature as 0.5–3000 (curve 1), (5×10^{-2})–300 (curve 2), (5×10^{-3})–30 (curve 3), (5×10^{-4})–3 (curve 4), and (5×10^{-5})–0.3 (curve 5). All the dependencies start from E_1 which directly follows from (6) subject to $\alpha = 0$. At higher conversions ($\alpha \rightarrow 0.3$), the value of E_α is determined by k_1/k_2 and reaches E_2 only when $k_1 < k_2$ (curve 5). Note, that the dependencies of E_α on α become steeper with decreasing k_1/k_2 at $\alpha \approx 0$. Nevertheless the variation of both E_2 and A_2 in (6) has not allowed one to obtain a dependence, the course of which is parallel to the experimental one.

Because of having one extra parameter, m, eq 7 gives rise to a wider diversity of E_α on α dependencies as compared to (6). Figure 4 displays how the shape of these dependencies changes when varying m. The values of Arrhenius parameters were kept constant (E_1

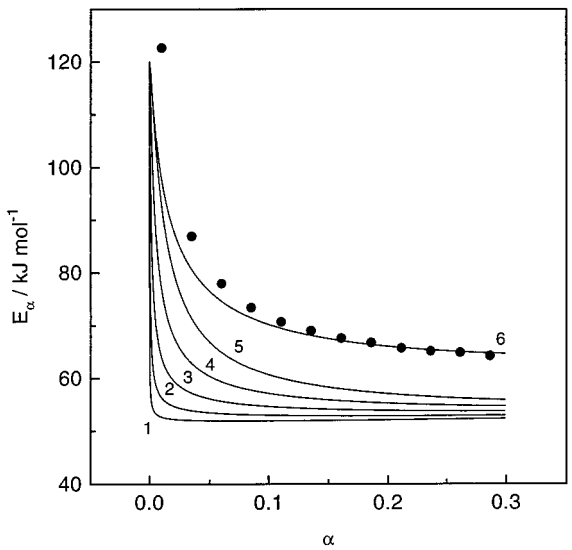


Figure 4. Dependencies of the activation energy upon conversion computed by eq 7 for different m (1, 0.7; 2, 0.9; 3, 1.1; 4, 1.3; and 5, 1.5) as compared to the actual value (●). Curve 6 represents the model dependence with $E_2 = 53$ kJ mol^{-1} and $m = 1.3$.

$= 120$ kJ mol^{-1}, $E_2 = 50$ kJ mol^{-1}; $A_1 = 10^{15}$ min^{-1}, $A_2 = 10^6$ min^{-1}). The dependencies were obtained analogously to those presented in Figure 3. It is worthy of note that a variation of m allows one to control steepness of the dependence of E_α on α without changing the ratio k_1/k_2. Thanks to this, a dependence, closely matching the experimental one (curve 6), can be obtained.

Therefore there are two options to evaluate the activation energy of the autocatalytic amine addition. As the first approximation, we can take a value of E_α corresponding to the conversion at which the actual dependence of E_α on α (Figure 2) violates a convex downward pattern characteristic of models 4 and 5. As shown in the next section, this violation is associated with the change of the cure to a diffusion regime. For the present system this occurs in the range of $\alpha = 0.3-0.5$, after which the dependence of E_α on α takes a convex upward shape. Since E_α is almost constant (about 64 kJ mol^{-1}) in the above range, we can use this value as an estimate for the activation energy of the autocatalytic amine addition. This value is in agreement with the literature values ascribed to the autocatalytic amine additions.[2,17,23] The variation of E_2 and m in (7) to fit the experimental dependence of E_α on α gives a lower value of 53 kJ mol^{-1}. This value is very close to the activation energies of the autocatalyzed process of both the primary[19] (55.1 kJ mol^{-1}) and the secondary[17] (52.3 kJ mol^{-1}) amine additions. It is worth noting that the activation energies of the primary and secondary amine addition were found to be equal for four different amines,[23] although substantially different values have also been reported.[17,19]

The main conclusion which can be drawn from the analysis of the cure models 4 and 5 is that both models lead to the dependencies of E_α on α similar to those actually found (Figure 2), provided $E_1 > E_2$. In all the studies,[7−12] the found values of E_1 were greater than E_2. Consequently, the isoconversional kinetic analysis, if applied to the cure data, might have discovered decreasing dependencies of E_α on α. Nevertheless we cannot deny the possible existence of increasing dependencies if $E_1 < E_2$. This might be a case when a small amount of an effective acid catalyst (HX) is initially present in a system. In such a case the cure may reveal a low E_α at $\alpha \approx 0$ which gradually increases with increasing the amount of hydroxylic molecules inducing the autocatalytic cure.

2. Diffusion-Controlled Cure. One of the first diffusion kinetic models was suggested in ref 35. The basic idea was to find the mean duration of coordination of two molecules as a sum of the mean durations of coordinations due to reaction and diffusion. This idea is also known as the law of the addition of kinetic resistances:[36,37]

$$k_{ef}^{-1} = k^{-1} + k_D^{-1} \tag{8}$$

where k is the intrinsic rate constant, k_D is the specific rate constant for diffusion, and k_{ef} is the effective rate constant. It has been shown[38] that the Arrhenius plot for a process complicated by diffusion is nonlinear. As a result, a characteristic convex upward dependence of E_α on α occurs.[24]

Let us accept the Arrhenius form for the temperature dependence of k_D:

$$k_D = D_o \exp(-E_D/RT) \tag{9}$$

This form has been suggested[39] in the theory of absolute reaction rates to analyze the effect of the temperature on both diffusion and viscosity. This equation, despite some possible limitations,[40] is very convenient to analyze the effect of the temperature because of an explicit relation between k_D and T. The effective activation energy of the process coupled with diffusion is

$$E_{ef} = -R\ \mathrm{d}\ln(k_{ef})/\mathrm{d}T^{-1} = (kE_D + k_D E)/(k + k_D) \tag{10}$$

Here E_{ef} is a function of the temperature and $E_{ef} = E_{ef}(T)$. The dependence of E_α on α may be found as $E_\alpha = E_{ef}(T_\alpha)$, i.e., by substituting the temperatures related to given conversions into (10) when computing the values of k and k_D.

The values of E and E_D necessary to model the E_α on α dependencies were taken with regard to the experimentally observed dependence. E and A have been taken to be 63 kJ mol^{-1} and 10^8 min^{-1}. E_α at $\alpha \to 1$ gives an upper estimate for E_D (43 kJ mol^{-1}). Generally E_D is considered[39] to not be greater than 20 kJ mol^{-1}. The latter value was used as an approximation for E_D. D_o was varied to display the influence of k/k_D on the shape of the dependencies of E_α on α. The dependencies are shown in Figure 5. The ratio of k/k_D varies with the temperature within the range $(2.9 \times 10^{-4})-(5.6 \times 10^{-2})$ (curve 1), $(2.9 \times 10^{-3})-0.56$ (curve 2), and $(2.9 \times 10^{-2})-5.6$ (curve 3). All these dependencies fail to reproduce the course of the actual dependence of E_α on α. Curves 1 and 2 start from E_α approaching the experimental value; however, at higher α they demonstrate a more slowly increasing contribution of diffusion. Curve 3 has a similar shape; however, it begins from an E_α value which is considerably lower than the modeled value. This suggests that for such a process the influence of diffusion would be detectable far before $\alpha = 0.3$.

Undoubtedly the temperature dependence of k_D is not the only reason responsible for the observed E_α on α dependence. Another crucial factor is the change of physical properties and primarily of viscosity in the epoxy system with degree of cure. Measurements[3] show that viscosity increases in 3 orders of magnitude when α increases from 0.1 to 0.6. A comparable decrease in

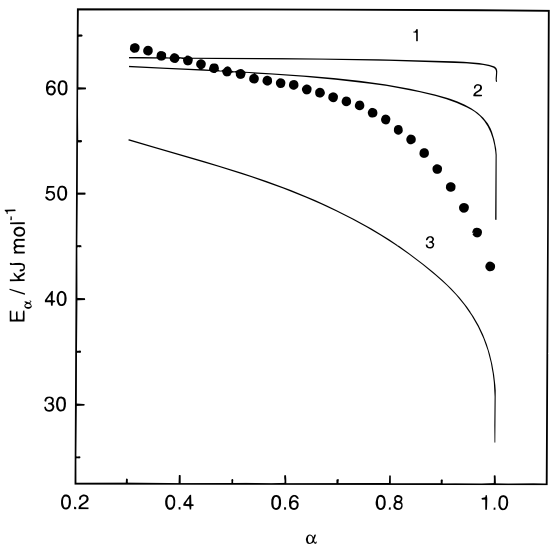


Figure 5. Dependencies of the activation energy upon conversion computed by eq 10 for different D_o (1, 10^4; 2, 10^3; and 3, 10^2 min^{-1}) as compared to the actual value (●).

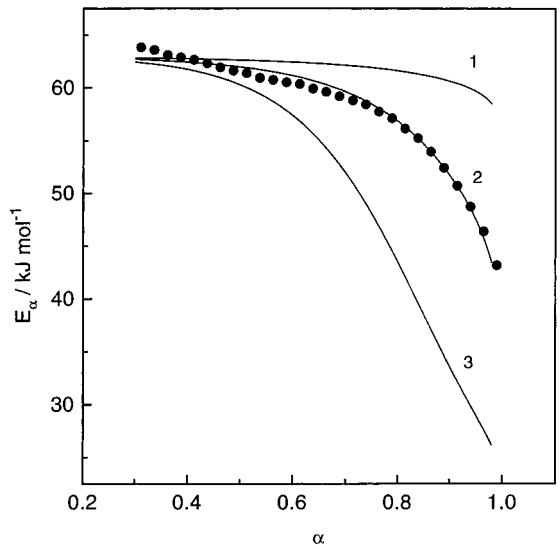


Figure 6. Dependencies of the activation energy upon conversion computed by eq 17 for different K (1, −2; 2, −4; and 3, −6) as compared to the actual value (●).

the diffusion coefficient may be expected due to the interrelations[39,40] between the coefficients of diffusion and viscosity.

The Doolittle equation:[41]

$$\mu = a \exp[b(v_o/v_f)] \tag{11}$$

relating viscosity (μ) with the free volume (v_f) of a liquid has been adopted[9] to adequately describe the kinetics of the diffusion-controlled cure. However eq 11 does not establish explicit dependencies on T and α. The temperature dependence has been introduced[9] using an expression for the fractional free volume:

$$f \equiv v_f/(v_o + v_f) = f_g + \alpha_f(T - T_g) \tag{12}$$

(f_g is the fractional free volume at T_g and α_f the thermal expansion coefficient of the free volume) derived[42] for amorphous polymers. Equation 12 has the only variable, T, and three constants of which f_g and α_f take respective values of 0.025 and 4.8×10^{-4} K^{-1}. The expression obtained[9] for the diffusion coefficient:

$$D = D_o \exp\{B[1 - (f_g + \alpha_f(T - T_g))^{-1}]\} \tag{13}$$

has been used[9,10] in kinetic computations. However its use presents a major problem. Equations 11 and 12 hold true for normal liquids for which v_o (occupied volume at 0 K) is constant and v_f increases with the temperature. Under these conditions, the constancy of f_g and α_f is a reasonable assumption. Substitution of (12) into (11) gives an inverse dependence of viscosity on the temperature which is not the case of epoxy-curing systems. For such systems the free fractional volume has to be a rather cumbersome function of both T and α different from (12). Attempts to tackle this problem and to employ (13) for kinetic computations involved the experimental determination of the dependencies of T_g on α[9] and D on α.[10] Nevertheless these practical expedients do not resolve the contradiction in application of eq 12 to epoxy-curing systems for which it is inappropriate.

The most convenient way to take into account the effect of both T and α on diffusion is to develop an equation with separable variables T and α:

$$k_D(T,\alpha) = D(\alpha)k_D(T) \tag{14}$$

where $k_D(T)$ is an explicit function of T as given by eq 9 and $D(\alpha)$ is an explicit function of α. The existence of the latter function is reinforced by experimental evidences. The first among them is direct measurements of $D(\alpha)$ which have shown either no[18] or almost no[10] dependence on the temperature. Another experimental evidence is that the average molecular weight (M_w and M_n) for an amino epoxy resin is a unique[6] (independent of the temperature) function of conversion. This fact also suggests the existence of a separate function, $D(\alpha)$, because at a given temperature the coefficient of diffusion is predominantly determined by the molecular weight.[4,43,44]

An equation with separable variables α and T:

$$\mu(T,\alpha) = \mu_o \exp(E_\mu/RT + K\alpha) \tag{15}$$

(where E_μ is the activation energy of the viscosious flow and K is a constant which accounts for the effect of the chemical reaction on the change in the reacting mass viscosity) has been mentioned in a review[45] and has been used[8] to describe a variation in viscosity with α of Hercules 3501-6 resin.

By analogy to (15), let us introduce eq 16:

$$k_D(T,\alpha) \equiv D(\alpha)k_D(T) = D_o \exp(-E_D/RT + K\alpha) \tag{16}$$

where K is a constant accounting for the effect of the chemical reaction on the change in diffusivity. Note that in eq 16 K is opposite in sign to that in (15). Equation 16 establishes explicit dependencies on T and α which gives it an evident advantage over (13). Inserting $k_D(T,\alpha)$ into (8) with following differentiation gives an expression for E_α:

$$E_\alpha = -R[\mathrm{d}\ln(k_{ef})/\mathrm{d}T^{-1}]_\alpha = (kE_D + k_D(T,\alpha)E)/(k + k_D(T,\alpha)) \tag{17}$$

Figure 6 presents dependencies of E_α on α obtained at different values of K. The values of Arrhenius parameters were kept constant (E = 63 kJ mol^{-1}, E_D =

Table 1. Computation of Arrhenius Parameters by the ASTM E698-79 Method

β (°C min^{-1})	T_m (°C)	α_m	log(A) (min^{-1})
1	71.7	0.447	8.42
2	83.4	0.452	8.38
5	96.3	0.436	8.42
E (kJ mol^{-1}) = 63.42			

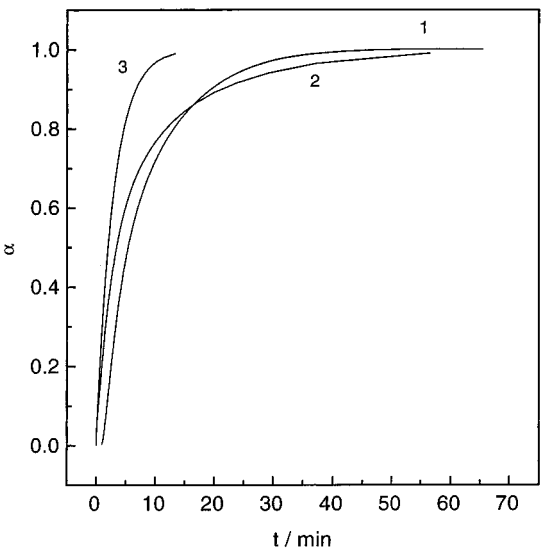


Figure 7. Conversion on time plot for the cure at 100 °C: 1, measured; 2, predicted by eq 24; and 3, predicted by ASTM E698-79 method.

20 kJ mol^{-1}, $A = 10^8$ min^{-1}, $D_o = 10^4$ min^{-1}). It is seen that the use of model 16, which accounts for the effect of both T and α on diffusion, allows to reproduce the course of the experimental dependence.

Predictions. The idea of predicting the isothermal behavior of a substance from nonisothermal data usually reduces to inserting nonisothermally estimated A, E, and $g(\alpha)$ into (18) which is the integral form of (1):

$$t = g(\alpha)/A \exp(-E/RT_o) \tag{18}$$

where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1}\, d\alpha$ and T_o is the temperature of interest.

It has been mentioned[1] that the kinetic methods using the variation of peak exotherm with the heating rate may give reasonable isothermal predictions for the cure progress. One of these methods is suggested by ASTM E698-79[46] according to which the activation energy is evaluated from the plot of $\ln(\beta_i/T_{m,i}^2)$ against $T_{m,i}^{-1}$, where $T_{m,i}$ are the temperatures corresponding to peak maxima at different heating rates. It is supposed[46] that the process being studied is a first-order reaction for which $g(\alpha) = -\ln(1 - \alpha)$. This assumption is also used[46] to evaluate the pre-exponential factor:

$$A_i = \beta_i \exp(E/RT_{m,i})E/RT_{m,i}^2 \tag{19}$$

The values of Arrhenius parameters for the epoxy−amine cure are given in Table 1. Substituting these parameters into (18) and varying α, dependencies of α on t at $T_o = 100$ °C have been obtained. Figure 7 shows the dependence (log A = 8.42) which best approaches the experimental one found by numerically integrating an isothermal DSC peak. The results of the predictions are rather unsatisfactory. However it is not surprising because ASTM E698-79 method treats the complex epoxy−amine cure as a single-step reaction of the first order. Compared to the results of the isoconversional analysis, the activation energy evaluated by this method is a single point on the dependence of E_α on α at $\alpha = \alpha_m$.

An original technique has been suggested[47] for the cure predictions. It does not use any kinetic calculations at all, only a transformation of experimental data. It has particularly shown that the time to reach α at T_o can be found as

$$t = \int_0^\alpha [(d\alpha/dt)_{T_o}]^{-1}\, d\alpha \tag{20}$$

where the reaction rates at T_o, $(d\alpha/dt)_{T_o}$, are taken from a series of DSC runs performed at different heating rates. This method has two obvious pitfalls. The first is that it requires to perform many nonisothermal runs to have the table dependence of $[(d\alpha/dt)_{T_o}]^{-1}$ on α sufficiently representative for numerical integration. This problem can be solved[48] by using the equation:

$$(d\alpha/dt)_{T_1}/(d\alpha/dt)_{T_2} = \exp[(E/R)(T_2^{-1} - T_1^{-1})] \tag{21}$$

at a constant α to compute E from two nonisothermal runs. The substitution of the found E and a constant T_0 into (21) gives a plot of $(d\alpha/dt)_{T_o}$ on α which is treated in the same way as experimentally obtained. Nevertheless the technique has the second pitfall because of the fact that the value $[(d\alpha/dt)_{T_o}]^{-1}$ inevitably tends to infinity at $\alpha \to 0$. This makes the determination of the initial area uncertain and has an impact on the whole predicted dependence of α on t. Comparisons of the predictions with the isothermal experiments have shown[47,48] significant disagreement especially at $\alpha > 0.5$.

An alternative technique has been developed[49] assuming that the reaction model, $g(\alpha)$, and Arrhenius parameters related to a given conversion remain the same when changing temperature. Under this assumption we can equate the expressions 22:

$$g(\alpha) = A_\alpha \exp(-E_\alpha/RT_o)t_\alpha \tag{22}$$

and 23 (the integral form of eq 2) related to a given conversion

$$g(\alpha) = (A_\alpha/\beta) \int_0^{T_\alpha} \exp(-E_\alpha/RT)\, dT \tag{23}$$

which hold true under isothermal and nonisothermal conditions, respectively. Simultaneous solution of (22) and (23) for t_α yields (24):

$$t_\alpha = [\beta \exp(-E_\alpha/RT_o)]^{-1} \int_0^{T_\alpha} \exp(-E_\alpha/RT)\, dT \tag{24}$$

Equation 24 enables the time at which a given conversion will be reached at an arbitrary temperature, T_o, to be computed. Note that the computations require only a dependence of E_α on α and experimental values of T_α.

Solving (24) for different conversions, the epoxy−amine cure at T_o = 100 °C has been predicted. A dependence of α on t is depicted in Figure 7. It is seen that the prediction made by eq 24 gives quite satisfactory results. This is primarily because the entire dependence of E_α on α being substituted into (24) implicitly takes into account the actual complexity of the cure.

Conclusions

The experimental dependence of E_α on α determined from the isoconversional kinetic analysis of nonisother-

mal DSC data on epoxy−amine cure can be adequately interpreted in the terms of the reaction mechanisms with the help of the generally accepted models 5, 8, and 9. Equation 9, however, has been modified by inducing a term which accounts for the effect of the cure on diffusivity (eq 16). The experimentally evaluated values of E_α are reasonable and consistent with the literature estimates for the activation energies of the primary amine addition initiated by HX molecules (at $\alpha \rightarrow 0$), of autocatalyzed epoxy−amine addition (at α where the cure starts to change from a kinetic to a diffusion regime), and of diffusion (at $\alpha \rightarrow 1$). Furthermore, eq 24 suggests that the dependence of E_α on α is the only information necessary to satisfactorily predict the isothermal cure.

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MA951162W